University of Naples Federico II



DEPARTMENT OF INDUSTRIAL ENGINEERING

Ph.D. Thesis

Evaporative Emissions from a Gasoline Fueled Vehicle: Predictive Models of Fuel Evaporation from Tank and Canister Dynamics

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«Science is but a perversion of itself unless it has as its ultimate goal the betterment of humanity.»

Nikola Tesla

Abstract

Fuel evaporative emissions from a vehicle fuel tank have long been known to be an important source of pollution, and international regulations on automotive Volatile Organic Compounds (VOCs) are becoming increasingly stringent every year, because of their effects on human health and environment. The most cost-effective and widely adopted solution for limiting the release of VOCs to the environment is the use of an EVAP system, which commonly consists of a canister filter filled with activated carbons that stores fuel vapors, by means of adsorption, to make them available for the combustion in the engine cylinders. However, as the automotive world is moving towards hybrid electric solutions, the role of the EVAP system is becoming even more important, because of limited possibilities of canister filter purging.

In the present study, the problem of VOCs formation from gasoline vehicle and the EVAP system functioning have been analyzed, under three different aspects. Gasoline evaporation inside the vehicle fuel tank has been experimentally tested by using a VT Mini-SHED, under different environmental temperature conditions, in order to study the fuel vapor formation and leakage from the tank due to diurnal temperature variations (DBLs), when the vehicle is in parking conditions. A 0D semi-empirical model has been developed in MATLAB[®] environment, that is able to predict the amount of fuel vapors that escapes the tank under different environmental temperature conditions, fuel tank dimensions, filling level and gasoline vapor pressure (RVP). Fuel vapors adsorption and desorption phenomena have been analyzed by means of an experimental activity performed on a European-type canister filter, by measuring its mass variation and internal temperatures changes due to the phenomena themselves. A 1D model has been developed in MATLAB[®] environment, to simulate the adsorption phenomenon by evaluating the adsorbed mass

and temperature variations during time. Evaporative emissions due to the tank refueling process have also been studied and experimentally measured by using a VT Mini-SHED. A 3D CFD simulation of the refueling process has been carried out, by adding suitable equations to evaluate and predict the fuel vapor quantity that escapes the tank during refueling.

The present work is the result of a collaboration among the Department of Industrial Engineering of the University of Naples Federico II (Naples, NA, IT), the R&D division of Stellantis N.V. (Pomigliano d'Arco, NA, IT) and the Center for Automotive Research of the Ohio State University (Columbus, OH, USA).

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Nomenclature

Symbols

ASVP	Air saturated vapor pressure (Pa)
$A_C(x)$	Cross-sectional area of the carbon bed (m^2)
A_s	Evaporation surface area (m^2)
\vec{B}_f	Body force (gravity, buoyancy and extra terms for non-intertia reference
	frame)
b_1	Henry's law constant of component 1 $(mol/(kg \cdot Pa))$
b_{01}	Temperature-independent calibration parameter, characterizing each
	adsorbate-adsorbent system $(mol/(kg \cdot Pa))$
C_{BET}	Brunauer, Emmett and Teller constant
C_d, C_l	Linear and quadratic drag coefficients for pressure loss vs. flow curve
C_{f}	Fuel vapor concentration (mol/m^3)
C_L	Langmuir constant
\widetilde{c}_{pg}	Gas-phase molar heat capacity $(J/(mol \cdot K))$
c_{ps}	Solid-phase heat capacity $(J/(kg \cdot K))$
$c_{v,a}, c_{v,f}, c_{v,c}, c_{p,p}$	Specific heat capacity of air, vapor fuel, activated carbons, and plastic
	wall of canister $(J/(kgK))$
$C_{1\epsilon}, C_{2\epsilon}, C_{\mu}$	Empirical modeling constants, $k - \epsilon$ model
DVPE	Dry vapor pressure equivalent (Pa)
D_f, D_a	Fuel vapor in air (inert) mass diffusion coefficient, air (inert) self-diffusion
	coefficient (m^2/s)

$D_{pe,i}, D_{pi}, D_{si}$	Effective diffusion coefficient in porous media, porous diffusion coefficient
	and surface diffusion coefficient of component $i \ (m^2/s)$
E, E_0, E_1, E^*, v	*, n Curve fitting parameters, according to Lavoie et al. (for ε evaluated
	in J/mol)
E	Internal energy in the canister bed (per lenght of carbon bed element)
	(J/m)
E(RVP, Z)	Slope of the line $\log P$ vs. $1/T$ (K)
e_a, e_f, e_c, e_p	Specific energy of air, vapor fuel, activated carbons, and plastic wall of canister (J/kg)
E_R	Evaporation rate
E_s	Specific energy of adsorbed phase, per mass of carbons (J/kgC)
f	Differential free energy of adsorption (J/m^3)
$f(\mathbf{x}, \mathbf{v}, t)$	Probability density function
f_0, f_1, f^*, v^*, n	Curve fitting parameters, according to Lavoie et al.
G_k	Turbulent production from stress and strain, $k - \epsilon$ model
h_a, h_f	Specific enthalpy of air and vapor fuel in canister bed (J/kg)
h_s	Heat transfer coefficient between gas and solid phase $(W/(m^2 \cdot K))$
h_W	Heat transfer coefficient between gas and can ister wall $(W/(m^2\cdot K))$
K	Constant characterizing adsorbent pore size distribution
k	Turbulent kinetic energy
k_C	Thermal conductivity of the carbon bed $(W/(mK))$
K_m	Mass transfer coefficient (m/s)
$K_{m,C}$	Overall mass transfer coefficient (adsorption), as defined by Cooney
	$(kg/(m^2\cdot s))$
$K_{m,HF,i}$	Effective mass transfer coefficient (adsorption) for component i, as defined
	by Huang and Fair (m/s)
$ar{m}$	Adsorbed fuel vapor mass per mass of activated carbons (kg/kg_C)
$m'_{a}, m'_{f}, m'_{f,i}, m'_{f,i}$	$f_{f,exit}$ Specific mass of air (inert), fuel vapor, component <i>i</i> , and fuel vapor

exiting the tank, per volume of dispensed fuel (kg/m^3)

m_a, m_f	Air and fuel vapor mass in vapor space (kg)
\dot{m}_a,\dot{m}_f	Air and fuel vapor mass flow in canister bed (kg/s)
$m_{a,FILL}$	Mass of air (inert) that enters the tank during refueling (kg)
$\dot{m}_{aX}, \dot{m}_{fX}$	Air and fuel vapor mass flow exiting the tank (kg/s)
M_{D1}, M_{D2}	Mass of HCs after first and second day of diurnal test (g)
M_{HS}	Mass of HCs recorded during hot soak test (g)
M_{TOT}	Total mass of HCs for the GTR EVAP test (g)
$\dot{m}_{FILL}, \dot{m}_{sup/ret}$	Fuel mass filling, supply and return flow rate (kg/s)
m_L	Liquid fuel mass (kg)
\dot{m}_{pq}	Mass transfer from the p -th phase to the q -th phase
m_{VL}	Tank vapor generated mass (kg)
\dot{m}_{VL}	Tank vapor generated mass flow rate (kg/s)
M_{3w}, M_{20w}	Mass of HCs after 3 and 20 weeks of permeability test (g)
N	Molar flux (mol/s)
\bar{n}	Adsorbed fuel vapor moles per volume of activated carbons (mol/m_C^3)
\dot{N}_{a}	Air (inert) molar flow (mol/s)
n_a', n_f'	Specific number of moles of air (inert) and fuel vapor, per volume of dispensed fuel (mol/m^3)
$\dot{N}_{conv}, \dot{N}_{diff}$	Convective and diffusive fuel molar flow (mol/s)
n_f, n_a, n_i	fuel vapor, air and i -th component number of moles (mol)
$N_{\mathbf{x},\mathbf{v}}$	Number of molecules in a determined space and with a determined velocity
PF	Permeability factor (g)
P_a, P_f, P_i	Air, fuel and <i>i</i> -th component partial pressure (Pa)
P_{amb}, P_{env}	Environmental pressure (Pa)
$P_C(x)$	Cross-sectional perimeter of the carbon bed (m^2)
$P_{FILL}, P_{tank}, P_{ex}$	Fuel vapor partial pressure of the dispensed fuel, the in-tank fuel, and the fuel vapor exiting the tank (Pa)

P_{foc}	Fuel focal pressure (Pa)	
$P_{sat}, P_{sat,i}$	Total saturation pressure and saturation pressure of component i (Pa)	
q, q_i	Solid-phase adsorbate concentration (mol/kg)	
q^*	Equilibrium solid-phase adsorbate concentration (mol/kg)	
Q_c, Q_k, Q_l	Convection, conduction energy fluxes, and energy lost through canister	
	plastic wall (W)	
\dot{Q}_C	Convective heat from environment (W)	
q_i^∞	Limiting amount adsorbed of component $i \ (mol/kg)$	
\dot{Q}_{pump}	Heat generated by the fuel pump (W)	
\dot{Q}_R	Radial heat from tank underbody (W)	
q_{01}^{∞}	Temperature-independent calibration parameter, characterizing each	
	adsorbate-adsorbent system (mol/kg)	
r	Saturation ratio	
R	Universal gas constant $(J/(mol \cdot K))$	
RVP	Reid vapor pressure (Pa)	
R_C, R_R	Convective and radial resistances of the fuel tank (K/W)	
RVP_{FILL}, RVP_{to}	a_{nk} Reid vapor pressure of the dispensed fuel and the in-tank fuel (Pa)	
8	Slope of the fuel distillation curve at 10% evaporated	
S/N	Signal to Noise ratio for DFSS tests	
Sc	Schmidt number	
S_q	Source term of phase q	
Т	Temperature (° C, K)	
$T1, T2, T3, T4, T_{skin}$ Temperatures recorded from thermocouples installed in and on the		
	can ister filter (° C)	
TVP	True vapor pressure (Pa)	
T_b	Normal boiling point (° C, K)	
$T_{FILL}, T_{tank}, T_{exit}$ Temperature of the dispensed fuel, the in-tank fuel, and the fuel vapor		
	exiting the tank (K)	

T_{foc}	Fuel focal temperature (K)
T_g, T_s, T_W	Gas, solid and wall temperature in canister (K)
T_{in}, T_{target}	Initial and target test temperature (° C, K)
T_l, T_v	Liquid and vapor temperature in tank (K)
T_p	Canister plastic wall temperature (° C, K)
T_{RVP}	Temperature at which RVP is evaluated $(37.8^{\circ}C)$
U_C	Convective heat transfer coefficient between canister and environment $(W/(m^2K))$
U_{ext}	Overall heat transfer coefficient between canister and environment $(W/(m^2K))$
$ec{V}$	Velocity
$\mathbf{v} = [v_1, v_2, v_3]^T$	Molecule velocity in positon \mathbf{x} (m)
$\mathbf{v_A},\mathbf{v_B};\mathbf{v_A\prime},\mathbf{v_B\prime}$	Velocities of molecules A and B , before and after their collision $[m/s]$
$V_{a,FILL}^{\prime}$	Specific volume, per volume of dispensed fuel (m^3/m^3)
V_d	Volume distilled percentage (carburetor bowl) (m^3)
V_L	Liquid fuel volume (m^3)
V_U	Ullage space volume (m^3)
V_0	Limiting amount of adsorbed phase volume (m^3)
WC	Activated carbons working capacity (but ane or gasoline) (kg/m_C^3)
Wt_d	Weight loss during distillation (carburetor bowl)
W_a, W_f, W_i, W_l	Molecular weight of air (inert), fuel vapor, $\it i-th$ component and fuel liquid phase (kg/mol)
$\mathbf{x} = [x_1, x_2, x_3]^T$	Molecule Euclidean position in space (m)
x_i	Molar fraction of component i in solution
Y, Y_f, Y_i	Gas-phase adsorbate molar fraction
$ar{y}$	Average value for DFSS noise tests
Ζ	Fuel vapor mass fraction evaporated
Z_{RVP}	Fuel vapor mass fraction evaporated, in RVP conditions

Greek Symbols

α	Air solubility in fuel
α_B	Bunsen coefficient
$lpha_q$	Volume fraction of phase q
$\alpha_{1v} \ (\alpha_{ij})$	VSM-FH parameter describing nonideality due to interaction between
	component 1 and vacancy (in general, components i and j)
β	Affinity coefficient, adsorbability of a given vapor on a given carbon with
	respect to benzene
Г	Diffusion coefficient
γ_i	Activity coefficient of component i
γ_v^s	Activity coefficient of vacancy in the adsorbed phase
$\Delta H_A, \Delta H_L$	Heat of adsorption and condensation (J/mol)
ΔH_{vap}	Heat of vaporization (J/mol)
ΔH_m	Molar enthalpy for fuel vaporization (J/mol)
ϵ	Void fraction
ϵ_k	Turbulence dissipation rate
ϵ_T	Refueling thermal efficiency
ε	Adsorption potential (J/mol)
heta	Ratio between adsorbed quantity and maximum adsorbable quantity
	(surface coverage)
Λ_{ij}	Wilson equation parameters
μ,μ_t	Viscosity, turbulent viscosity
$ ho_{app}$	Apparent carbon density (kg/m^3)
$\widetilde{ ho}_g$	Gas-phase molar density (mol/m^3)
$ ho_L$	Fuel liquid density (kg/m^3)
$ ho_q$	Density of phase q
$ ho_s$	Adsorbent density (solid-phase) (kg/m^3)
$\sigma_k, \sigma_\epsilon$	Turbulent Prandtl numbers

$\sigma(u,\mu)$	Differential cross section of scattering through angle $\bar{\theta}$
ϕ_i	Fugacity coefficient of component i

Abbreviations

AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
ATEX	Atmospheres Explosible
BE	Best Engineerign (DFSS)
BV	Bed Volume
BWC	Butane Working Capacity
CARB	California Air Resources Board
CFD	Computational Fluid Dynamics
DBL	Diurnal breathing loss
DDT	dichloro-diphenyl-trichloroethane
DFSS	Design For Six Sigma
ECU	Engine Control Unit
ETBE	Ethyl t-butyl ether
EVAP	Evaporative emission control system
FID	Flame Ionization Detector
FLVV	Fill Limit Vent Valve
FTIV	Fuel Tank Isolation Valve
FVSMOD	Fuel Vapor system model
GHG	Greenhouse Gas
GTR	Global Technical Regulation
GWC	Gasoline Working Capacity
HC	Hydrocarbon
HDPE	High density polyethylene
IDDOV	Identify, Define, Develop, Optimize, Verify (DFSS)

Nomenclature

LDF	Linear Driving Force
MTBE	Methyl tert-butyl ether
NAFTA	North American Free Trade Agreement
NEDC	New European Driving Cycle
NMVOC	Non Methane VOC
OBD	On Board Diagnostics
ODE	Ordinary Differential Equation
ORVR	Onboard Refueling Vapor Recovery
PCV	Purge Control Valve
PDE	Partial differential equation
RDE	Real Driving Emissions
ROV	Roll Over Valve
SAE	Society of Automotive Engineers
SHED	Sealed Housing for Evaporative emissions Determination
SVOC	Semi Volatile Organic Compound
U.S. EPA	United States Environmental Protection Agency
UNECE	United Nations Economic Commission for Europe
UNIFAC	Universal Functional Group Activity Coefficients
UNIQUAC	Universal Quasichemical
VLE	Vapor-liquid equilibrium
VOC	Volatile Organic Compound
VSM	Vacancy Solution Model
VTSHED	Variable Temperature Sealed Housing for Evaporative emissions Deter- mination
VVOC	Very Volatile Organic Compound
WHO	World Health Organization
WLTP	Worldwide Harmonized Light Vehicle Test Procedure

Introduction

Air pollution is one of the most important issues for the human health and environment, and during the last years it is at the center of attention of almost every industrialized country. Global warming is one of the most important effects of air pollution, which is regulated by the Paris Agreement, an agreement signed by 196 countries, with the target of keeping the rise in global average temperature to well below 2.0 °C above pre-industrial levels (preferably 1.5 °C).

The vehicle transportation field is responsible for the 17.5% of the global production of air pollutants. Pollutant emissions from vehicles propelled by an internal combustion engine are due to two main causes. Fuel combustion that occurs inside the engine cylinders is not ideal, therefore it produces various types of pollutants (CO, NO_x , HC, soot, etc.), named *exhaust emissions*. The fuel itself (especially gasoline) is made for having a certain volatility, to realize a better combustion inside the engine, but this property also have the negative effect of unburned hydrocarbons dispersion in the environment, named *evaporative emissions*. These two sources are potentially dangerous for the global ecosystem in which the human species lives, for several reasons, one of them being global warming. Therefore, these emissions are limited by several devices, like the 3-way catalytic converter for the exhaust emissions and the EVAP system for the evaporative emissions, which is the main focus of this work.

Evaporative emissions are generally referred to gasoline-propelled vehicles, since diesel components are heavier than the gasoline ones and, therefore, they are not interested in evaporation, since their volatility can be considered negligible at environmental temperatures. On the other hand, a commercial gasoline is composed by more than 120 constituents, many of which can be classified as Volatile and Very Volatile Organic Compounds (VOCs and VVOCs), which have many effects on human health and environment. For this reason, emissions are subject to many national and international regulations, which were imposed during the last few decades and which become more stringent every year: from January 2020, new approved vehicles must comply with Euro 6d requirements. This standard has adopted the new Worldwide harmonized Light-duty vehicles Test Procedure (WLTP) as a standard for evaluating tailpipe emissions, along with the Real Driving Emissions (RDE) cycle, that evaluates the effective emissions that are produced by a real vehicle driven on a real route. These two procedures have replaced the NEDC (New European Driving Cycle). Regarding evaporative emissions, the WLTP EVAP procedure has been adopted, which states that the vehicle cannot have a total amount of evaporative emissions greater than 2.0 g on a 2-day diurnal test cycle (the previous regulation imposes the same limit for a 1-day diurnal test cycle).

Most of the evaporative emissions are produced from the gasoline vehicle fuel tank, which must be connected to the external environment, to avoid unacceptable pressure variations. The Evaporative Emission Control (EVAP) system is the apparatus that prevents fuel vapors produced inside the tank to go in the atmosphere. The main element of the EVAP system is the carbon canister filter, that adsorbs fuel vapors coming from the tank and makes them available for combustion in the engine, through the canister purging process, which is executed when the engine is working. However, this operation cannot always been executed, especially in the case of an hybrid vehicle, when the thermal engine is not functioning. In this case, the canister filter can rapidly reach the saturation, thus losing its ability to store fuel vapors, that then escape into the environment. With the spreading of hybrid vehicles, that have become the best solution in dealing with the emission regulations (full electric vehicles excluded), this issue is becoming more relevant, and it has represented one of the most important levers for reaching the strategical targets defined in Horizon 2020 program.

This work is focused on studying the evaporative emission control system, by experimentally analyzing its behavior under different conditions and by developing computational models that are able to predict this behavior. In particular, three main aspects have been examined: fuel evaporation inside a gasoline fueled tank; carbon canister adsorption phenomenon and capacity; emissions produced during the refueling operation. The present elaborate is organized as follows:

- *Chapter 1* focuses on the main aspects of the evaporative emission problem, describing the effects of hydrocarbons on the human health and environment and pointing out the main causes of evaporative emissions. An in-depth analysis of the EVAP system is made, with a focus on the fuel tank and the carbon canister filter. Finally, a broad picture of the worldwide regulations that limit evaporative emissions is reported.
- *Chapter 2* provides an exhaustive description of the main modeling approaches that were developed during the years to study and predict the in-tank fuel evaporation and the canister adsorption and desorption behaviors. Examples of 3D CFD approaches to refueling emissions are also reported.
- *Chapter 3* reports the activities performed to develop a fuel evaporation model: a comprehensive experimental activity has been carried out, and measurements of fuel evaporation under various conditions (different fuel tanks, temperature, tank filling levels, etc.) have been performed. Then, a semi-empirical, lumped parameters model has been developed, coded and solved in MATLAB[®] environment.
- *Chapter 4* describes the experimental activity performed on a European-type carbon canister filter, to study the adsorption and desorption phenomena inside the carbon bed. Then, a 1D model has been developed to simulate the canister adsorption phase and estimate the adsorbed quantity and canister saturation time under specific conditions. Again, the model has been coded and solved in MATLAB[®] environment, then, it has been optimized by means of a DFSS activity.
- *Chapter 5* reports the experimental activity on the refueling losses, as well as the 3D CFD model developed (by using the commercial software SimericsMP+[®]) for studying the formation of these losses and predicting the evaporative emission quantity.

The whole project has been made from a collaboration between the Department of

Industrial Energy of the University of Naples Federico II (Naples, NA, IT), the R&D division of Stellantis N.V. (Pomigliano d'Arco, NA, IT) and the Center for Automotive Research of the Ohio State University (Columbus, OH, USA). In particular, the experimental activities have been performed at the Stellantis N.V. laboratories of the Pomigliano Technical Center, while the tank evaporation model and the refueling model have been developed at the University of Naples; finally, the canister model has first been developed at the Ohio State University and then optimized at the Pomigliano Technical center and the University of Naples.

The project is part of the industrial research described by the challenges of Horizon 2020, and fits in the national smart specialization strategy (SNSI), in accordance with the two targets, "Smart urban mobility systems for logistics and people" and "Systems for the safety of the urban environment, environmental monitoring and prevention of critical or risk events". In particular, the proposed activity matches the area of expertise "Sustainable mobility" (defined in the SNSI). The study also arises as a result of the European Union policy about air pollution from vehicles, which aims at a drastic reduction in vehicle exhaust and evaporative emissions and also to modify the type approval cycles, bringing them closer to the vehicle real driving conditions.

Chapter 1

Vehicle Evaporative Emissions

It is well known that road transport is one of the most important sources of air pollution and greenhouse gas emissions. The *GHG* (Greenhouse Gas) emissions caused by vehicle transportation has been estimated to be around 12 % of the total amount produced by anthropogenic sources (data updated for the year 2016) [1], while the contribute regarding air pollutants (carbon monoxide, unburned hydrocarbons, nitrogen oxides, particulate) from this sector is more than 17.5 % of the total production, on average, with a peak for NO_x from thermal engine vehicles tailpipe of 30 % of the overall emission (data update for the year 2018) [2].

Pollutant emissions from vehicles can be divided in two main categories: exhaust (or tailpipe) emissions and evaporative emissions. The first type regards the products of combustion and the pollutants that survive the after-treatment processes (e.g. 3-way catalytic converter), which are usually carbon monoxide (CO), nitrogen oxides (NO_x), unburned hydrocarbons (HC), sulfur oxides (SO_x), particulate (SOOT). Being these elements harmful for human health and environment, their production and emission from vehicles has been regulated over the years [3, 4]. Carbon dioxide (CO_2) is not part of vehicle pollutant emissions, being a natural product of the hydrocarbon combustion, but it gives the major contribution to the greenhouse effect (if the contribution of gases to global greenhouse effect is quantified as carbon dioxide-equivalents, the pure CO_2 represents the 74.4 % of the total amount [5]). Therefore, carbon dioxide production and, in general,

greenhouse gas emissions have also been regulated [6, 7].

Evaporative emissions are essentially unburned hydrocarbons that evaporate from the fuel tank and the fuel supply system of a gasoline-filled vehicle¹. Commercial gasoline is a mixture of over 120 compounds [8], many of them, called Volatile Organic Compounds, have a very low vapor pressure and can easily evaporate at environment conditions. Thus in the fuel tank the vapor headspace above the liquid gasoline is almost always saturated with hydrocarbons. This environment must be connected to the external ambient to avoid unacceptable pressure variations, which are caused by thermal excursion during daytime and fuel evaporation/condensation. Therefore, gasoline vehicles must be equipped with a suitable system that captures fuel vapors and limits their emissions towards the environment.

In this chapter there will be a characterization of Volatile Organic Compounds and a classification of evaporative emissions. A description of the vehicle fuel and evaporative emissions control system will follow, with a detail on the canister filter. Finally, a general framework of the regulations adopted around the world to limit these emissions will be presented.

1.1 Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are carbon-based chemical compounds that can easily evaporate at room temperature, thanks to their high vapor pressure. Their definition varies through the world. For instance, in Italy VOCs are defined as any organic compound that has a vapor pressure equal to or higher than 0.01 kPa at the temperature of 293.15 K (20 °C). European Union states that VOCs are "any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101.3 kPa" [9]. The U.S. Environmental Protection Agency (EPA) distinguishes between *indoor* VOCs, which are organic compounds that evaporate under normal indoor atmospheric conditions, and *outdoor* VOCs, which are "any compound of carbon, excluding carbon

 $^{^1{\}rm For}$ diesel vehicles, evaporative emissions are considered negligible, thanks to the low vapor pressure of diesel.

monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions" [10].

The World Health Organization [11] categorizes VOCs by considering the boiling temperature of the compound at a standard pressure of 101.3 kPa (normal boiling point:

- Very Volatile Organic Compounds (VVOCs), which have a T_b between 0 °C and 50 °C (e.g. propane, butane, methyl chloride);
- Volatile Organic Compounds (VOCs), which have a T_b between $50 \div 100 \ ^{\circ}C$ and $240 \div 260 \ ^{\circ}C$ (e.g. formaldehyde, toluene, acetone, ethanol);
- Semi Volatile Organic Compounds (SVOCs), which have a T_b between 240 ÷ 260 °C and 380 ÷ 400 °C (e.g. DDT, plasticizers, fire retardants).

Apart from petroleum treatments and gasoline evaporation, anthropogenic sources of VOCs include chemicals produced in the manufacture of paints, pharmaceuticals, and refrigerants; they can be found as industrial solvents (trichloroethylene), fuel oxygenates (MTBE), by-products of chlorination in water treatment (chloroform); they are components of hydraulic fluids, paint thinners, and dry cleaning agents.

VOCs represent a serious problem for human health and environment. Emission of carbonyl and aromatic compounds in air leads to various short-term and long-term diseases, depending on their concentration level in the air. Short-term effects can be headaches, sickness, atopic dermatitis, dizziness, sleepiness, irritation in skin and eyes. Long-term effects can be way more dangerous, since long exposures can lead to lung cancer, leukemia, and reduced pulmonary function. Indeed, some carbonyl compounds are considered hazardous to human health [12]. Moreover, VOCs can react with sources of oxygen molecules such as nitrogen oxides (NOx), and carbon monoxide (CO), in the atmosphere in the presence of sunlight, to form tropospheric ozone, which is a constituent of photochemical smog, and secondary organic aerosol [13, 14]. VOCs also react with stratospheric ozone causing its reduction and increasing the hole in ozone layer which protects life from ultra violet rays. This will expose people to dangerous ultra violet rays and cause eyes and skin cancer [15]. About 142 Tg of carbon per year in the form of VOCs is emitted by anthropogenic sources [16]. Fuel evaporation from gasoline tanks is one of the main sources of VOC production from road vehicles. The U.S. National Emission Inventory reports that the quantity of VOCs produced by USA on-road vehicles in 2014 was equal to 1.68 million tons, that is 6.7% of the total amount of pollutants from vehicles, after carbon monoxide (77.5%) and oxide nitrogen (13.9%) [17]. Furthermore, the Emission Database for Global Atmospheric Research reports that in 2015 the quantity of Non-Methane Volatile Organic Compounds produced by road transportation on a global scale is the 20% of worldwide NMVOC production [18]. This drives the need to limit VOC emissions from vehicles by directly acting on the fuel tank geometry and materials, and by developing efficient containment systems, as described below.

1.2 Gasoline and Evaporative Emissions Classification

Unburned hydrocarbon emissions are mainly due to gasoline evaporation from vehicle fuel tanks. Commercial gasoline is designed and produced to have a certain level of volatility, in order to be able to form a mixture with air as uniform as possible in the short time that goes from the fuel injection to the ignition in the combustion chamber. Of course, the volatility is determined by the gasoline composition. Gasoline is a homogeneous mixture of over 120 different components, many of them being small and lightweight hydrocarbons ranging from 4 to 12 atoms of carbon per molecule, typically paraffins, olefins and cycloalkanes [19]. Its composition varies according to the country, the regulations enfoced and the season (for instance, during the winter and/or in a cold weather country, a more volatile gasoline is needed to guarantee its evaporation in the engine). It is common to blend gasoline with oxygenate compounds, like methanol and ethanol, since their usage as alternative fuels has proven to be cost effective, thanks to their reduced production cost, and to reduce the pollutant tailpipe emissions of carbon monoxide and hydrocarbons, thanks to the higher concentration of oxygen. Ethanol-blended gasolines are adopted in many countries around the world, with different ethanol percentages, that goes from 5% to 85% (volume of ethanol with respect to the volume of the gasoline mixture); these ethanol-gasoline mixtures are

indeed named after their ethanol concentration, with an "E" followed by the percentage (e.g. E5, E20, E85). In Europe, thanks to the introduction of the new regulation Euro 6D, the content of ethanol in the commercial gasoline is gradually shifting from 5% to 10%.

The parameter that is used for classifying a gasoline for its volatility is the saturation vapor pressure, which is evaluated experimentally, under specific conditions of temperature and volume. The experimental procedure changes among the regulations, therefore, this property can be named Reid Vapor Pressure (RVP, commonly used in North America), Dry Vapor Pressure Equivalent (DVPE, commonly adopted in Europe), True Vapor Pressure (TVP) and Air Saturated Vapor Pressure (ASVP), but, generally, it is evaluated at a constant temperature of T = 37.8 °C (which corresponds to 100 °F), by placing a sample of gasoline in a movable piston chamber and expanding its volume until the volumetric ratio between the vapor and the liquid phases is equal to 4: the fuel vapor pressure corresponds to the desired value [20–23]. A higher vapor pressure corresponds to a higher volatility of the gasoline. However, this is of course a disadvantage for evaporative emissions, which increase with the vapor pressure.

While tailpipe emissions are classified based on their chemical composition, evaporative emissions, which are essentially HCs, are classified according to the way they are produced and released in the environment. Typically, evaporative emissions sources are of five types:

- *Running losses* occur when the vehicle is in motion. They are mainly caused by two factors: the liquid fuel sloshing, inside the fuel tank, which increases the vapor-liquid interface and, more important, increases the kinetic energy of the fuel itself, thus giving the fuel more opportunity to evaporate; the heat coming from the engine cooling system (which is usually placed in front of the vehicle, while the tank is on the back), which increases the temperature of the fuel inside the tank and brings the fuel to evaporate. For this reason, fuel tanks can be equipped with baffles that limit the fuel sloshing effect, and can also have insulation covering to prevent the fuel to be excessively heated by the engine and the surrounding environment.
- *Hot soak losses* are caused by the engine latent heat during the engine cooling down phase, immediately after the vehicle has been parked. The hot soak period lasts for

about $1 \div 2 h$ after the engine is shut down, until the whole vehicle has reached the environmental temperature. This type of emissions interests not only the fuel tank, but the entire fuel system, i.e. the high pressure fuel pump, the injectors and the hoses of the fuel delivery and return lines, in which remains some fuel and which are closer to the engine.

- *Permeation losses* are due to the fuel vapor permeation through plastic and rubber elements that compose the fuel system. Generally, the fuel tank is built with a material (or a layered composition of different materials) that minimizes the permeation, but if it is mainly made of plastic (e.g. high density polyethylene) the fuel permeation cannot reach negligible values. For this reason, metallic tanks are spreading during the last years, that are able to drastically reduce permeation losses, at least for the tank system, since the other components of the fuel delivery system are still made of plastic.
- Diurnal breathing losses (DBLs) are the most important losses in terms of potential quantity. They occur when the vehicle is parked and are caused by the oscillation of the thermal conditions of the environment in which the vehicle is placed. A fuel tank temperature rise causes two effects, which are the fuel evaporation and the increase in specific volume of the air-vapor mixture that fills the volume of the fuel tank that is not occupied by the liquid fuel (ullage volume). These two effects contribute to the increase of the total vapor pressure inside the fuel tank, which can reach unsafe values (that can cause fuel tank deformation or even structural failures) if the tank is isolated from the environment. Hence, the tank must communicate with the environment, in a way that avoids the fuel vapors to be released in the ambient (this system is described in the next session). On the other hand, when the temperature drops, the fuel vapor condensates and the vapor specific volume reduces, allowing for external air to enter the tank (hence, breathing). If the vehicle remains in these conditions for a long time (more than 2-3 days), the fuel vapor quantity that can be released in the environment due to fuel tank breathing could be a serious danger in terms of pollution. Therefore, different systems are used to contain DBLs.
- Refueling losses are generated during the refueling operation, which is the most



Figure 1.1: Techniques adopted to reduce refueling losses: (a) Stage II; (b) ORVR.

critical situation in terms of hydrocarbon release quantity. The fuel tank ullage space is occupied by a mixture of air and fuel vapor in equilibrium with liquid gasoline, which, during the normal functioning of the vehicle, always remains in the fuel tank. During the refueling operation, fresh fuel coming from the gas station enters the fuel tank and pushes out most of the vapor mixture in few seconds, generating a high fuel vapor flow. Hence, different strategies are commonly adopted to avoid this source of pollution. In general, two techniques have been adopted during the years to control this source of pollutants: Stage II and ORVR. The former, currently used in Europe [24], consists in recovering petrol emissions by the suction through the fuel delivery nozzle and subsequent deposit inside the underground fuel tank of the gas station (Figure 1.1(a)). The fuel vapor will then be stored in the tanker that supplies new fuel to the gas station (Stage I). On the other hand, ORVR (Onboard Refueling Vapor Recovery), widely adopted in USA [25], is a car-integrated system, which consists of using a filter connected to the tank in order to store vapors (Figure $(1.1(b))^2$. The Stage II system has the advantage of rapid implementation and no need of vehicle fleet retrofitting, while the ORVR cannot be installed on vehicles that do not have fuel vent systems. However, Stage II requires significant capital investment and maintenance costs, and it is less efficient than ORVR [26].

This work will focus on the last two types of emissions, and on how to predict them in

²The ORVR configuration also requires the use of a particular receptacle, equipped with a Venturi nozzle, that creates a small depression when the fuel passes inside it, which also sucks air from the nearby environment, in order to avoid fuel vapors to escape through the receptacle itself.



Figure 1.2: Different fuel tank shapes.

order to optimize the design of the components of the evaporative emission control system to limit the hydrocarbon emissions.

1.3 Fuel Tank and EVAP System

The fuel tank is the main component of the fuel system on a combustion-engine powered vehicle: along with the engine fuel efficiency, it is the element that characterizes the driving range of the vehicle, which is dependent on its maximum fuel capacity. Fuel tanks can have very different shapes, as shown in Figure 1.2, since they do not usually need to have a particular shape for their purpose. Therefore, unless in the case of specific applications, the fuel tank is designed after the definition of most of the components of the vehicle. Hence, for each vehicle a specific fuel tank is developed, in order to optimize the available space. Moreover, different fuel tank systems are developed for the same vehicle, depending on the fuel type used by the engine and the region (Europe, North America, etc.) in which the vehicle will be sold.

In general, the fuel tank is made of high density polyethylene (HDPE), shaped by



Figure 1.3: Schematic representation of a common fuel tank.

blow molding. HDPE is a thermoplastic polymer made from ethylene, characterized by a high strength-to-density ratio and a moderate resistance to high temperatures (usually, up to 120 $^{\circ}C$). Its properties make the HDPE a very common used plastic for applications that require a certain level of robustness. However, HDPE is permeable to most of the hydrocarbons that compose the gasoline, hence, fuel tanks walls are often composed by several layers of HDPE and other materials, to reduce the permeation losses. Another common technique is to realize fuel tanks by welding metal (steel or aluminum) into stamped sheets. A common material used for this applications is the Nickel-chromium steel, type AISI 304 and 316L. Advantages in using this type of material for tanks are of course a higher resistance to mechanical shocks and reduced permeability to hydrocarbons. However, they have an increased cost and weight with respect to the HDPE ones, which are two factors that are highly considered in the design and the production of an automotive vehicle.

A simplified, schematic representation of the main components of a common fuel tank system is given in Figure 1.3. The fuel pump, positioned at the bottom of the fuel tank, gives a certain preload to the fuel, to deliver it to the engine system (main pump and injectors). It is equipped with a system that detects the fuel level and, hence, the remaining fuel quantity (usually, this system is composed by a floating element that moves a rotating element, which varies the resistance of an electric circuit), which is communicated to the ECU and the user/driver. The headspace (also called vapor dome, or ullage space) is the part of the fuel tank that is not occupied by liquid fuel. It has a minimum volume, determined by the tank geometry and by the position of the Fill Limit Vent Valve and the Roll Over Valves, to guarantee a certain tolerance to fuel expansion and to preserve the canister filter functioning. The Fill Limit Vent Valve (FLVV) is a ventilation valve that puts the tank headspace in communication with the fuel vapor vent line, the canister filter and, therefore, with the environmental pressure. A common fuel tank headspace must be connected to the environment in order to avoid unwanted pressure differences between the vapor dome and the environment itself, which are caused by internal pressure variations due to temperature changes. A rise of the internal tank temperature causes a volumetric expansion of the vapor and also the evaporation of the fuel itself, which can increase the internal tank pressure of more than 300 mbar, if the fuel tank is isolated from the environment, bringing the system to an unsafe condition. On the other hand, a decrease of the internal temperature leads to under-pressures caused by the opposite phenomena, and, again, the pressure difference with the environment can reach unsafe values. The tank is also equipped with several Roll Over Valves (ROVs), which hermetically close the fuel tank if the tank is overturned, for instance, in case of an accident, to avoid the gasoline leakage in dangerous situations. The FLVV is also put in communication with the fuel line receptacle: during the refueling operation, when the fuel level inside the tank reaches the FLVV, it closes a floating system inside the valve that communicates a pressure increase through this pipe and up to the receptacle; this pressure variation is then perceived by a sensor on the gas nozzle that interrupts the fuel delivery (by releasing the gas nozzle trigger) and stops the refueling process. Some tanks can also have baffles, to reduce the fuel sloshing and hence the running losses.

Given the need of tank headspace connection with the environment, and also the containment of the fuel vapors inside the vehicle system, the totality of the modern gasoline vehicles are equipped with an evaporative emission control system (called EVAP system). The most common EVAP system strategy consists of storing hydrocarbon vapors from the fuel tank in a canister filter, by adsorbing them in a porous structure made of activated carbons, when the vehicle is stationary (Figure 1.4(a)). Since the canister filter



Figure 1.4: Schematic representation of the EVAP system [27]: (a) canister loading phase; (b) canister purging phase.

capacity is limited, the adsorbed fuel vapor must be periodically purged (Figure 1.4(b)), and this is done by opening the Purge Control Valve (PCV), which is a solenoid valve controlled by the Engine Control Unit (ECU). This valve opening puts in communication the canister filter with the engine intake manifold, therefore, when the engine is on, the depression generated in the intake manifold allows for fresh air coming from the environment to flow through the canister filter and purge the activated carbons, thus making the fuel in vapor form available to the engine for combustion. The PCV is activated by the ECU when certain engine operating conditions are met, which are defined by the specific purging strategies developed by the vehicle manufacturer. In some conditions (e.g. when the engine is idling) the fuel vapors quantity that comes from the carbon canister can significantly change the air-fuel ratio that enters the engine, thus, the purging phase commonly requires the engine to be in closed loop conditions (the fuel injection is regulated depending on the data of the oxygen concentration in the exhaust gas, acquired by the lambda probe placed downstream the engine), in order to always have a stoichiometric mixture that burns into the cylinders (this is necessary for the correct functioning of the 3-way catalytic converter). The fuel tank is also vented by connecting it with the engine manifold, in order to contain the running losses. However, if the vapor generated during driving conditions is higher than the purging flow rate, it will eventually go to the canister and then contribute to its loading even during its purging phase. This system is also used for collecting refueling emissions in the North American vehicles, that must comply with the ORVR regulations, while in Europe the Stage II system is commonly adopted. In addition to the "active" purging performed when the vehicle is running, the canister can be also passively purged during parking events, when the environmental temperature decrease generates a depression inside the fuel tank that allows for fresh air coming from outside to go through the canister and then in the tank itself, partially purging the carbons. However, passive purging has a relatively small influence compared to the active one.

Finally, according to the in-force regulations (e.g. On Board Diagnostics II North American regulation, OBDII), a diagnostic system is required to be installed, that is able to detect the presence of leaks in the evaporating system (for instance, for OBDII the minimum leak required to be detected is equivalent to a 0.5 mm diameter hole). Commercial leakage detection systems usually consist of a solenoid valve placed downstream the canister that, when activated, closes the EVAP system, thus allowing the system to have small pressure increases or decreases, due to environmental temperature changes, after the engine is shut down. A possible leakage is detected by comparing the pressure evolution inside the fuel tank with predefined values. Pressure variation can also be realized by active components: an external actuator can realize positive or negative pressures inside the EVAP system, while negative pressure can also be obtained by connecting the system with the intake manifold.



Figure 1.5: Fuel Tank Isolation Valve.

1.3.1 Sealed Tanks

The most effective solution to limit evaporative emissions could be to use a sealed fuel tank, which can prevent hydrocarbons from escaping the fuel system. Sealed tanks are designed to resist to positive and negative pressure variations (up to 350 *mbar*) due to volumetric expansions and contractions, respectively, of the vapors inside the tank itself, which are caused by temperature variations (depending on the engine heat and the environmental temperature changes during the daytime), and to fuel evaporation and fuel vapor condensation, also caused by thermal variations. In order to fulfill these requirements, a sealed fuel tank must be properly designed for resisting higher pressures without excessive deformations. This usually requires two steps: the adoption of more resistant materials than HDPE, like steel, and the optimization of the tank geometry, that can no longer be shaped based on the available space, but needs to have a more "rounded" shape, to resist overpressures, and/or internal structures that help to avoid unsafe deformations.

Furthermore, the sealed tank is required to have a relief valve that avoids the vapor dome to reach unsafe pressure values and prevents the system failure (a sealed tank is designed to resist to a certain level of pressure, after that level it can have leakages or even deformations). This function is guaranteed by the Fuel Tank Isolation Valve (FTIV, Figure 1.5), which is a valve placed downstream the FLVV: it acts as a relief pressure valve in case of high positive pressures, and allows for back flow in case of excessive negative pressures. Moreover, this valve is also controlled electronically by the ECU, since it must always be opened before the refueling process: before the tank cap is opened, the pressure inside the fuel tank must be equal to the ambient pressure, to avoid the fuel vapor inside the tank (or even liquid fuel) to be ejected through the receptacle. Therefore, the sealed tank cannot be used without an EVAP system, that manages the vapors that escape the tank through the FTIV, even if the canister can be smaller than a non-sealed fuel tank case, since it does not need to store emissions during the entire functioning cycle of the vehicle.

The sealed fuel tank strategy has the advantage of drastically reducing the permeation losses and also limiting the DBLs, but of course it is more costly that the non-sealed one, in terms of the design of the components, materials, weight and complexity of the whole system, and does not allow to avoid the use of a canister filter and, hence, the necessity of its purging. Therefore, it is generally not adopted unless for specific cases, like hybrid applications. On a hybrid vehicle, the internal combustion engine can remain unused for a certain amount of time, depending on the capacity of the electric batteries. In some cases, like when the vehicle is used for short routes, the thermal engine does not have the possibility to purge the canister, which can easily reach the saturation and let the fuel vapors escape to the environment, when the vehicle is parked a second time. Hence, there is the necessity of a sealed tank system.

1.4 Canister Filter

The carbon canister filter is the main component of the EVAP system, the one that effectively prevents the fuel vapors to go outside the vehicle and into the environment as hydrocarbon VOCs. A carbon canister is essentially a plastic box filled with activated carbons. Activated carbons have a highly developed porosity and an extended interparticulate surface area. Activation is almost exclusively carried out by the pyrolysis of carbonaceous raw material at temperatures lower than 1000 °C.



Figure 1.6: Activated carbons: (a) example of carbonaceous material; (b) porous structure.

Carbon preparation usually involves two steps: the carbonization of carbonaceous raw material at temperatures below 800 $^{\circ}C$ in an inert atmosphere, and the activation (or oxidation) of the carbonized product. During the carbonization process, most of the non-carbon elements (e.g. oxygen, hydrogen, nitrogen) are eliminated as volatile gaseous species by the pyrolytic decomposition of the raw material. The residual carbon atoms are grouped into stacks of flat, aromatic sheets arranged in a random manner. This irregularity gives the material a porous structure, which makes activated carbons excellent adsorbents. During carbonization, these pores are filled with the tarry matter or the products of decomposition or at least blocked partially by disorganized carbon. This pore structure in carbonized char is further developed and enhanced during the activation process, which converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various sizes and shapes, giving rise to an extended and extremely high surface area of the product. Activation process is made by exposing the carbonized material to an oxidizing atmosphere at high temperatures (usually, between 950 $^{\circ}C$ and 1000 $^{\circ}C$). This process gives to carbonaceous material a highly developed porous structure and a very high specific surface area, which is usually between 800 m^2/g^3 and 1500 m^2/g for the most widely used activated carbon adsorbents, but can reach 2500 m^2/g for some particular applications [28].

Activated carbons performance is strongly dependent on the raw material and the

³Square meters of surface area per gram of activated carbons.

activation process, as well as the internal pore distribution (Figure 1.6(b)). Pores can be classified according to their dimensions: macropores (radii that exceed 50 nm), micropores (radii that do not exceed 2.0 nm) and mesopores (intermediate dimensions) [29]. Most of the adsorption occurs in micropores and a small amount in mesopores, while macropores only act as ducts for hydrocarbon molecules.

Adsorption is the result of unbalanced molecular forces that are present on every solid surface (the adsorbent), which tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atoms, or ions of the gas or liquid (the adsorbate). Adsorption involves two types of forces, physical forces and chemical forces, and, depending on these forces, the adsorption can be classified as: physical adsorption (or physisorption), in which the adsorbate is bound to the adsorbent surface by relatively weak Van der Walls forces, similar to molecular forces of cohesion; chemisorption, which involves electrons exchange or sharing between adsorbate and adsorbent molecules, resulting in a chemical reaction and, thus, generating a much stronger bond than the previous one. The most important difference between the two kinds of adsorption is the magnitude of the enthalpy of adsorption, which is the heat released during the adsorption process (and thus is also a



Figure 1.7: Examples of different canister geometries.

reference value for the energy required by the desorption process): for physisorption the enthalpy of adsorption is of the same order as the heat of liquefaction (usually less than $10 \div 20 \ kJ/mol$), whereas in chemisorption the enthalpy change is generally one order of magnitude higher than the previous $(40 \div 400 \ kJ/mol)$. Furthermore, while physisorption can occur between any adsorbate-adsorbent systems, chemisorption only occurs for specific systems (because of the chemical nature of the bond), therefore, it is possible, with chemisorption, to isolate and adsorb specific components from a fluid mixture, and that is the reason why this phenomenon is of great interest in pollution treatment. The adsorption process is highly dependent on adsorbent and adsorbate temperature conditions, and in general, adsorption performances decrease with increasing temperature; therefore, the process intrinsically decreases its performance, because of the heat released during the process itself.

A common carbon canister for automotive applications consists of a bed of activated carbons that are specifically treated to react with hydrocarbons coming from the fuel tank. As shown in Figure 1.7, automotive canisters can have different shapes and sizes, which can significantly change between different countries and world regions, since they must comply with different regulations. One of the main differences in shape is given by the difference in regulation regarding the refueling losses: canister designed for EVAP systems that must



Figure 1.8: Carbon canister filter, schematic representation: (a) loading phase; (b) purging phase.
comply the ORVR regulations (e.g. North American vehicles) usually have a bigger carbon bed volume (generally, $2 \div 3 L$) than the ones mounted on vehicles that circulate in regions in which the Stage II is adopted (e.g. European vehicles). The carbon bed is usually divided in several sections, or pockets, that are put in communication with each other; this structure helps the flow that comes from the fuel tank to gradually saturate each part of the canister before starting to be adsorbed by the successive section. Canisters are also equipped with a liquid separator, that prevents the liquid fuel to go inside the carbon bed (which drastically decreases the adsorption performance of the carbons), and an air filter for cleaning the air flow coming from outside during the purging phase.

As represented in Figure 1.8, a canister for vehicle applications has three gates, connected to the tank, to the engine intake manifold and to the environment, respectively. During the loading phase, the air-fuel vapor mixture flows from the tank gate through the canister bed, where the hydrocarbons are adsorbed, then, clean air exits towards the external ambient. During the purging phase, fresh air comes from outside through the environment gate and flows in the carbon bed, usually following a reverse path with respect to the loading one, exiting the canister to go to the engine intake manifold (the engine gate is often placed close to the tank one). Of course, the carbon canister storage is limited by the quantity of activated carbons that are present in it as well as the type of carbons. If a gasoline vehicle is parked for a long time, the canister can easily reach the saturation [30] and then all the fuel vapors coming from the tank are released in the atmosphere. That is the reason why the canister filter and, in general, the adsorption phenomenon are the subjects of numerous studies and regulations, as described in 2.3.

1.5 Evaporative Emissions Regulations

Given the impact of the unburned hydrocarbons on the human health and environment, several regulations have been developed during the years to limit the evaporative emissions by acting on their formation and their containment in the vehicle system. The United States, and in particular, the State of California began to introduce regulations about evaporative emission from light-duty vehicles since the late 1960s [31]. The State of California enforced

the first tailpipe emissions standards in 1966, and a year later the California Air Resources Board (CARB) was established [32], which still remains a worldwide reference in terms of pollutant emission from automotive vehicles. The U.S. Environmental Protection Agency follows the State of California in 1971, when gasoline vehicles were enforced to be equipped with an evaporative emissions control system designed to store and dispose of fuel vapors preventing them from escaping into the atmosphere [33]. Following these developments, other agencies around the world have enacted regulations related to fuel volatility and evaporative HC emissions. Japan started around the same time as the US but eventually adopted the EPA standards, suitably modified to reflect Japanese conditions, in 1978 [34]. Many countries of the European Union started in 1989 to adopt UN regulation n. 83 [35], on the evaporative emissions control, while only in 1998, with the regulation 98/69/EC[36], limitations on evaporative emissions were enforced with the directives Euro 3 and 4. The UN regulation n. 83 later evolved in the UNECE Global Technical Regulation n. 19 [37]. The GTR-19 was the first attempt to unify the regulations regarding evaporative emissions on a global scale: it uses the U.S. EPA and Japanese standards as a basis, but it is less stringent due to regional differences, that regard average temperature, refueling emissions requirements and fleet composition of each region. This regulation has been enforced with the WLTP EVAP from September 2019. Figure 1.9 gives an overview of the main regulations about evaporative emissions, currently adopted around the world. It is possible to notice the presence of two main regulations, which are the North American EPA Tier x standards⁴ and the European Euro x standards, differently applied in the totality of the developed countries, with some modifications to adapt the restriction to the local climate and resources (e.g. gasoline).

The evaporative emissions regulations have in common the use of specific equipment to evaluate hydrocarbon emissions from a vehicle: the use of a Sealed Housing for Evaporative Emissions determination (SHED) is mandatory for most of these regulations (Figure 1.10). A SHED is a sealed, explosion-proof chamber, generally made of steel, in which a light-duty vehicle is placed, generally after one or more preconditioning drive cycles, in order to

 $^{^4{\}rm The}$ EPA Tier 3 has the same emission limits of the CARB LEV III, to harmonize the federal certification testing with California requirements.



Figure 1.9: Overview of the evaporative emissions regulations adopted worldwide [38].

evaluate the total amount of unburned hydrocarbons produced by the vehicle during parking conditions (hot soak losses and DBLs). It is equipped with a conditioning system that allows for temperature changes, in order to simulate the diurnal temperature variations to which a common vehicle is exposed, along with a pressure compensation system that regulates the pressure during temperature variations. Evaporative emissions are evaluated by means of a Flame Ionization Detector (FID), which measures the concentration of organic species in the SHED environment by detecting the ions formed during the combustion of organic compounds in a hydrogen flame. It is also equipped with an air recirculating system and several safety devices.

In Figure 1.11 it is reported the flowchart of the test procedure for hot soak and DBL determination, according to the UNECE GTR-19. Before the beginning of the hot soak tests (point 6.5.7 in the flowchart, which lasts for 1 h), the sampled vehicle must go through several preparation steps, that includes two soaks, various fuel tank drain and refills, and a preconditioning drive (which follows the WLTP cycle). Moreover, the canister filter must also be preconditioned, with an "ageing" procedure that consists of several temperature variation cycles (where temperature goes from -15 to $60 \ ^{\circ}C$), vibration cycles and loading/purging cycles with n-butane and nitrogen⁵. Permeation

⁵According to the regulation, the canister must be loaded with n-butane at a flow rate of 40 g/h, in



Figure 1.10: Variable Temperature Sealed Housing for Evaporative Determination [39].

losses are estimated by means of a permeability factor (PF), which is evaluated with a soak test that totally lasts 20 weeks⁶. The hot soak test is executed inside the SHED at a temperature $T = 23 \div 31 \ ^{\circ}C$, where the vehicle is placed immediately after a dynamometer test (where follows a driving cycle which depends on the vehicle class) and the quantity of hydrocarbons is recorded (M_{HS}) . Then, the diurnal breathing losses are evaluated, during two cycles of 24 h in which the SHED temperature is changed to simulate daily conditions (temperature goes from 20 to 35 $^{\circ}C$ and back to 20 $^{\circ}C$ in 24 h). The hydrocarbon emissions are evaluated for each day $(M_{D1}$ and M_{D2} , respectively). Finally, the total evaporative emission contribution of the sampled vehicle is evaluated as follows:

$$M_{TOT} = M_{D1} + M_{D2} + M_{HS} + 2 \cdot PF \tag{1.1}$$

mixture with nitrogen at 50% in volume, and then purged with pure nitrogen at a flow rate of 25 L/min for a total volume equal to 300 times the carbon bed volume. This cycle mus be applied for a total of 300 times, to evaluate the Butane Working Capacity (BWC, see also chapter 4).

⁶The sampled vehicle with a tank filled at 40% of its nominal capacity is soaked at T = 40 °C for 3 weeks, then the tank is drained and refilled, and the vehicle is soaked for the remaining 17 weeks, at the same temperature. After 3 weeks and then after 20 weeks, the hydrocarbons are evaluated with the same procedure applied for the first day of the diurnal test (mass of HC). The permeability factor is given by the difference: $PF = M_{20w} - M_{3w}$.



Figure 1.11: UNECE GTR-19 test procedure for hot soak and DBL determination [37].

and this quantity must be less than 2.0 g, to comply the regulation. It is possible to notice that sealed fuel tank must be tested with a slightly different procedure, to also consider the so-called puff losses, which are the losses derived by the FTIV opening.

Other regulations slightly differ from this pattern, for instance, the previous European regulation (Euro 6c) requires only one diurnal cycle, with the same limit on the total mass of hydrocarbons, while the U.S. EPA regulation requires three days for the diurnal test, with an higher temperature variation.

It is clear that the EVAP system performance must be continuously improved because of these regulations, that become more stringent every year. The research activity presented in this thesis has the objective of providing useful tools to simulate and develop the tank and the EVAP canister in order to reduce VOCs emission and comply with the regulations.

Chapter 2

EVAP modeling

2.1 Evaporation and discussion on complexities to model fuel evaporation

Evaporation is a non-equilibrium phase transition that involves simultaneous exchange of both heat and mass. At the vapor-liquid interface, molecules can detach from the liquid surface and become vapor at any temperature as long as the molecules can acquire enough kinetic energy to break free from intermolecular forces [40].

Studies of the evaporation process can generally be divided into "microscopic" and "macroscopic" approaches. Based on kinetic molecular theory and statistical physics, microscopic modeling of evaporation estimates the distribution of molecular velocity and uses the estimated distribution function to derive the conservation equations of mass, momentum and energy [41]. An illustration of the vapor-liquid system is in Figure 2.1 [42].

The velocity distribution in the non-equilibrium transition layer should satisfy the Boltzmann equation. In short, the Boltzmann equation describes the time evolution of $f(\mathbf{x}, \mathbf{v}, t)$, the probability density function at time t in the phase space (\mathbf{x}, \mathbf{v}) , where $\mathbf{x} = [x_1, x_2, x_3]^T \in \mathbb{R}^3$ represents the 3D Euclidean space and $\mathbf{v} = [v_1, v_2, v_3]^T \in \mathbb{R}^3$ represents velocities in corresponding coordinates. The total number of molecules which



Figure 2.1: Illustration of vapor-liquid two-phase system [42]

have positions and velocities in a region of the phase space is:

$$N_{x,v} = \int_{velocities} \int_{positions} f(\mathbf{x}, \mathbf{v}, t) d\mathbf{x} d\mathbf{v}$$
(2.1)

The Boltzmann equation for rarefied monoatomic molecules with no external force field is:

$$\frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{x}} = \left(\frac{\partial f}{\partial t}\right)_{coll} \tag{2.2}$$

The right hand side of eq. 2.2 $\left(\frac{\partial f}{\partial t}\right)_{coll}$ is the collision term corresponding to forces acting between particles in collision, a nonlinear integral of $f(\mathbf{x}, \mathbf{v}, t)$ only with respect to **v**:

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int \int g\left(u, \frac{\mathbf{un}}{u}\right) \left[f(\mathbf{v}_A')f(\mathbf{v}_B') - f(\mathbf{v}_A)f(\mathbf{v}_B)\right] d\mathbf{v}_B d\mathbf{n} \frac{\partial f}{\partial t} + \mathbf{v} \frac{\partial f}{\partial \mathbf{x}}$$
(2.3)

with:

$$\mathbf{u} = \mathbf{v}_A - \mathbf{v}_B , \ u = |\mathbf{u}| , \ g(u, \mu) = u\sigma(u, \mu) ,$$

$$\mathbf{v}'_A = \frac{1}{2}(\mathbf{v}_A + \mathbf{v}_B + u\mathbf{n}) , \ \mathbf{v}'_B = \frac{1}{2}(\mathbf{v}_A + \mathbf{v}_B - u\mathbf{n})$$
(2.4)

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where \mathbf{v}_A and \mathbf{v}_B are the velocities of two arbitrary molecules A and B before collision; \mathbf{v}'_A and \mathbf{v}'_B are their velocities after collision; the relative velocity of these particles has been acquired as a result of collisions in a direction along the unit vector $\mathbf{n} \in R^3$, and $d\mathbf{n}$ is the element of area of the surface of the unit sphere in R^3 . The function $\sigma(u,\mu)$ is the differential cross section of scattering through angle $\bar{\theta} \in [0,\pi]$ in the center-of-mass system of the colliding molecules, where u > 0, $\mu = \cos \bar{\theta}$ are the arguments. The quantity $\sigma(u,\mu) > 0$ depends on the chosen model of molecules [41, 43].

Due to the complexity of the Boltzmann equation, it is hard to solve the velocity distribution analytically, unless significant simplifications are made [40]. The velocity distribution function at the surface of the condensed phase (to be understood to mean "liquid" in the remainder of the paper) surface may be described by two half-Maxwellian distributions - one for the molecules emitted by the liquid surface into the liquid-vapor transition layer, and the other for the ones incident on the surface from the bulk vapor space. When more molecules are emitted than incident, the net mass transfer goes to the vapor from the liquid. With further simplifications, the velocity distribution is usually a function of: molecular mass, temperature at the liquid surface and the corresponding vapor (saturation) pressure at that temperature, molecular velocity at the surface, pressure, temperature, and hydrodynamic velocity in the bulk vapor space [41, 43–46]. Furthermore, the existence and uniqueness of exact solutions are not guaranteed and they have been extensively investigated in various disciplines for different applications [47–51].

The molecular velocity distribution in the liquid-vapor transition layer sets the boundary condition for the bulk vapor region, where one may continue to apply microscopic modeling methods [40]. On the other hand, macroscopic modeling is usually applied to represent fluid dynamics of evaporation in the vapor space. Fluid dynamic parameters, e.g. density and pressure, that are defined according to conventional rules of statistical averaging cannot fully describe the nonequilibrium character of evaporation near the condense-phase surface in the Knudsen layer. However, gas dynamics equations are sufficient to capture the behavior in the bulk vapor space, with carefully determined boundary conditions [41].

The evaporation of liquid hydrocarbon fuels, which is the focus of this thesis, has been the subject of studies related to: the environmental impact of hydrocarbon spills on land and water; the evaporation of fuels within the context of combustion engines (with emphasis on droplet and spray formation at high temperature and pressure); and the evaporative emissions associated with combustion fuels used in ground vehicles.

The term "evaporation rate" is often used in macroscopic modeling of the evaporation process. A generic semi-empirical rate of air-boundary-layer regulated evaporation, such as water evaporation, can be represented as:

$$E_R \ge KCT_u S \tag{2.5}$$

where E_R is the rate in mass per unit area, K is the mass transfer rate at given conditions, C is the mass of the evaporating fluid per unit volume, T_u is a factor indicating the intensity of turbulence and S is a factor affected by the boundary layer above the liquid [52]. It is highly dependent on the physical properties of the evaporating liquid as well as environmental conditions.

Sutton's model for water evaporation is:

$$E_R = K C U^{7/9} d^{-1/9} S c^{-r} (2.6)$$

where U is the wind speed, d is the area of evaporation surface, r is an empirical value in the range [0, 2/3], and Sc is the Schmidt number [52, 53]. Mackay et al. adapted Sutton's model for Cumene (C_9H_{12}) evaporating from a pool of water and derived the corresponding heat transfer dynamics for liquid and vapor temperatures [52, 54]. They also developed the evaporative molar flux N, mole per unit time, driven by the difference between the pressure of hydrocarbon vapor at the liquid surface (P) and in the bulk gas phase (P_{∞}) . For a single hydrocarbon, the molar flux is:

$$N = K_m A_s (P - P_\infty) / (R T_l)$$

$$(2.7)$$

where: K_m is an empirical coefficient lumping all transport conditions which may include turbulence speed and Schmidt number of the hydrocarbon; A_s is the evaporation surface area; R is the gas constant; and T_l is the liquid temperature [54, 55]. When P_{∞} is smaller than P, the net mass transfer is from liquid to vapor. If P_{∞} reaches P, the flux becomes zero and the net mass transfer from liquid to vapor is zero. Since the liquid-vapor interface region very close to the liquid surface is almost saturated at vapor pressure P_{sat} , P is assumed to be equal to P_{sat} . Therefore, when the vapor space and the evaporating liquid are at the same constant temperature, generation of vapor will continue until equilibrium vapor pressure is reached in the entire vapor space.

Evaporation is a complicated process to model even for a pure compound. The following section will discuss how gasoline, a mixture of over 100 constituents, and a storage system like a fuel tank in an automobile requires more sophisticated modeling to determine the key factors contributing to evaporation such as vapor pressure and surface area.

Vapor pressure or equilibrium vapor pressure of a liquid is the pressure exerted by a vapor in thermodynamic equilibrium above its liquid in a closed system. The equilibrium vapor pressure of a material is a physical characteristic that depends on the liquid temperature. The higher the liquid temperature is, the more kinetic energy molecules have on average and the higher the vapor pressure. For pure substances, there exist semi-empirical correlations between vapor pressure and temperature. There are several well-established formulas to approximate saturation water vapor pressure, like the Arden Buck equation which has been proved to be most accurate in the range [-80, 50] °C:

$$P_{sat}(T_v) = 0.61121 exp \left[\left(18.678 - \frac{T_v}{234.5} \right) \left(\frac{T_v}{257.14 + T_v} \right) \right] , \text{ over water, } T_v > 0$$

$$P_{sat}(T_v) = 0.61115 exp \left[\left(23.036 - \frac{T_v}{333.7} \right) \left(\frac{T_v}{279.82 + T_v} \right) \right] , \text{ over ice, } T_v < 0$$
(2.8)

where T_v is air temperature in $^{\circ}C$ and P_{sat} is the saturation pressure of water in kPa. The standard testing methods such as ASTM D323A can be used to determine a fuel sample's vapor pressure, Reid Vapor Pressure (RVP), at 37.8 $^{\circ}C$ with vapor space to liquid ratio of 4 [56]. Another standardized vapor pressure measure is Dry Vapor Pressure Equivalent (DVPE) as defined in ASTM D5191. Nowadays, DVPE has become more popular and widely used compared to RVP, because the test procedure for DVPE is faster and DVPE is considered more precise than RVP [21]. EPA provides a general correlation of true vapor pressure with RVP of refined petroleum stocks using additional information from ASTM D86 distillation curve for a specific fuel type:

$$P_{sat}(T_l) = exp\left\{ \left[0.7553 - \left(\frac{413}{T_l + 459.6}\right) \right] s^{0.5} log_{10}(RVP) - \left[1.854 - \left(\frac{1042}{T_l + 459.6}\right) \right] \cdot s^{0.5} + \left[\left(\frac{2416}{T_l + 459.6}\right) - 2.013 \right] log_{10}(RVP) - \left(\frac{8742}{T_l + 459.6}\right) + 15.64 \right\}$$

$$(2.9)$$

where P_{sat} is in psi, T_l in ${}^{\circ}F$, s is the slope of the distillation curve at 10% evaporated, in degrees Fahrenheit per percent, and RVP is in the range $[1, 20] psi [57]^1$.

Other approaches to model fuel vapor pressure are usually based on individual constituent vapor pressure, fuel blend composition information and experimental data for calibration [58–63]. The equilibrium vapor pressure for various pure organic compounds can be estimated by the Antoine equation,

$$P_{sat} = 10^{A - \frac{B}{C + T_l}} \tag{2.10}$$

where A, B, C are empirical coefficients that can be found in chemistry hand-books such as the National Institute of Standards and Technology Chemistry WebBook [64]. Multiple sets of coefficients corresponding to multiple temperature intervals are often used to represent pressure correlations over a greater temperature range below critical point [65]. However, the tank temperature increases at most 20 °C from the controlled starting temperature of 35 °C after several standard US driving cycles [66]. European vehicles show similar behavior during various driving cycles as their tank temperatures fluctuate from 20 °C

¹By using P_{sat} and RVP in kPa, and T_l in K, the equation becomes:

$$P_{sat}(T_l) = exp\left\{ \left[0.6333 - \left(\frac{192.4}{T_l}\right) \right] s^{0.5} log_{10}(RVP) - \left[1.854 - \left(\frac{579}{T_l}\right) \right] s^{0.5} + \left[\left(\frac{1125}{T_l}\right) - 1.688 \right] log_{10}(RVP) - \left(\frac{4857}{T_l}\right) + 13.71 \right\}$$

to 40 °C, indicating an increase about 20 °C [67]. During the course of 24 hours, the combined effects of diurnal temperature change and driving cycles may cause the fuel tank temperature to fluctuate from 15 °C to 54 °C [68]. It is therefore usually sufficient to use one set of Antoine equation parameters corresponding to one set of temperature range when calculating vapor pressures of constituents in fuel. For example, the [272.66, 425] K section for n-butane is able to cover most operating conditions.

Finding the vapor pressure of mixtures of liquids can be difficult. If the intermolecular forces between similar molecules are identical to those between dissimilar molecules, the heat of mixing is zero and the solution is called ideal. In an ideal solution, the activity of a constituent is proportional to its composition. Vapor pressure of an ideal solution obeys Raoult's law [69], which is the sum of all the products of the vapor pressure of pure constituents, $P_{sat,i}$, and their corresponding mole fractions in the solution, x_i :

$$P_{sat} = \sum_{i} P_{sat,i} x_i \tag{2.11}$$

On the other hand, the vapor pressure can deviate from Raoult's law in a non-ideal solution. If the attraction between dissimilar molecules is weaker than similar molecules, molecules of each kind will have greater tendency to escape from the solution into the vapor than from each pure liquid. The result is a positive deviation, that is the partial pressure of each constituent is higher than the one predicted from Raoult's law. Large positive deviations are observed in mixtures of liquids which differ distinctly in polarity, internal pressure, length of hydrocarbon chain and degree of association, e.g. an alcohol and a hydrocarbon. Negative deviations exist as well when the reverse process happens in systems like chloroform-acetone and water-nitric acid [70].

To better approximate the properties of non-ideal solutions, a dimensionless correction factor called activity coefficient is used to account for the deviations from ideal scenario [70]. In any appropriate formulae, a constituent's 'strength', i.e. mole fraction, concentration or partial pressure, is replaced by its respective 'activity' that is the product of the activity coefficient and the 'strength'. For ideal solutions, the activity coefficient approaches one for every constituent and 'activity' is equal to 'strength'. Otherwise, a positive deviation is represented by an activity coefficient greater than 1; and negative, smaller than 1. Activity coefficients are often empirically calculated for a constituent at a given temperature and a given composition. The vapor pressure of a solution can then be approximated by:

$$P_{sat} = \sum_{i} P_{sat,i} x_i \gamma_i \tag{2.12}$$

where γ_i is the empirical activity coefficient for constituent *i*.

Determining the vapor pressure of a binary solution can already be challenging in physical chemistry, let alone to estimate the vapor pressure of gasoline, a mixture over 100 compounds. Automotive gasoline composition varies from region to region and season to season to meet different requirements such as combustion quality, fuel economy and emission standards [71]. Moreover, detailed fuel composition is only available in a laboratory environment; information of certain constituents, e.g.: ethanol percentage may be available, but refiners do not usually disclose information of major influential constituents to the public, e.g.: n-butane whose boiling point is -1 °C, and is therefore a critical element when considering fuel evaporation.

In addition to equilibrium vapor pressure and liquid temperature, surface area also affects the rate of evaporation. The same amount of liquid solution will evaporate faster if the surface area is larger between liquid and vapor. When the liquid is sitting still, the surface area does not change significantly. When waves form, e.g. fuel sloshing, the area fluctuates considerably and swiftly, while it is also difficult to determine. Other factors in evaporation include the number of molecules in the liquid that can evaporate. Fuel level can be an indicator. However, automotive fuel tanks rarely have geometries whose volume and surface are that can be easily calculated at any fuel level. In addition, any vent or adsorption mechanism in the storage system will affect the evaporative mass transfer rate by influencing the vapor space pressure.

As a result, evaporation modeling of fuel in an automotive fuel tank system merits particular theoretical and experimental work. The next section concentrates on this special case of evaporation modeling.

2.2 Tank evaporation modeling

Through the years, many mathematical models have been developed in order to estimate the fuel evaporation losses from a vehicle fuel system. The first attempts were made by Wade and Koehl at the end of the 1960's, when regulations about air pollution were adopted for the first time in California and the California Air Resources Board (CARB) was established.

Wade [72] split the evaporation problem in two parts, analyzing the fuel losses from the carburetor and the fuel tank in different ways. Since the carburetor has become obsolete, a study of fuel losses from it is not relevant for the scope of this research, but the approach used to analyze them can still be interesting. Laboratory tests were conducted by using a distillation apparatus connected to a carbon canister, whose weight was monitored by a precision weight scale (see Figure 2.2). This approach demonstrated that the evaporation from a carburetor bowl can be represented by one plate distillation curves. A one plate distillation curve can be evaluated by approximation from the equilibrium flash vaporization curves of the fuel components. That implies knowledge of the composition of the fuel and the equilibrium data for all of them, which are not easy to obtain. However, for an evaporative analysis, the principal compounds of interest are the ones with less than 8 carbon atoms, which represent the major fraction of an automotive fuel; therefore, the heavier compounds can be lumped into groups, with characteristics approximated by those of similar known species.

Then, Koehl [73] also compared the weight loss percentage from a carburetor bowl $(\%Wt_d)$ and the volume distilled percentage $(\%V_d)$ at the peak bowl temperature (T), according to ASTM distillation method D216 (now updated in D86), by using a linear correlation:

$$\% W t_d = a \ \% V_d - b \tag{2.13}$$

The slope a and the intercept b must be evaluated empirically for each carburetor. An experimental analysis on different types of carburetors and fuels was performed, to obtain



Figure 2.2: One-plate distillation apparatus, after [72].

average values of a and b capable of representing the average behavior of the passenger vehicle fleet at the time of the study.

Wade [72] and Koehl [73] considered the bulk vapor flow during temperature cycles as the principal mechanism of fuel tank losses, neglecting the diffusion contribution, as they also did in carburetor loss analysis. According to their study, when the tank temperature rises, either due to engine heat or to daily temperature increase, the vapor in the tank expands and flows out of the tank, since the tank is vented to the atmosphere. Furthermore, the equilibrium fuel vapor pressure rises with temperature, so the liquid fuel vaporizes to restore equilibrium. As consequence of both the factors, some fuel vapor will be expelled by the tank into the atmosphere. Since the fuel vapor quantity changes with temperature, it cannot be treated directly. However, since no new air mass is generated, the air quantity (n_a) expelled during the temperature increase from T_1 to T_2 is given by a simple balance on the vapor tank volume (V):

$$n_a = \left[\frac{\left(P_{tank} - P_f\right)V_u}{R T_v}\right]_1 - \left[\frac{\left(P_{tank} - P_f\right)V_u}{R T_v}\right]_2$$
(2.14)

where P_{tank} and P_f are total and fuel vapor partial pressures in the tank. If all the vapor escaped from the tank is collected in a large bag (at constant pressure P_{atm}), the quantities of air (n_a) and fuel vapor (n_f) in that bag are:

$$n_a = \frac{(P_{atm} - P_{f,bag}) \ V_{bag}}{R \ T_v} ; \qquad n_f = \frac{P_{f,bag} \ V_{bag}}{R \ T_v}$$
(2.15)

Combining equations (2.14) and (2.15) and considering a compressibility factor to correct for non-ideality, the quantity of collected fuel vapor in the bag can evaluated as follows:

$$n_f = \frac{P_{f,bag}}{\left(P_{atm} - P_{f,bag}\right)C_f} \cdot \left[\left[\frac{\left(P_{tank} - P_f\right)V_u}{R T_v} \right]_1 - \left[\frac{\left(P_{tank} - P_f\right)V_u}{R T_v} \right]_2 \right]$$
(2.16)

The compressibility factor (C_f) was evaluated by Wade and Koehl as an empirical function of molecular weight of fuel vapor (W_f) , density of condensed vapor $(\rho_L$, which is assumed equal to the fuel density) and vapor pressure [74], but it could be evaluated in different ways.

The difficulty with this method described in [74] is how to determine the fuel partial pressure. For small temperature increases, the fuel partial pressure $P_{f,bag}$ in the bag can be assumed equal to the average of the partial pressures at $T_{v,1}$ and $T_{v,2}$. There are several methods for determining P_f ; one of these is described by the American Petroleum Institute [74]: it involves the conversion of RVP to true vapor pressure at 37.8 °C, by knowing the slope of the ASTM distillation curve at 10% evaporated, and a series of tables and equations for estimating the pressure at the desired temperature.

This model has a fairly good agreement with the experimental data, but it has some limitations. It requires that fuel liquid and vapor be in equilibrium, and that implies a slow change of the temperature. Furthermore, the model works only under non-boiling conditions. In addition, total tank pressure must be constant, in general, equal to the ambient pressure, but this is not always true: if the tank is equipped with a relief valve, the pressure must reach the relief value (by thermal expansion and evaporation) before it starts to lose vapor fuel; so, the evaluation of losses should start in that moment. Because of the increasing interest in oxygenated gasolines, new studies and models were developed to take into account the effects of alcohol as a gasoline-blending component. It has been shown [75–77] that alcohol (methanol and ethanol) increases the octane quality of unleaded gasoline and reduces tailpipe CO and HC emissions, but of course increases gasoline volatility and consequently evaporative emissions.

A study by Reddy [78] aimed to describe the evaporative behavior of oxygenated fluid blends by evaluating the fuel vapor pressure as the sum of the partial pressure of the fuel components. The partial pressure of the i-th component is given by the following equation:

$$P_i = \frac{\gamma_i x_i}{\phi_i} P_{sat,i} \tag{2.17}$$

where x_i is the mole fraction of the *i*-th component, $P_{sat,i}$ is its pure vapor pressure (calculated by using the Antoine equation, [64, 79]), γ_i is the activity coefficient and ϕ_i is the fugacity coefficient, used to correct the non-ideality of the vapor phase. It could be estimated by different non-ideal equations of state [80]: in his model, Reddy cited the Redlich-Kwong equation, but subsequent studies [81] showed a better agreement with experimental data by using the Soave modification of the Redlich-Kwong equation.

The activity coefficient was evaluated by the UNIFAC theory (Universal Functional Group Activity Coefficients, an extension of the UNIQUAC quasi chemical theory of liquid mixtures) [82]. This method is based on the group-contribution concept: a physical property of a fluid is given by the sum of the contributions made by each functional group that forms the molecule of the compound. Therefore, it is possible to evaluate the activity coefficient of each of the hundreds of hydrocarbons that compose a common fuel by knowing some geometrical and interactional parameters of a little number of functional groups.

For evaluating the fuel losses, Reddy used a similar approach of the one developed by Wade and Koehl, but he evaluated the evaporated number of moles (eq. (2.16)) for each component:

$$n_{i} = \frac{P_{i,bag}}{(P_{atm} - P_{f,bag})} \left[\frac{(P_{tank} - P_{f})_{1}}{R T_{v,1}} - \frac{(P_{tank} - P_{f})_{2}}{R T_{v,2}} \right]$$
(2.18)

in which $P_f = \sum P_i$. As before, for tanks without any pressure controls, initial tank pressure, final tank pressure and total pressure in the bag are equal to the atmospheric pressure, while if the tank has a pressure relief valve, then they are all equal to the relief pressure. Finally, the total mass of hydrocarbons that escapes from the tank is given by the sum of every n_i times its molecular weight (W_i) , without the approximation given by the evaluation of an average fuel vapor molecular weight (W_f) , necessary in Wade equation.

This model has similar limitations as the one described previously: it is not applicable at temperatures greater than the fuel boiling point and it requires the equilibrium between liquid and vapor fuel implying, as before, a slow temperature increase. Furthermore, it requires knowledge of the fuel composition. However, in a fuel mixture only one hundred components are present in appreciable quantities, and some of them are isomers, which are represented as a single component since the UNIFAC method makes no distinctions between them. With these considerations, Reddy was able to analyze a common alcohol-blended fuel with only 37 components and 16 functional groups, obtaining a very good agreement with experimental data performed on several fuels (oxygenated and non-oxygenated) under both hot soak and diurnal cycle tests. From these studies, Reddy derived some nomographs [83] for evaluating the fuel vapor generation from a fuel tank, normalized with respect to the vapor volume space, in function of temperature and RVP (Figure 2.3).

It is possible to notice a quasi-linear trend between the temperature increase and the logarithm of tank vapor generation. It has also been noticed in a previous work [84] that diurnal vapor generation increases exponentially with the fuel RVP. Combining these two effects, the tank vapor generation, per unit of ullage volume, can be written as follows:

$$\frac{m_{VL}}{V_u} = Ae^{B(RVP)} \cdot \left(e^{C \ T_2} - e^{C \ T_1}\right)$$
(2.19)



Figure 2.3: Nomographs for estimating tank vapor generations: (a) with gasolines; (b) with 10% ethanol blends compared to gasolines of matched RVP [83].

A, B and C were evaluated for alcohol and non-alcohol blends and for different ambient pressures by comparing eq. (2.19) with the results that can be found by using the model described by eq. (2.18) and the UNIFAC method.

This equation was then validated with SHED test experiments and other laboratory tests. Its agreement to experimental data was also compared with the one of the EPA modified Wade equation [85], showing an excellent agreement ($R^2 = 0.97$), while the Wade-EPA model overestimated the experimental data ($R^2 = 0.57$).

This equation was then recently used by Mellios et al. [86], as a part of an empirical model developed by the authors for estimating evaporative emissions from a vehicle during parking conditions. The authors performed several tests on different cars by following the European Standard SHED test procedure, in which the temperature varies from 20 to $35^{\circ}C$ and then returns to $20^{\circ}C$ in 24 h, and also many tests made by changing the temperature interval $(25 - 40^{\circ}C \text{ and } 10 - 25^{\circ}C)$. By measuring the canister weight before and after each test and adding the measured diurnal emissions, they obtained the data

needed for calibrating the Reddy equation (e.g. values of A, B, C) and then validating it. However, the agreement with experimental results found in this study was not so high as the one found by Reddy in his studies, even if it still remains fairly good ($R^2 = 0.65$).

Other studies have demonstrated the lack in predictivity of the Reddy equation. In particular, after having performed a series of experimental tests by means of a SHED, Hata, Yamada et al. [87] have evaluated the same agreement of the Reddy equation with experimental data as the one found by Mellios. Starting from the assumption of ideal gas for the fuel vapor in the ullage space, they derived a theoretical correlation between the vapor generated and the minimum and maximum temperature values. RVP is considered by using the Clausius-Clapeyron equation. However, since this correlation is generally derived for pure components, its introduction to a complex system such as gasoline generates a mathematical error. Therefore, an exponential dependence between RVP and fuel vapor generate is applied:

$$P_f = RVP^{1/2} \cdot exp(\alpha_{RVP} \cdot RVP) \tag{2.20}$$

Then, it is possible to derive the following:

$$\frac{m_{VL}}{V_m} = \frac{W_f \cdot P_f}{\Delta H_m} \left[exp\left(\frac{\Delta H_m}{R} \cdot \left(\frac{1}{T_{RVP}} - \frac{1}{T_2}\right)\right) - exp\left(\frac{\Delta H_m}{R} \cdot \left(\frac{1}{T_{RVP}} - \frac{1}{T_1}\right)\right) \right]$$
(2.21)

in which ΔH_m is the molar enthalpy for fuel vaporization (J/mol), estimated by a linear correlation with RVP ($\Delta H_m = -157 \cdot RVP + 39415$, in which RVP is in kPa). V_m is the sum of the tank ullage volume (V_U) and the parameter $V_e x$, which represents the tank backup volume and the refueling pipe inner volume; since there is less information about this value, it is treated as a calibration parameter, along with α_{RVP} in (2.20). This equation has a better agreement ($R^2 = 0.80$) with the experimental data collected by the authors in previous studies [88] than the Reddy correlation, and it has only two calibration parameters to evaluate. However, since the study was mainly conducted on vehicles available in the Japanese market, the authors do not exclude the possibility that this equation could improve the estimation of fuel vapor generation only in this context. This equation was then implemented in a step model of the EVAP system, which estimates the breakthrough emissions along with the canister loading level [89].

The models presented so far are all based on the vapor-liquid equilibrium (VLE) and they are relatively accurate in predicting evaporated fuel vapor and its composition [73] [78], but they are not easy to use, because they require the fuel composition as an input data, along with the properties of most of the components, which evolve with the fuel evaporation itself.

Lavoie et al. [62] developed a simpler approach to determine the fuel vapor pressure and then the evaporated fuel quantity, which also includes the weathering effect (FVSMOD). They based their model on the empirical observation, made by Edmister and Okamoto [90], that, for a given fuel, the relationship between its vapor pressure (P_{sat}) and temperature (T) at fixed mass fraction evaporated (Z^2) can be represented by straight lines on a log Pvs. 1/T plot. Furthermore, all these lines, obtained for different values of Z, pass through a common focal point (P_{foc}, T_{foc}) . This result can be represented as follows:

$$P_{sat} = P_{foc} \cdot e^{-E(RVP, Z) \cdot \left(\frac{1}{T} - \frac{1}{T_{foc}}\right)}$$
(2.22)

where E is the slope of these lines, dependent on RVP and Z. Along with the focal point, another point is needed to determine the value of E. This could be given by an independent P,T,Z relationship.

The authors performed an experimental distillation analysis on several fuel types, using a distillation procedure that slightly differed from the ASTM D86 standard method, in order to have the same temperature in liquid and vapor phases: a pre-weighted fuel sample is heated in a water bath with slowly temperature increase (Figure 2.4).

After the bath reaches the desired temperature and liquid vapor equilibrium is established, the measured weight loss provides the fuel percent distilled at that temperature. This process is repeated to build up a distillation curve. It has been found that, under

 $^{^{2}}Z = m_{f}/m_{l,0}$; ratio between evaporated mass and initial liquid mass.



Figure 2.4: Equilibrium distillation apparatus, after [62].

equilibrium conditions, the distillation curve can be represented by a linear correlation between the boiling temperature T_b and Z, for Z < 0.2:

$$T_b(P,Z) = T_{b0}(P) + AZ$$
 (2.23)

in which $T_{b0}(P)$ is the Initial Boiling Point (IBP) at pressure P, which is empirically evaluated, along with the slope A. Then the distillation curve that passes through the point at which RVP is evaluated will be:

$$T(P_f = RVP, Z) = T_{RVP} + A \left(Z - Z_{RVP}\right)$$

$$(2.24)$$

where $T_{RVP} = 37.8 \ ^{\circ}C = 100 \ ^{\circ}F$ is the temperature at which the RVP is evaluated [20], while Z_{RVP} is the mass fraction evaporated during the RVP test, which can be estimated as follows³

$$Z_{RVP} = \frac{1}{1 + \frac{\rho_L R T_{RVP}}{4 RVP W_f}}$$
(2.25)

Inserting eq. (2.24) in eq. (2.22), it is possible to find E as a function of Z (and fuel properties A, P_{foc} , T_{foc} , RVP). Then the vapor pressure equation is:

$$P_{sat} = P_{foc} \cdot e^{\frac{ln\left(\frac{RVP}{P_{foc}}\right) \cdot \left(\frac{1}{T} - \frac{1}{T_{foc}}\right)}{\frac{1}{T_{RVP} + A \left(Z - Z_{RVP}\right)} - \frac{1}{T_{foc}}}}$$
(2.26)

This equation can be used to evaluate the vapor generation during time.

Lavoie et al. [91] assumed that the evaporation driving force is the difference between the fuel vapor pressure, in equilibrium with its liquid phase at a specific temperature and mass fraction evaporated, and the partial pressure in the fuel tank (P_f) , which in general are not equal because of the finite rate of evaporation. The vapor mass generation rate is:

$$\dot{m}_{VL} = K_m \frac{W_f}{R T} A_s (P_{sat} - P_f)$$
 (2.27)

It is also proportional to the liquid - vapor interface (A_s) and to the mass transfer coefficient (K_m) , which includes the effects of diffusive resistance in both liquid and gas phases⁴. P_f can be evaluated by the ideal gas law along with the air partial pressure $(P_a)^5$, assuming the fuel vapor behavior not to be so different from the ideal, for small

$$Z = \frac{m_f}{m_{l,0}} = \frac{m_f}{m_f + m_L} = \frac{1}{1 + \frac{m_L}{m_f}} = \frac{1}{1 + \frac{V_L}{V_u} \frac{\rho_L \ R \ T_v}{P_f \ W_f}}$$

where, in the RVP test, the ratio V_u/V_l is 4.

 ${}^{4}K_{m}$ was found empirically by the authors, as a calibration parameter; it is equal to 0.1 m/s.

³With the hypothesis of ideal gas, the mass fraction evaporated can be estimated as:

⁵In evaluating P_a , it was also considered the dissolved air in fuel, described by a Henry's law behavior [62, 92]; the Bunsen coefficient α_B is assumed equal to 0.185.

evaporations:

$$P_f = \frac{m_f R T}{W_f V_u} \quad ; \qquad P_a = \frac{m_a R T}{W_a \left(V_u + \alpha_B \left(\frac{T}{273 K}\right) V_l\right)} \tag{2.28}$$

 m_f and m_a are fuel vapor and air mass in the tank vapor space (ullage), and they are evaluated by mass balances on the ullage space, in which \dot{m}_{fX} and \dot{m}_{aX} are fuel vapor and air mass flows exiting the tank (which are dependent on the fuel vent system).

Suitable models for filling, supply-return and vent lines were added to this model. Finally, an equation for estimating the evolution of the mass fraction evaporated was carried out⁶:

$$\frac{dZ}{dt} = \frac{(1-Z)\,\dot{m}_{VL} + \frac{1-Z}{1-Z_{FILL}}\,(Z_{FILL}-Z)\cdot\dot{m}_{FILL}}{m_L}\tag{2.29}$$

A fuel vapor system was built up using equations (2.26) to (2.29), along with other balance equations (for m_L , m_{aU} , m_{fU} dependent on \dot{m}_{FILL} , $\dot{m}_{sup/ret}$), a suitable energy conservation equation and a canister model. This approach led to a good agreement with

$$\frac{dZ}{1-Z} = \frac{dm_f}{m_L} = \frac{-dm_L}{m_L} \qquad or \qquad d\left[\frac{m_L}{1-Z}\right] = 0 \tag{a}$$

If the composition of the fuel through the evaporation only depends by Z, the liquid fuel carries the memory of its original mass, that is the specific property $\eta = 1/(1-Z)$ (because the quantity $m_L/(1-Z) = m_{L,0}$ is constant). In contrast, vapor carries no memory of it. Therefore, a useful relation for Z can be derived from the conservation of the "specific" original fuel mass η :

$$d(m_L \eta) = -\eta \ dm_{out} + \eta_{in} dm_{in} \tag{b}$$

This is a general conservation equation, in which both input (from filling and return line) and output (supply line) are considered; for the output flow, of course, η is the same as the one of the liquid tank fuel, while in general the input one is different. The conservation on the liquid mass only is:

$$dm_L = -dm_{out} + dm_{in} - dm_f \tag{c}$$

Combining equations (b) and (c):

$$m_L d\eta = \eta \ dm_f + (\eta_{in} - \eta) \ dm_{in} \tag{d}$$

and substituting $\eta = 1/(1-Z)$ leads to eq. (2.29).

⁶For evaluation of eq. (2.29), some considerations about Z must be done. First of all, for a given mass of fuel that evaporates only (no filling or supply flows), the rate of change of Z is $dZ = dm_f/m_{l,0} = dm_f(1-Z)/m_L$; this relation can also be written as follows:

experimental data obtained by a 3-day diurnal test, and a reasonable agreement was found in refueling emission tests with a low-temperature fuel and in running-loss tests.

The principal limitation of this model is that the fuel is considered as a "pseudo" single component, whose properties vary only because of the variation of Z, and the vapor composition remains constant. This is not strictly true, but it can be acceptable for small evaporation fractions (Z up to 20%) and for fuels that do not change significantly their composition during the evaporation. The accuracy of the model will be degraded if there will be considered mixing fuels of different RVP or highly oxygenated fuels.

More recently, Ghadirian et al. [93] developed a quasi-steady 1D model for fuel evaporation, that also considers the fuel vapor diffusion into air. The authors solved the Fick's second law for one spatial dimension, which is a 1D partial differential equation for the fuel vapor concentration C_f (evaluated in mol/m^3) along the coordinate z (the distance from the liquid- vapor interface):

$$\frac{\partial C_f(z,t)}{\partial t} = D_f \cdot \frac{\partial^2 C_f(z,t)}{\partial z^2}$$
(2.30)

with the initial and boundary conditions as follows:

$$C_f(z,0) = C_{f,i}$$
 (2.31a)

$$C_f(0,t) = C_{f,sat} = \frac{P_{sat}(T)}{RT}$$
 (2.31b)

$$\frac{\partial C_f(L,t)}{\partial z} = 0 \tag{2.31c}$$

where D_f is the mass diffusivity coefficient of fuel vapor in air (m^2/s) , $C_{f,sat}$ and P_{sat} are the saturation fuel vapor concentration and pressure (the vapor is considered in equilibrium with its liquid phase at the liquid-air interface), while L is the maximum height of the vapor dome. Three methods for evaluating the saturation pressure were adopted and compared. The first method is the Antoine equation, the second and the third evaluate the saturation pressure by using an approach based on an American Petroleum Institute procedure [94], which involves the use of the normal boiling point T_b . The normal boiling point can be evaluated from an experimental distillation curve (second method) or by using RVP and the slope of the distillation curve (third method). This model was incorporated in the commercial software GT-SUITE, to implement the geometry of the fuel tank and solve the thermal equations for the wall and the liquid fuel. The mass diffusivity coefficient and a Scaling Factor for Normal Boiling Point were used as calibration parameters. The model was then calibrated and validated with the experimental results obtained by [83] and [91], by using an optimization tool included in the GT-SUITE software. Good results were obtained in evaluating the fuel mass evaporated and escaped from the fuel tank.

2.3 Canister modeling

A common vehicle canister consists of a bed volume of activated carbons that adsorb the fuel vapors generated from the fuel tank. Adsorption is an exothermic process in which a component in its fluid phase can be attracted on the surface of a solid material. This process is highly dependent on the temperature conditions: in general, adsorption performances decrease with the temperature. Activated carbons are very good adsorbents, mainly thanks to their large interparticle surface area and their pore distribution, that involves macro, meso and micropores in which the adsorbate molecules diffuse and then are trapped [95]. Adsorption and desorption phenomena are of great interest in pollution treatment, not only in the field of vehicle emissions [96]. Therefore, these phenomena have been subject of many studies, and many theoretical and empirical models have been derived. In general, the first approach is to analyze the equilibrium condition that can be established between an adsorbate in its fluid phase and in its adsorbed phase, under constant temperature (adsorption isotherm) [28]. In addition, the dynamic adsorption condition is also studied, which is usually considered as a transition phase between two equilibrium conditions, so that its discussion starts from the adsorption isotherm [97, 98].

2.3.1 Langmuir approach

The first contribution to the development of an adsorption isotherm was given by Langmuir [99, 100]. He derived an equilibrium equation assuming: the adsorbent surface is flat and homogeneous, so that the adsorption energy is constant on the surface; particles are adsorbed on surface at definite localized sites; each site can adsorb only one particle. From these hypotheses it can be derived that only one layer of adsorbate is possible and that an adsorbate particle has the same probability to be adsorbed on each vacant site. A dynamic equilibrium is assumed, and from the equality of adsorption and desorption rates the following equation can be derived:

$$\theta = \frac{C_L P_i}{1 + C_L P_i} \tag{2.32}$$

where θ is the fractional coverage, P_i is the pressure of the adsorbate in its gas phase and C_L is a constant⁷ that depends on temperature and heat of adsorption, that is the released heat during the exothermic process (equal to the activation energy necessary for desorption). The simplicity of this equation has made it very popular and many works based their equilibrium theory on this approach, although many deviations from this model were often noticed in several experimental data. That is mainly due to the ideality of its hypotheses, in particular the independence of the energy of adsorption from the coverage status. Even if the Langmuir equation (2.32) is of limited applicability, this approach has led to other more complex isothermal equations and non-equilibrium models.

Freundlich [101] and then Temkin [102] derived Langmuir-based equations that take into account the adsorption heat dependency on coverage. The Temkin equation considers a linear decrease of E_A :

$$\frac{\theta}{1-\theta} = C_L \ P_i \exp\left[\frac{E_A}{RT}\right] = C_L \ P_i \exp\left[\frac{E_{A0}(1-\alpha\theta)}{RT}\right]$$
(2.33)

 $^{{}^{7}}C_{L} = \frac{k_{ads}}{k_{des}} \exp\left(\frac{E_{A}}{RT}\right)$; parameters that must be found are only the ratio $\frac{k_{ads}}{k_{des}}$ (adsorption and desorption reaction rate multipliers) and the energy of adsorption E_{A} .

where E_{A0} is the value at $\theta = 0$.

Brunauer, Emmett and Teller [103] developed another Langmuir-derived isotherm equation, considering the multilayer adsorption and assuming that the particles in the second and subsequent layers are bounded by condensation forces: each layer acts as adsorbent for the following one.

$$\theta = \frac{C_{BET} P_i}{(P_{sat} - P_i) \left[1 + (C_{BET} - 1) P_i / P_{sat}\right]}$$
(2.34)

in which the constant $C_{BET} = exp[(\Delta H_A - \Delta H_L)/RT]$ depends on temperature and the difference between heat of adsorption and condensation. This approach is applicable for nonporous and macroporous surfaces, but not for microporous and non-homogeneous surfaces such as activated carbons. Furthermore, its applicability is within the relative pressure range (P_i/P_{sat}) of 0.05 \div 0.30 [28, 96].

The Langmuir adsorption isotherm was largely used also as a base for non-isothermal and non-equilibrium models, that are more similar to a real canister adsorption situation. Considering an adiabatic fixed bed of activated carbons filled with a single adsorbate (or a solution in which the solvent, or carrier gas, is considered not to interact with the sorbent surface, like nitrogen), many experimental and numerical investigations [97, 98, 104–106] showed that the interaction between mass transfer and heat generation and transfer phenomena during adsorption (or desorption) can lead to two principal situations in the adsorbed mass and temperature values along the fixed bed: (a) a wave on the temperature profile (temperature vs. space) precedes a single transfer zone in which both gas-phase concentration and temperature vary; (b) there are two zones in which there is a variation in both temperature and concentration, and between them a static region. The latter is the situation that mostly occurs. Regarding this situation, Cooney [97] developed a system built with two basic partial differential equations that represent continuity of solute (adsorbate) concentration and energy balance in time (t) and space (x):

$$\frac{\partial Y}{\partial t} + v \frac{\partial Y}{\partial x} + \frac{\rho_s \left(1 - \epsilon\right)}{\widetilde{\rho}_g \epsilon} \frac{\partial q}{\partial t} = 0$$
(2.35)

50

$$\frac{\partial T_g}{\partial t} + v \frac{\partial T_g}{\partial x} + \frac{\rho_s \ c_{ps} \ (1-\epsilon)}{\widetilde{\rho}_g \ \widetilde{c}_{pg} \ \epsilon} \frac{\partial T_s}{\partial t} + \frac{\Delta H_A \ \rho_s \ (1-\epsilon)}{\widetilde{\rho}_g \ \widetilde{c}_{pg} \ \epsilon} \frac{\partial q}{\partial t} = 0$$
(2.36)

where Y, q, T_g and T_s are gas-phase adsorbate molar fraction, solid-phase solute concentration, gas and solid temperatures and ϵ is the void fraction. Concerning the concentration in the adsorbed phase, a LDF approach was used, in which the adsorbed rate is given by the difference between the actual concentration and an equilibrium value (q^*) given by a Langmuir-like equilibrium equation:

$$\frac{\partial q}{\partial t} = \frac{K_{m,C} a_s}{\rho_s} (q^* - q)$$
(2.37)

$$q^* = \frac{0.15 \ C_L(T_s) \ Y}{1 + 40 \ C_L(T_s) \ Y}$$
(2.38)

$$\frac{\partial T_s}{\partial t} = \frac{h_s \ a_s}{\rho_s \ c_{ps}} \ (T_g - T_s) - \frac{\Delta H_A}{c_{ps}} \frac{\partial q}{\partial t}$$
(2.39)

The temperature dependence in the Langmuir equation is included in the constant C_L . The last equation is the energy balance for the solid phase. Solutions of this system pointed out some relevant differences between q and q^* , and T_g and T_s , to underline the non-equilibrium behavior of the adsorption phenomena.

Sircar and Kumar [98] simplified this approach, noting that the trend of the principal variables of the system $(Y, q \text{ and } T_g)$ in the adsorption "active" zones⁸ does not change significantly during time, but it only shifts towards the fixed bed. This so-called constant pattern behavior allows to simplify, under certain hypotheses, the two partial differential equations system into an algebraic system. This approach was then used by the authors to find analytical solutions for the bulk single-component adsorption and for the dilute adsorption, in which the single adsorbate component in the gas-phase solution has a very low concentration with respect to the gas mixture. The system is also solved numerically

⁸In which the space derivative is different from 0.

for evaluating the multi-component adsorption of a binary mixture in which the two species have different selectivity⁹. This approach allows to greatly simplify the system resolution and leads to interesting analytical and numerical solution. However, it represents a strong approximation of the phenomenon, applicable only when the adsorbed mass and temperature trends can be well approximated by the constant pattern model.

Generally, in a bulk component adsorption case, the interaction between vapor concentration and temperature generates more complex profiles. Therefore, a general numerical approach to the phenomenon is more realistic. Hwang et al. [107] proposed a nonequilibrium, non-adiabatic and non-isothermal model for a bulk single component system, using a Langmuir-like adsorption isotherm and adopting the LDF model for both mass and heat transfer rates. However, there are relevant differences between this model and the one developed by Cooney [97]. First, the system is diabatic, so that an energy balance equation is added to describe the heat exchange between the carbon column and the external environment. Then, the flow velocity is considered as an unknown variable: in a dilute-sorption case, the mass flow rate changes in the gas flow due to adsorption are negligible, so that it is possible to consider negligible the velocity in equations (2.35) and (2.36); however in the bulk-sorption case its variation can be relevant, so that it was added as unknown variable. A six coupled-PDE system was derived, with the following variables: adsorbent concentration in the bulk gas (c_i) , gas velocity (v), adsorbate concentration in solid phase (q), gas, solid and wall temperatures (T_g, T_s, T_w) .

The system was first used to compare the profiles of the dependent variables derived from the isothermal and the adiabatic conditions to the ones evaluated for a non-equilibrium, non-isothermal, non-adiabatic condition, showing how complex the dependence of the adsorbed mass on the temperature could be. Then, the dependence on the values of the transport parameters was investigated: mass transfer coefficient $(K_{m,C})$, heat transfer coefficient between gas and wall (h_w) , heat transfer coefficient between gas and solid phase (h_s) and heat transfer coefficient between wall and ambient (U_a) . The values of $K_{m,C}$ and h_w have a strong influence on the profiles of the variables, while the values of h_s and U_a

⁹The selectivity S_{ij} is defined as the measure of the competitiveness of adsorption between the components of a gas mixture.

have a little influence, except for gas and solid phase temperatures.

System outputs were then compared with experimental results. Equilibrium adsorption isotherms for carbon dioxide and activated carbons were measured by using a volumetrictype apparatus (with a method which is similar to the one described in Appendix A), obtaining results which are consistent with those from previous studies [108]. Another apparatus was used for the non-equilibrium tests, in which a carbon dioxide flow, premixed with helium at various molar fractions, is injected in a column of activated carbons. Temperature is measured at the half of the column, and a breakthrough measurement was realized by means of a thermal conductivity detector. The system was then calibrated, by evaluating mass and heat transfer coefficients, K_p and h_w , and validated with these data, showing a correct trend prediction of the total sorbed quantity and middle-bed temperature during time.

Another interesting experimental analysis was realized by Fiani et al. [109]. It was carried out on a very small activated carbon sample (a 30mg carbon cylinder), filled with a n-butane/nitrogen mixture, whose temperature and weight were dynamically measured by a micro-thermocouple and a TGA¹⁰ apparatus. Regarding a modeling description of the experimental results, the small dimensions of the carbon sample, combined with a high gaseous mixture flow rate, allows to neglect the effects of internal and external diffusion of the adsorption rate and to consider a uniform temperature in the sample and a forced convection through the sample surface, so that the derived model only consists of a 0D time-dependent energy balance and an equation for the adsorption and desorption quantities (k and k' are kinetic constants for adsorption and desorption processes, evaluated by the Arrhenius law):

$$\frac{\partial \theta}{\partial t} = k P_i (1 - \theta) - k' \theta \qquad (2.40)$$

Good agreement is found between the simulated and measured results, although this

¹⁰Thermogravimetric Analysis.

analysis is limited to a very small carbon sample, not considering the effects of a larger bed, diffusion and slower heat dispersion.

Recently, a Langmuir adsorption/desorption kinetic mechanism was introduced by Smith et al. [110] in a 1D model developed and solved in a fluid-dynamic software (GT-SUITE) that represents the whole vehicle vent system, and so the carbon canister, in order to support the design and development of the EVAP system and optimization of Engine Management Systems strategies. The canister model was developed by using a flow-through catalyst substrate to represent the porous media, on which chemical reactions were applied to simulate the hydrocarbon adsorption/desorption. Reaction rates follows the Langmuir mechanism of kinetic equilibrium. This system was then validated with results from an experimental adsorption/desorption analysis executed on a NAS¹¹ carbon canister put on a precision weight scale and filled with a desired n-butane and nitrogen mixture flow, until breakthrough; the desorption phase was realized by using a purging flow of pure nitrogen.

The interesting part of such approach is that there is the opportunity to couple this model to a 1D engine model to simulate the canister purging realized by the engine suction phase. This coupling was realized by the authors to simulate a 2.0L GTDi engine vehicle subject to an FTP-75 driving test cycle, which was also experimentally emulated. Comparisons on purge flow rate and canister temperatures show a good correlation between model and experimental data.

2.3.2 Vacancy Solution Model

The Langmuir method is seen to be one of the most important theoretical approaches to the adsorption equilibrium, but since it mostly refers to ideal solutions cases it is seen to have some lacks in prediction of the adsorption behavior. Suwanayuen and Danner [111] proposed a solution theory model which involves a hypothetical solvent called "vacancy", that is defined as the vacuum space that can be filled by the adsorbate molecules. Therefore, the pure-component adsorption can be seen as a phase equilibrium between two solutions

¹¹North America Specification.

of different compositions, one for the gas phase, the other one for the adsorbed phase, in which the vacancy acts as a solvent. So that an equilibrium equation can be derived by equating the two chemical potentials of the gas and adsorbed solutions¹²:

$$P_1 = \left[\frac{q_1^{\infty}}{b_1}\frac{\theta}{1-\theta}\right] \left[\exp\left(-\int \frac{d\ln\gamma_v^s}{\theta}\right)\right] \left[\lim_{\theta\to 0}\exp\left(\int \frac{d\ln\gamma_v^s}{\theta}\right)\right]$$
(2.41)

where it can be noticed that the first RHS term represents the ideal Langmuir isotherm $(q_1^{\infty} \text{ is the limiting amount adsorbed of component 1, which is the unique component in the pure adsorption case), while the other two are functions of the activity coefficient <math>\gamma_v^s$ of the vacancy in the adsorbed phase and the surface coverage θ . Suwanayuen and Danner evaluated that coefficient by using the Wilson equation, so that equation (2.41) can be written as follows:

$$P = \left[\frac{q_1^{\infty}}{b_1}\frac{\theta}{1-\theta}\right]f(\Lambda_{1v}, \Lambda_{v1}, \theta)$$
(2.42)

in which the non-ideality term can be evaluated by means of the Wilson parameters (Λ_{ij}) .

This model was seen to be effective in prediction of experimental data¹³ Cochran et al. [112] proposed a different approach to evaluate the activity coefficient: the Wilson parameters have found to be highly correlated $(\Lambda_{1v} \cdot \Lambda_{v1} \rightarrow 1)$, so that they used the Flory-Huggins theory, that introduced a correlation parameter α_{1v} , defined by means of molar surface areas of the adsorbed species (a_1) and the vacancy (a_v) :

$$\alpha_{1v} = a_1/a_v - 1 \tag{2.43}$$

 $^{^{12}}$ Eq. (2.41) is obtained combining the state equation derived from equating the two chemical potentials with an isothermal relation based on the Gibbs adsorption approach [95, 112].

¹³Experimental data were taken by other authors data, who evaluated isotherms by means of similar experimental apparatuses, based on the difference in gas volume between initial and equilibrium adsorbed conditions. Experimental procedures are summarized in Appendix A, but it is complex to apply, and it is not able to explicitly include the effect of temperature.

Therefore, the VSM-FH equation for a single-component adsorption becomes:

$$p = \left[\frac{q_1^{\infty}}{b_1}\frac{\theta}{1-\theta}\right] \cdot \exp\left(\frac{\alpha_{1v}^2 \theta}{1-\alpha_{1v}^2 \theta}\right)$$
(2.44)

in which the calibration parameters $(q_1^{\infty}, b_1, \alpha_{1v})$ can be evaluated by experimental data, regressing individual isotherms (isothermal method) or regressing multiple isotherms simultaneously (temperature correlation method), by determining the values of q_{01}^{∞} , r_1 , b_{01} , ΔH_A , m_1 from the equations:

$$b_1 = b_{01} \exp\left(-\frac{\Delta H_A}{RT}\right)$$
 $q_1^{\infty} = q_{01}^{\infty} \exp\left(\frac{r_1}{T}\right)$ $\alpha_{1v} = m_1 q_1^{\infty} - 1$ (2.45)

An interesting aspect of the VSM approach is that it is possible to evaluate equilibrium distribution of the i-th gas species in a multi-component adsorption condition starting from the single-component parameters. This aspect was analyzed for both the Wilson [113] and Flory-Huggins [112] approaches. In particular, the VSM-FH approach was able to predict wide range of binary and ternary adsorption equilibria, with a better accuracy than any previous models.

As showed before with the Langmuir model, also the VSM-FH model was used as a theoretical basis for describing a non-equilibrium, non-isothermal and non-adiabatic adsorption and desorption, as Huang and Fair did [114]. They proposed a dynamic model for describing the multi-component adsorption on a fixed-bed adsorbent, under several hypotheses: constant pressure, dilute gas phase (adsorbate molar fraction from 0 to 1.5 %), no carrier gas adsorption, negligible radial gradients (1D approach), gas heat capacity negligible compared to the solid one, all transport coefficients independent of concentration, mutual interactions taken into account only through isothermal equation. A PDE for each component is derived based on concentration balance in the gas phase, along with energy balances for the gas phase, the solid phase and the whole column wall. An LDF model is used in deriving the non-equilibrium mass transfer rate between gas and adsorbed phases, which is similar to the one expressed in eq. (2.37), but based on the gas concentration difference:

$$\frac{\partial q_i}{\partial t} = \frac{K_{m,HF,i} \ a_s \ (1-\epsilon)}{P_s} \ (y_i - y_i^*) \tag{2.46}$$

The mass transfer mechanism is described in detail, in order to derive a suitable value for the overall mass transfer coefficient $K_{m,HF,i}$:

$$\frac{1}{K_{m,HF,i}} = \frac{1}{k_{fi}} + \frac{R_p}{5 \ D_{pe,i}}$$
(2.47)

$$D_{pe,i} = D_{pi} + D_{si} \ \rho_s \frac{\partial q_i}{\partial c_i} \tag{2.48}$$

The mechanism includes four steps: fluid-film transfer, pore diffusion, surface adhesion and surface diffusion. In general, surface adhesion is essentially instantaneous, so that its rate is not considered, while the other contributions are fluid-film mass transfer coefficient k_{fi} , porous diffusion D_{pi} and surface diffusion D_{si} .

The five parameters for describing the single-component adsorption $(n_{01}^{\infty}, r_1, b_{01}, \Delta H_A, m_1)$ were found for both propane and ethane, on a specific activated carbon, by means of an experimental activity, which involves a test bench with two FIDs for evaluating equilibrium. Then, this model was validated with experimental data obtained by the adsorption and desorption of a two-component mixture, propane and ethane, strongly dilute with helium or nitrogen, on a fixed bed of activated carbons¹⁴. The model is seen to have a good agreement with experimental data, even if the temperature is often overestimated because of the neglection in model of the radial heat conduction and the heat conduction along the wall (in axial direction).

¹⁴Comparison parameters were temperature at middle and final points of the adsorbent bed and concentration of propane and ethane exiting the bed (breakthrough quantity in the adsorption phase, purge quantity in the desorption phase), during time.
2.3.3 Potential Theory

The potential theory of adsorption was first introduced by Polanyi [115, 116] and then modified and developed by Dubinin and Coworkers [117, 118]. This theory is based on the idea that molecules are attracted by the adsorbent depending on their distance from the adsorbent surface. This dependence is represented by the adsorption potential ε . Each equipotential surface encloses a volume V between itself and adsorbent surface (the maximum volume is enclosed by the last equipotential surface, for which $\varepsilon \to 0$):

$$\varepsilon = f(V) \tag{2.49}$$

The fundamental assumption is that this relationship is temperature-independent. The adsorbate that goes from $\varepsilon = 0$ to a generic ε is compressed. Therefore, the potential energy is equal to the inverse of differential Gibbs free energy, that is the isothermal work required for increasing pressure from the component partial pressure P_i to the desired pressure at given ε :

$$\varepsilon = -\Delta G = RT \ln\left(\frac{P}{P_i}\right) \tag{2.50}$$

With the hypotheses of vapor acting like an ideal gas, temperature well below vapor adsorbate critical temperature and incompressible liquid, the adsorption potential is:

$$\varepsilon = RT \ln \left(\frac{P_{sat,i}}{P_i}\right) \tag{2.51}$$

Dubinin [119] noted that adsorption potential curves $\varepsilon = f(V)$ for different gases and solutes on different adsorbents are related to each other, for a wide range of ε . Therefore, for a given pair of vapors, volume V and all the other conditions assumed equal:

$$\varepsilon\left(V\right) = \beta \cdot \varepsilon_0\left(V\right) \tag{2.52}$$

where β is a suitable affinity coefficient, that is a measure of the adsorbability of a given

vapor on a given carbon with respect to a standard vapor one (which is benzene). He described the adsorption isotherm using the Weibull probability distribution¹⁵:

$$V = V_0 \exp\left[-K \ \left(\varepsilon_0\right)^n\right] = V_0 \exp\left[-K \ \left(\frac{\varepsilon}{\beta}\right)^n\right]$$
(2.53)

Substituting eq. (2.51), for a given adsorbent/adsorbate, the Dubinin-Asthakov equation can be obtained:

$$V = V_0 \exp\left[-\left(\frac{RT}{E_D} \ln\left(\frac{P_{sat,i}}{P_i}\right)\right)^n\right]$$
(2.54)

where V_0 is the limiting value of the adsorbed volume phase, while $E_D = \beta^{\frac{1}{n}}/K$. This equation relates the equilibrium adsorbed quantity (V or V/V_0) with the gaseous partial pressure of the adsorbate, at different temperatures, once evaluated the calibration parameters V_0 , E_D and n.

Lavoie et al. [121] used the same method to determine a suitable adsorption isotherm, relating the relative adsorbed volume $v = V/V_0$ (dimensionless adsorbed volume per mass of carbons, with respect to the saturation volume) with the differential free energy of adsorption per unit volume of adsorbate (as liquid) $f = \frac{\rho_L RT}{W_l} \ln \left(\frac{P_{sat}}{P}\right)$:

$$v = \begin{cases} A^* e^{\left(-\frac{f}{f_1}\right)^n} & f \ge f^* \\ B^* \left(1 + \frac{f_0}{f}\right) & f < f^* \end{cases}$$
(2.55)

where f_0 , f_1 , n, f^* , v^* and V_0 are calibration parameters, and were determined by fitting an experimental isotherm data of the n-butane adsorption on activated carbons.

Starting from this adsorption isothermal equation, in order to describe a two-component non-adiabatic and non-isothermal adsorption, Lavoie derived a system of three PDEs, a mass transport equation for each component and a thermal transport (energy balance)

¹⁵No satisfactory theoretical base has been found for the Dubinin-Asthakov equation, which is rather a semi-empirical function, but Chen and Yang [120] derived it by an adsorption isotherm equation found by statistical mechanical principles.

equation. In this model, the finite-rate mass transfer was not considered, but a local equilibrium adsorption is assumed, in which the transient adsorbed quantity is considered equal to the equilibrium one. This assumption was made because finite-rate mass transfer effects on the adsorption results can be neglected for the low flow rates encountered in a vehicle carbon canister adsorption cycle¹⁶. Furthermore, it is assumed that the energy of adsorption per unit liquid volume is not affected by the composition of the adsorbate and that the adsorbate mixture is an ideal solution. The heat of adsorption ΔH_A is derived from an analogy with the Clapeyron relation for the heat of vaporization; it was found as a function of the heat of vaporization ΔH_{vap} and the differential free energy of adsorption f. This model was then validated with data obtained by an experimental analysis on a gasoline-aged carbon canister, by using a mixture of n-butane and nitrogen for the loading phase and pure nitrogen for the purging phase: in general, a very good agreement was found between predicted and measured load and breakthrough mass. This model, coupled with the FVSMOD [91] was then used to integrate experimental analysis that aimed to evaluate the influence on the adsorption behavior of the canister geometry and initial conditions |122|.

Bai et al. [123] used the Dubinin-Polany potential theory as the basis of a twodimensional adsorption and desorption CFD model. 2-D PDEs for total mass, momentum, energy balance (for both solid and gas phases) and species conservation are written and solved by means of FLUENT, but, unlike Lavoie, an LDF model is used to describe the adsorption rate. It configures as a source term in mass and species conservation, while the heat of adsorption¹⁷ is the source term in the solid phase energy balance equation. This model was then used to compare adsorption under different inlet concentrations: results show the presence of two adsorption fronts, which move through the carbon bed, as affirmed by Cooney [97] and Sircar [98], but the interesting thing is the presence of two-dimensional effects: as a consequence of the heat exchange towards the external environment, the temperatures are lower near the walls, so that the adsorption is higher

¹⁶This assumption is applicable only under low flow rates (40g/h). If the flow rate is considerably higher it will be necessary to apply a finite-rate mass transfer theory [97]. In a real vehicle carbon canister this condition could be verified during the tank filling phase.

¹⁷Taken from Lavoie model.

in these zones. However, this analysis is not supported by experimental data.

Attempts to apply the isothermal theory of adsorption on a 3D CFD model were also made. Among the others, Lin et al. [124] used the Dubinin-Asthakov equation coupled with a two-dimensional Lagrange Interpolating Polynomial for describing the adsorption behavior of n-butane on an activated carbon fixed bed. The Lagrange interpolating polynomial relates the gas phase concentration and temperature with the amount of the adsorbed vapors (in each cell of the computational domain and for each timestep): it has been seen that a quadratic dependence on each variable is enough for describing the process, so that the model is calibrated starting from 9 activated carbon equilibrium points, 3 for gas concentration times 3 for temperature. Several experimental analyses were made for validating the model, and a fairly good agreement was found for the load phase, but it lacks in the prediction of the purge phase.

2.4 Refueling modeling

In order to correctly dimensioning a carbon canister filter for the ORVR system, it is useful to have an estimation of the fuel vapor that comes from the fuel tank during refueling. Several empirical and mathematical models were developed in literature for predicting the amount of fuel vapor generation. Here are reported some examples of 0D theoretical and semi-empirical models that are able to perform this estimation with a certain level of accuracy.

Shiller [125] proposed a computational model (developed in BASIC, for the Fortune 32:16 microcomputer) that was able to evaluate gasoline RVP and, consequently, refueling losses, along with hydrocarbon reactivity in forming tropospheric ozone. He based his theory on the hypothesis of gasoline being a nearly ideal mixture and, therefore, it obeys Raoult's law (equation 2.11). However, since the law is derived from the assumption of molecules of similar size, that do not attract or repel each other, this hypothesis cannot be applicable for alcohol-blended gasolines, due to their non-ideal mixture behavior, which were excluded from the study. With this hypothesis, by also assuming that the fuel vapors obey the ideal gas law, it is possible to evaluate the RVP by knowing the composition

of the liquid fuel, and by iterating the computation, because of changes in the molar fraction of each component of the liquid fuel, due to its evaporation and, hence, reduction in the liquid mixture. To evaluate the vapor pressure at different T for each component (which is then used in Raoult's law), several relations were adopted, nearly one for each component of interest (van Kranen and van Nes, Riedel, Antoine, Frost-Kalkwart-Thodos, etc.). Photochemical hydrocarbon reactivity was calculated starting from a hydrocarbons reactivity scale based on hydrocarbon OH reaction rate data (relative to methane reaction rate, which was set to 1). The model considered 35 hydrocarbons (number of carbon atoms that goes from 3 of the propene to 11 of the diethiltoluene) in the gasoline mixture, which are the major constituents in common gasoline mixtures. RVP was evaluated for 9 different gasoline mixtures, which composition was accurately measured from previous studies (conducted at the U.S. National Institute for Petroleum and Energy Research): results shows a good agreement with the RVP evaluated experimentally (by following the procedure described in [20]), with an error of less than 5%. The same technique was used for evaluating the quantity of vapors of benzene (mq per gallons of liquid gasoline) that are present in a fuel tank, at a constant temperature of 85 °F (= 29.4 °C), obtaining a fairly good agreement with the experimental data (error less than 13%). The disadvantages of this type of model are of course the limiting hypothesis of gasoline ideal mixtures, that excludes the possibility of using the model for alcohol-blended gasolines (such as ethanol-blended gasolines, which are widely used around the world), and the need of precisely knowing the gasoline composition, at least for the most important hydrocarbon species.

Lockart [126] adopted a similar approach, based on Raoult's law, to evaluate the vapor quantity that escapes the fuel tank during refueling as mass of hydrocarbons per volume of liquid fuel dispensed in the tank itself, which is also the volume previously occupied by the vapors escaping the tank. The model was developed based on the following hypotheses: gasoline is considered as an ideal mixture (for Raoult's law application); fuel vapor and air are considered as ideal gases (for ideal gas law application); composition of the dispensed and the pre-filled gasoline is the same; tank contents (fuel and air-vapor mixtures) are in thermal, mechanical and material equilibrium. Therefore, the vapor mass of a single hydrocarbon component $m'_i (kg/m^3)$ can be evaluated as follows:

$$m'_{f,i} = \frac{m_{f,i}}{V} = \frac{P_{f,i}W_i}{RT}$$
(2.56)

where $m_{f,i}$ is the actual mass of the *i*-th component in the volume V, W_i is the molecular weight of the component, and $P_{f,i}$ is the vapor pressure of the component, which is evaluated by means of the Raoult's law ($P_{f,i} = P_{sat,i}x_i$). Therefore, the specific mass of fuel vapors (per volume of vapor space) is the sum of these values. Furthermore, the specific mass of air inside the vapor dome can be evaluated as:

$$m'_{a} = \frac{m_{a}}{V} = \frac{(P_{tot} - \sum_{i} P_{f,i})W_{a}}{RT}$$
(2.57)

where P_{tot} can be considered equal to P_{amb} and, therefore, a constant. During the refueling, ORVR type tanks also ingest air, which causes other fuel to evaporate (for the hypothesis of equilibrium, more fuel must evaporate in the presence of fresh air). Hence, the specific fuel vapor mass that escapes the tank during refueling, is:

$$m'_{f} = \sum_{i} m'_{f,i} + m_{a,FILL} \cdot \frac{\sum_{i} m'_{f,i}}{m'_{a}}$$
(2.58)

where $m_{a,FILL}$ is the mass of air that enters the fuel tank with the filling gasoline. This model was compared with another approach, that uses the studies from [62] to evaluate the fuel vapor pressure, as in 2.26, instead of Raoult's law:

$$m'_{a} = \frac{(P_{tot} - P_{f})W_{a}}{RT}$$
(2.59)

$$m'_f = \frac{P_f W_f}{RT} \cdot \left[1 + \frac{m_{a,FILL}}{m'_a} \right]$$
(2.60)

The two approaches were compared with results derived from refueling experiments, performed by regulating the inlet mass flow rate of both the liquid fuel and the air. However, the evaluated accuracy of the model was poor, being the error committed between 10% to 29% of the measured value (the second approach gave an error between 2% to 14%).

Reddy [127] proposed a simplified method to evaluate the fuel vapor pressure depending on RVP and fuel temperature, which is the following equation:

$$P_{sat} = A \cdot T \cdot RVP \cdot \exp\left(-\frac{B}{T}\right) \tag{2.61}$$

where constants A and B have been evaluated by correlating fuels RVP, temperature and vapor pressure values obtained by a more detailed model, developed by the same author [78] for determining fuel vapor pressure by using Raoult's law and activity coefficients. This equation implies to consider gasoline as a single component hydrocarbon. Since it is almost always possible to consider the fuel tank not completely emptied, the vapor headspace can be considered filled of fuel vapors that are in equilibrium with their liquid phase, hence the evaluation of HC mass that escapes the fuel tank during refueling operations consists of determining the mass of hydrocarbons that fills the volume which will be occupied by the fresh fuel. Therefore, by considering an ideal gas behavior of the fuel vapor, the specific vapor mass (per volume of vapor space) that escapes the fuel tank can be evaluated as:

$$m'_{f} = \frac{W_{f}}{RT} \cdot \left[A \cdot T \cdot RVP \cdot \exp\left(-\frac{B}{T}\right) \right]$$
(2.62)

However, this equation (and also the previous models) does not take into account the possibility of having a refueling gasoline with a different RVP or a different temperature with respect to the already in-tank gasoline. These two circumstances happen quite often, since the gasoline RVP changes among the gas stations, and the in-tank gasoline, which is heated up by the in-tank fuel pump and by air that comes from the engine cooling system, has a temperature that is generally higher than the dispensed fuel, which is stored underground. Reddy developed his model by also considering these variations. Furthermore, he provided two approaches to the problem, which depend on the position of the inlet check valve at the end of the fuel line, whether it is at the top of the fuel tank

(top-fill tank) or underneath the liquid-vapor interface (bottom-fill tank)¹⁸.

During refueling, there is a quantity of fresh air that is ingested in the fuel tank; hence, the total air quantity involved in the process, expressed in specific number of moles (per volume of dispensed fuel) is:

$$n'_{a} = \frac{V'_{a,FILL}P_{amb}}{RT_{FILL}} + \frac{P_{a}}{RT_{tank}}$$
(2.63)

where T_{FILL} and T_{tank} are the temperature of the filling gasoline and the in-tank gasoline, respectively (filling air and in-tank air temperatures are considered equal to the fuel temperatures, respectively), while $V'_{a,FILL}$ is the specific volume (per volume of dispensed fuel) of the filling air (which is dimensionless). The partial pressure of air inside the tank is the difference between total (ambient) pressure and fuel partial pressure, evaluated with equation 2.61, being $T = T_{tank}$ and $RVP = RVP_{tank}$. For a top-fill tank, the filling gasoline enters in contact with the whole quantity of air, evaluated in 2.63, therefore, the moles of fuel vapor (per volume of dispensed fuel) that goes in equilibrium with air, are as follows:

$$\frac{n'_f}{n'_a} = \frac{P_{FILL}}{P_a} = \frac{P_{FILL}}{P_{amb} - P_{FILL}}$$
(2.64)

where P_{FILL} is the fuel saturation pressure of the filling gasoline, which is evaluated with equation 2.61, being $T = T_{FILL}$ and $RVP = RVP_{FILL}$. Combining and rearranging equations 2.61 to 2.64, the mass of fuel vapors that escapes the fuel tank during refueling $(m'_{f,exit}, \text{ per volume of dispensed fuel})$ is:

$$m'_{f,exit} = W_f \cdot \left(\frac{V'_{a,FILL}P_{amb}}{RT_{FILL}} + \frac{P_{amb} - P_{tank}}{RT_{tank}}\right) \cdot \left(\frac{P_{FILL}}{P_{amb} - P_{FILL}}\right)$$
(2.65a)

¹⁸If the inlet check valve is in an intermediate position, which is above the liquid-vapor interface in the first part of the refueling, but below in the second part, this approach can still be used by dividing the refueling in two parts.

$$P_{tank} = A \cdot T_{tank} \cdot RVP_{tank} \cdot \exp\left(-\frac{B}{T_{tank}}\right)$$
(2.65b)

$$P_{FILL} = A \cdot T_{FILL} \cdot RV P_{FILL} \cdot \exp\left(-\frac{B}{T_{FILL}}\right)$$
(2.65c)

This model supposes that the vapor dome mixture reaches the thermal equilibrium with the dispensed fuel, hence, the fuel vapor that escapes the tank is at the same temperature of the filling gasoline. To take into account the non-ideality of the thermal exchange, a thermal efficiency can be considered, being the ratio: $\epsilon_T = (T_{tank} - T_{exit})/(T_{tank} - T_{exit})$. The system 2.65 is then modified by replacing P_{FILL} with P_{exit} , which is evaluated as following:

$$P_{exit} = A \cdot T_{exit} \cdot RV P_{exit} \cdot \exp\left(-\frac{B}{T_{exit}}\right)$$
(2.66a)

$$T_{exit} = T_{tank} + \epsilon_T \left(T_{tank} - T_{FILL} \right) \tag{2.66b}$$

$$RVP_{exit} = RVP_{tank} + \epsilon_T \left(RVP_{tank} - RVP_{FILL} \right)$$
(2.66c)

Finally, for a bottom-fill tank, being no thermal exchange between filling gasoline and vapor dome, the thermal efficiency is equal to 0 and, then, the system 2.65 is evaluated by considering $P_{FILL} = P_{tank}$. Results comparison with experimental data gives a fairly high level of accuracy, however, for applying this model it is necessary to know the thermal efficiency and the volumetric ratio between air that enters the tank and filling gasoline (along with the "classical" inputs, that are RVPs and temperatures of the two fuels), which are hard to measure and usually supposed a-priori.

Several three-dimensional CFD models were also developed to study the refueling process, but most of them are mainly focused on studying the liquid fuel motion and detecting the pressure developed in the fuel tank and in the other fuel system components. The main focuses of a CFD analysis in this field are: to study the pressure field realized in the fuel receptacle, that must generate a sufficient depression to avoid the tank fuel vapors to escape towards the receptacle; to analyze the shut-off of the gas nozzle, which ends the refueling process, and premature shut-off events, both triggered by a pressure increase in the fuel tank and line (and also, in some cases, in the vent piping system). These behaviors cannot easily been simulated without a 3D simulation of the fluid flow inside the fuel tank and receptacle. However, a complete and accurate simulation of the totality of events that occur inside the fuel tank and receptacle (which eventually lead to shut-off) is challenging, since it requires high computational power and time. This has been clearly pointed out by Sinha et al. [128], who performed a qualitatively CFD simulation by dividing the refueling process in some key subprocesses to make detailed analyses in a reasonable computational time, and to study the chain of events that lead to a premature shut-off. More recently, Stoker et al. [129] performed a more complete simulation of the tank and the vent system during refueling operation: the complete geometry of fuel tank, fuel line, receptacle and vent line was discretized¹⁹ and simulated to analyze the flow field and pressure increases. Simulations were performed for different filling gasoline flow rates, for the first and last seconds of the refueling process (only one case was simulated for the entire refueling process, to prove that reduced simulations do not affect the final pressure result), on a non-uniform mesh (which presents refining zones near the critical areas of the systems) composed by 2.2 million cells. Pressure results were compared with experimental data obtained by the same authors, with a good agreement in both increasing pressure magnitude and timing. However, authors chose not to consider the fuel evaporation, by performing experiments and simulations with Stoddard solvent and indolene, which have a low vapor pressure.

Banerjee et al. [130] also developed a 3D CFD model for the refueling process, which involved a simplified geometry, a cuboid shape fuel tank and a simple fuel line²⁰, in order to study the fuel and air flow in two different conditions of fluid dynamics resistance caused by the tank vent pipe. Then, the same authors [131] proposed a modification of this CFD

¹⁹The vapor return line, that connects the vent line to the receptacle, was not simulated. Instead, its boundaries (to the vent line and to the receptacle) were modeled by a field function based on experimental flow bench data.

 $^{^{20}\}mathrm{However},$ they did not consider the vapor return line either.

model that also evaluate the refueling emissions, by considering the liquid fuel and the vapor as ideal mixtures. A continuous thermodynamics approach [132] was adopted for this study, that, with the hypothesis of ideal mixture, allows to use a monovariate distribution function to characterize the properties of the fuel mixture, instead of determining these properties for each component of the mixture. Therefore, the concentration of the species and then the vapor transport equation are written in terms of a distribution function, which must respect the condition of integration on the whole domain being equal to 1 (the distribution function adopted in this work was the Γ -distribution function, chosen for its ability to represent gasoline mixtures). The vapor-liquid equilibrium was evaluated by the Raoult's law and the Clausius-Clapeyron relation, while the saturation vapor pressure was defined by the Clausius-Calpeyron equation and Trouton's Rule (which relates the boiling molar enthalpy of a substance with its normal boiling point). However, to reduce the model complexity, some important assumptions were made: isothermal system, gas phase viscosity and species diffusivity independent of the local mixture fraction, natural convection being neglected, and absence of interphase mass transfer (i.e. the fuel evaporation from the liquid gasoline was not considered, being negligible with respect to the quantity present in the air-vapor mixture). This approach was implemented in FLUENT to simulate the fuel and the air-vapor mixture flow inside a fuel tank line, receptacle and gas nozzle. The mesh, developed in GAMBIT, counted less than 60'000 hexahedral and tetrahedral cells. Boundary conditions were: constant pressure inlet and atmospheric conditions on the exposed part of the receptacle, constant pressure outlet at the end of the fuel line, constant liquid flow rate at the inlet of fuel nozzle. This model was then used to study the behavior of the air-vapor mixture flow: it was discovered that, for the sampled geometry of the fuel line, the vapor tends to escape through the exposed side of the receptacle, at very high gasoline dispense rates, which is an unwanted behavior. This approach was then used to design a new geometry of the fuel line that prevents this fuel vapor escape, showing an effective utility of the computational simulation of the fluid dynamics in refueling phase.

Chapter 3

Tank evaporation model

Diurnal Breathing Losses from gasoline-filled vehicles are an important source of pollutant hydrocarbon emissions: during the daily period, when the engine is turned off, the environmental temperature variation leads to a continuous evaporation of fuel inside the vehicle tank and vapor flowing outside the tank itself, due to volumetric expansion of the vapor-air mixture that fills the tank vapor dome. Therefore, these emissions are subject of various studies and various regulations around the world, as illustrated above. Purpose of the research activity described in this chapter is to develop a physical model able to predict the vapor generation from the vehicle fuel tank, in order to have a tool that can be used for both the tank design and the canister purging strategies.

In this chapter, a comprehensive experimental analysis will be exposed, made in collaboration with Stellantis N.V. at the Pomigliano Technical Center, and results will be discussed. This activity has been used as basis for the developing of the semi-empirical tank evaporation model, which will be described later in the chapter.

3.1 Experimental Activity

3.1.1 Setup

The evaporative emission test is designed to evaluate hydrocarbon diurnal breathing losses and hot soak emissions. For this purpose, a SHED chamber is commonly used. The tested vehicle is moved immediately after a test-driving cycle, for hot soak emissions evaluation. It is also kept in the SHED for several days, with temperature variation cycles, for DBLs evaluation.

For this experimental activity a different model of the SHED has been used, called VT Mini-SHED (Variable Temperature Mini-Sealed Housing for Evaporative Determination, Figure 3.1), which incorporates all the functionalities of a common SHED, but it has reduced dimensions (internal dimensions: $2.0 \ m \ge 1.5 \ m \ge 1.0 \ m$). The chamber is used for the evaluation of hydrocarbon evaporation from vehicle fuel system components and/or for fuel permeation tests from fuel tanks, EVAP systems and gasoline supply systems. It is also used for testing VOCs evaporation from other vehicle parts, such as types and internal trims, which can produce hydrocarbon emissions if thermally stressed. It is designed to facilitate applications that require a medium-sized envelope, with the ability to detect a low emission concentration, in order to improve emission readings and reduce thermal inertia, allowing for a faster temperature change. It includes a tedlar bag as volumetric compensation device, a FID analyzer, an air recirculating and purging system and several safety devices. The access door is equipped with a pneumatic closing system, to guarantee a perfect sealing. An external water heating/cooling system allows the temperature to be changed within 15 °C and 45 °C, with a heating/cooling gradient greater than 0.2 °C/min (guaranteed value). Temperature is controlled by several thermocouples placed inside the chamber, to which an external thermocouple is added, to check the external laboratory temperature. The chamber is also accessible through a gate that allows for refueling operations and ORVR tests (this type of test will be described in Chapter 5). The system is controlled by a dedicated software that can automatically program temperature profiles and thus allows for complete execution of EVAP test cycles.



Figure 3.1: Variable Temperature Mini-Sealed Housing for Evaporative Determination. Stellantis N.V. laboratories.

However, in this activity this system has been used for determining the fuel vapor generation inside a fuel tank and the quantity that flows outside it. It would have been impossible to use the FID analyzer to measure this quantity, since it would have run out of scale almost immediately. Therefore, a different system has been adopted: a carbon canister filter has been connected to the fuel tank and its weight has been monitored with a precision weight scale during the test.

The test bench scheme is represented in Figure 3.2. The experimental testing procedure is described below:

- 1. A suitable aluminum support is built and prepositioned inside the Mini-SHED, in order to avoid the contact between the sample tank and the Mini-SHED floor (a minimum distance of 0.2 m has been guaranteed to let the air flow freely underneath the tank).
- 2. The sample fuel tank is equipped with 2 K-type thermocouples (appendix B, device 1) for measuring the internal temperatures of liquid fuel and vapor dome during the test. Internal Mini-SHED temperature is also constantly measured during the test through another K-type thermocouple. For some tests, the tank has also been equipped with a differential pressure transducer (appendix B, device 2) to monitor



Figure 3.2: Experimental setup for evaporation test.

pressure variations inside the vapor dome, to measure the pressure loss generated by the carbon canister filter and the vent system. However, this pressure has been proven to be negligible, therefore the measurement system has been removed¹.

3. A barrel of fresh² certified fuel is pre-conditioned inside the Mini-SHED, in order to bring the fuel temperature to the desired initial temperature of the test. Two types of fuel have been used for these tests, E5 and E10, which are gasoline-blended fuels with ethanol at 5% and 10%, respectively. This choice is in line with the European Directive EN 228 [133], which allows to add fuel of petroleum origin with 10% ethanol (ethyl alcohol), usually produced by fermentation of the sugars contained in vegetables (sugar cane, biomass, cereals, marc). Ethanol, thanks to its high octane index (120 Research Method), and oxygen content, adequately replaces oxygenated additives such as MTBE (Methyl-Ter-Butyl-Ether) and ETBE (Ethyl-T-Butyl-Ether), contained in lead-free gasoline in a proportion of 10% to increase the octane number and reduce CO and HC emissions (unburned hydrocarbons).

¹The carbon canister and the whole vent system do represent a pressure drop, but during the diurnal test the mass flow rate is minimal. Therefore, the pressure variation that can be observed does not have appreciable influence on the evaporation phenomenon (the maximum pressure variation registered is 90 Pa).

²i.e. not already used for other evaporation tests



Figure 3.3: Sampled tank placed in MiniSHED chamber.

- 4. The fuel tank is emptied completely through a fuel pump system and then filled with a predetermined certified fuel volume, outside the Mini-SHED and with good air-recirculating conditions, for safety reasons.
- 5. The filled fuel tank is placed inside the Mini-SHED, with its support, and the tank vapor vent is connected to a carbon canister filter, placed outside the Mini-SHED, through a common-use canister flow pipe (Figure 3.3).
- 6. A carbon canister for NAFTA (North American Free Trade Agreement) automotive applications (Figure 3.4(a)) is connected to the flow pipe and positioned outside the Mini-SHED on a precision weight scale, which monitors its weight changes (Figure 3.4(b)). A high precision weight scale (appendix B, device 3) has been used for this purpose. Its mass variation is considered to be equal to the vapor mass that escapes from the fuel tank, which is the target data of the experiment. This assumption is based on the hypothesis that the vapors leaving the tank are wholly adsorbed by the active carbons inside the canister filter, and not emitted in the environment. For this purpose, an American-type canister is used, which has a higher capacity than a European-type one, since it must comply with the On-board Refueling Vapor



Figure 3.4: (a) American-type canister used for evaporation test; (b) test bench scale and measurement systems.

Recovery regulation for refueling emissions. Hence, it is likely that the canister does not reach its saturation condition during the tests performed in this analysis and thus the assumption is fulfilled. This assumption has also been confirmed by placing another canister downstream the first one and by verifying its weight variations to be negligible during the test. Carbon canister is purged before each test to free it from vapors inside, and it is periodically replaced with a new one. Purging is realized by a constant air flux (~ 25 L/min), for a time long enough to consider the canister fully purged (> 4 h). The canister starting weight is not the same for each test. However, this is not relevant for the experimental purpose because, as said, what is important in this experiment is its mass variation during time. Before being connected to the test bench, the canister is pre-weighed by an external weight scale (appendix B, device 4, referred as "spare" scale in the text below).

7. The Mini-SHED chamber is pre-conditioned to bring the fuel and tank temperature to the desired initial value. The system is brought to a stationary thermal condition and kept in this state for about 15 *min*, to properly set the initial conditions for the tank and the canister filter.

- 8. The test begins by imposing the desired temperature variation (thermal profiles are described below). Inside-tank liquid and vapor temperatures, Mini-SHED environmental temperature, tank vapor space pressure and canister mass variations are measured during time with a frequency of 0.1 Hz. During the test, the FID analyzer checks for the presence of leakages in the system.
- 9. The test finishes when different conditions are fulfilled, depending on the thermal profile adopted for the test. After the test, the tank is disconnected from the vent system and emptied by an external pump. The canister is weighed with the "spare" scale and the difference with the pre-weighing value gives the total amount of vapor mass that escaped from the tested tank. This value is needed for correcting the in-test weight measurements which can be affected by the vent pipe weight and tension changes due to temperature variations. Then, the canister is purged for the next experimental test.
- 10. Experimental results are described by means of internal tank temperature and canister adsorbed mass during time.

Two thermal profiles have been adopted for this analysis:

- Ramp: starting from the initial value (T_{in}) , the temperature is changed in order to reach the target value (T_{target}) as quick as the MiniSHED can do. The test lasts until the system has reached the thermal equilibrium and it is kept in this condition for at least the same duration of the transitory phase.
- Variable: a standard 24 *h* diurnal thermal cycle is applied on the system, for 2 or 3 consecutive times. For this activity a standard CARB thermal cycle has been adopted [134], in which temperature is changed between 65 °*F* (= 18.3 °*C*) and 105 °*F* (40.6 °*C*). The thermal profile is reported in Table 3.1 and shown in Figure 3.5.

In the next session, tested tanks will be described and experimental results will be presented and discussed.

Hour	0	1	2	3	4	5	6	7	8	9	10	11	12
°F °C	65.0 18.3	$\begin{array}{c} 66.6 \\ 19.2 \end{array}$	$72.6 \\ 22.6$	$\begin{array}{c} 80.3\\ 26.8\end{array}$	$86.1 \\ 30.1$	$90.6 \\ 32.6$	$94.6 \\ 34.8$	$98.1 \\ 36.7$	$101.2 \\ 38.4$	$103.4 \\ 39.7$	$\begin{array}{c} 104.9\\ 40.5 \end{array}$	$\begin{array}{c} 105.0\\ 40.6\end{array}$	$104.2 \\ 40.1$
Hour	13	14	15	16	17	18	19	20	21	22	23	24	
°F °C	$ 101.1 \\ 38.4 $	$95.3 \\ 35.2$	$88.8 \\ 31.6$	$84.4 \\ 29.1$	$80.8 \\ 27.1$	$77.8 \\ 25.4$	$75.3 \\ 24.1$	$72.0 \\ 22.2$	$70.0 \\ 21.1$	$68.2 \\ 20.1$	$\begin{array}{c} 66.5 \\ 19.2 \end{array}$	$65.0 \\ 18.3$	

Table 3.1: CARB thermal cycle.



Figure 3.5: CARB thermal cycle, graphical representation for 24 h.

3.1.2 Results and Discussion

HDPE Tanks

The experimental setup previously described has been derived from several experimental attempts. The first test has been executed on a commercial tank (Figure 3.6), made available by Stellantis N.V. and mounted on a gasoline-fueled vehicle of the group³. The sampled tank wall is made of a multi-layer material mainly composed of high density polyethylene (HDPE), which is commonly used for this type of applications [135]. It has a useful fuel capacity of 47 L and a minimum vapor dome volume of 6.6 L.

The tank is filled with E5 type gasoline for the 40% of its useful capacity (i.e. 18.8 L). A ramp test has been executed on this sample, with an initial temperature of $T_{in} = 20 \ ^{\circ}C$ and a target temperature of $T_{target} = 40 \ ^{\circ}C$. For this test only the canister mass variation has been recorded and for a limited period of 6.5 h, which corresponds to the transitional

³For NDA reasons, it is not possible to name the model of the vehicle.



Figure 3.6: Sampled tank n. 1.



Figure 3.7: Tank 1: fuel vapor adsorbed quantity in canister filter after a thermal variation from 20 $^{\circ}C$ to 40 $^{\circ}C$.



(b)

Figure 3.8: Sampled tank n. 2: (a) CAD geometry; (b) in the MiniSHED, during the test.

phase of the test. Results have been reported in Figure 3.7. As expected, an increase of the canister filter mass has been recorded, which is due to vapor mass generation as a consequence of fuel temperature increase during the test and fuel specific volume variation. After 6.5 h the evaporated fuel quantity adsorbed in the canister filter is equal to $m_{f,final} = 43.02 \ g$. It is possible to see the principle of an asymptotic trend of the fuel vapor mass, as the system is approaching to the thermal equilibrium. Furthermore, the evaporation is more intense in the first part of the test: after 3 h, the evaporated quantity is about 70% of the total amount of fuel vapors. This suggests a strong influence on the fuel evaporation of temperature variations (and not the temperature itself).

For this reason, new *ramp* tests have been performed, also by recording the fuel temperature inside the tank. Results presented below refer to a second commercial fuel tank for gasoline vehicles applications, made of HDPE (Figure 3.8). It has a useful capacity of 55.0 L and a minimum vapor dome volume of 12.1 L. The tank has once again been filled with fresh E5 type certified gasoline, for the 40% of its useful capacity (i.e. 22.0 L). Temperature has been changed, by following the *ramp* strategy, from $T_{in} = 20 \ ^{\circ}C$ to $T_{target} = 35 \ ^{\circ}C$. This test lasts for 24 h, therefore, as can be noticed from Figure 3.9, the system reaches the thermal equilibrium after $7 \div 9$ h. What is interesting is that the fuel evaporation follows the fuel temperature increase and has a peak of 33.2 g at around the



Figure 3.9: Tank 2: (a) liquid fuel temperature; (b) fuel vapor adsorbed quantity in canister filter after a thermal variation from 20 °C to 35 °C;

same time in which the system reaches the target temperature, then it stabilizes at a constant value. A small reduction of mass variation has been recorded between the peak and the final constant value of 31.7 g (which is less than 5% of the final value). This phenomenon has not been observed in other tests, or for other sampled tanks, it may have been due to a relaxation of tensions in the vent pipe that connects the fuel tank to the canister filter placed on the weight scale. Therefore, to reduce the possibility of this type of systematic error on the measurement of the vapor mass, for further tests the canister

has been weighed in stationary conditions, before and after the test, as described above.

Stainless-steel Tank

Several tests have also been performed on a commercial, stainless-steel gasoline tank for hybrid applications. As said, for this applications the sealed fuel tank strategy is more effective for reducing evaporative emissions and avoiding the canister saturation. However, in order to be able to withstand delta pressures of more than 300 *mbar*, fuel tanks need to be designed with a different geometry and built with different materials. Hence, the third sampled tank is made of 1.2 mm tick stainless steel sheet (nickel-chromium steel, graded AISI316L according to the SAE steel grade system [136]) and it also has a rounded shape, if compared with the tanks previously described 3.10. It has a useful capacity of 36.7 L and a minimum vapor dome volume of 6.5 L.

A series of three experimental tests have been performed on this tank according to the *variable* procedure, which has been repeated for 2 times to study the fuel evaporation behavior in a fuel tank of a gasoline car parked for a total period of 48 h. The three tests differ for the initial fuel filling levels, which are 8 L, 16 L and 24 L respectively, to analyze the evaporated fuel variation with the vapor dome volume. An E5 certified gasoline has been used for these tests. In Figure 3.11 an example of the experimental results obtained by these tests has been reported. The fuel vapor quantity adsorbed by



Figure 3.10: Sampled tank n. 3: (a) CAD geometry; (b) in the MiniSHED, during the test.



Figure 3.11: Tank 3: filled with E5 gasoline at 16 L, diurnal CARB test cycle, 48 h: fuel vapor adsorbed quantity in canister filter for the first and the second day compared.

filling level (L)	1st day peak (g)	after 24 h (g)	2nd day peak (g)	after 48 h (g)
8.0	39.8	32.7	71.4	64.9
16.0	26.9	24.0	50.2	45.7
24.0	20.1	18.4	35.0	31.4

Table 3.2: Tank 3, diurnal CARB test cycle, 48 h, results.

the carbon canister increases in the first half of the day, as the fuel temperature increases, until it reaches a peak at around 13 h and then it gradually decreases. This phenomenon is called natural purging of the canister, or *breathing*, and it is due to the reduction of the temperature inside the ullage space, which brings to a specific volume reduction of the vapors inside the tank and then a backflow of fresh air coming into the tank from the external environment through the canister filter, that partially purges the canister itself, thus resolving in reduction of canister mass. In the same figure, there is a comparison between the fuel evaporated mass during the first 24 h and the second ones: it is interesting to notice that the mass evaporated during the second day is slightly reduced with respect to the first day (24.0 g after 24 h, 21.7 g after 48 h). This can be explained as the effect of fuel aging, which is the tendency of the gasoline to evaporate less during time, as the more volatile compounds have already evaporated.

Results of the test are reported in Figure 3.12. As can be seen in Figure 3.12(a), the



Figure 3.12: Tank 3, filled with E5 gasoline at 8 L, 16 L and 24 L, diurnal CARB test cycle, 48 h: (a) liquid fuel temperatures, compared with environmental temperature imposed by the cycle; (b) fuel vapor adsorbed quantity in canister filter.



Figure 3.13: Tank 3: filled at 16 L, diurnal CARB test cycle, 48 h: E5 and E10 type gasoline compared.

temperature delay of the liquid fuel inside the tank, with respect to the environmental temperature, increases with the filling, because of thermal inertia, while the total adsorbed fuel vapor mass decreases. Of course, a lower maximum temperature leads to a lower fuel evaporated mass, but this is not enough to explain the differences between measured adsorbed mass in the three tests, in fact values from the 24 L filling test are about half of the ones recorded from the 8 L filling test (Table 3.2). This behavior is also due to the vapor dome volume decrease with filling: all other conditions being equal, a bigger ullage volume needs a greater amount of vapor in order to reach the equilibrium condition with its liquid phase. Furthermore, the same temperature variation applied on a bigger vapor volume leads to a bigger volume variation (assuming a constant total pressure) or, in this case, to a bigger exiting flow of air and vapor. Of course this behavior also influences the "natural" purging phase: the bigger is the ullage volume, the more is the amount of canister purging, that is shown in a different line slope in Figure 3.12(b) for the three tests in the second half of the days.

The diurnal test on this fuel tank has been repeated by filling the tank with 8 L of E10 fuel, which has a higher ethanol concentration. Figure 3.13 shows that the E5 type gasoline has a slightly higher evaporation than the E10 one, around 5% of the adsorbed



Figure 3.14: Sampled tank n. 4: (a) CAD geometry; (b) in the MiniSHED, during the test.

vapor mass after 48 h. This result is in line with what found in [137] and [138]: the evaporation capacity (represented by the fuel RVP) increases with ethanol percentage in gasoline until it reaches a maximum value between 5% and 10% of ethanol concentration. Therefore, the evaporated fuel quantity in the two cases analyzed is quite similar (after 48 h of diurnal test, the difference between the results of the test with E5 and with E10 is around 3.2 g on the recorded canister mass variation).

Prototype Tank

Fuel evaporation and tank breathing losses are influenced by many factors, in which the tank shape is included: by varying the filling level, it is inevitable in a commercial tank to vary the interface between liquid fuel and vapors, which affects the evaporation phenomenon itself (by influencing the liquid-vapor equilibrium). Therefore, a fuel tank of a simpler geometry has been built for this work. It is made of 1.5 mm tick stainless steel sheet (nickel-chromium steel, graded AISI304 according to the SAE steel grade system [136]) and has a cuboid geometry, which internal dimensions are 400 mm \times 300 mm \times 200 mm for a total volume of 24 L (Figure 3.14). This shape allows to determine the influence of volumetric variations of liquid and vapor phases without having significant changes in the air-fuel interface.

For this experimental activity, the fuel tank has been filled with various quantities of E10 certified gasoline. Several tests have been performed, according to the *ramp* procedure,



Figure 3.15: Tank 4, filling level of 3.6 L, $T_{in} = 20^{\circ}C$, $T_{target} = 40^{\circ}C$, fresh vs recycled fuel: (a) canister mass variation; (b) vapor temperature profiles.

with different filling levels equal to 3.6 L, 7.2 L and 14.4 L (which correspond to 15%, 30% and 60% of the total internal volume, respectively) and different target temperatures of 30 °C, 35 °C and 40 °C (initial temperature has been set to $T_{in} = 20$ °C for all the tests). Furthermore, tests have also carried out with "recycled" or "aged" fuel, already used in a previous test. In an "aged" gasoline, the more volatile fractions have already evaporated, so the results in terms of generated vapors from the tank are lower. Summary of the tests performed is shown in Table 3.3.

The most severe condition in terms of fuel mass evaporation is expected to be the one applied in test $3.6L_{40}$, in which there is the higher variation of temperature between initial and target and the higher vapor dome volume. Results of this test are presented

N°	Filling level (L)	T_{target} (°C)	Fuel	Duration (hh:mm:ss)	$\begin{array}{l} \mathbf{Adsorbed} \\ \mathbf{mass} \ (g) \end{array}$	Notes	Label
1	3.6 (15%)	30	Fresh	21:50:40	6.85	-	$3.6L_{30}$
2	3.6~(15%)	30	Recycled	23:54:10	5.22	red. 24%	$3.6L_{30}R$
3	3.6~(15%)	35	Fresh	23:02:20	11.54	-	$3.6L_35$
4	3.6~(15%)	35	Recycled	23:51:40	9.18	red. 20%	$3.6L_{35}R$
5	3.6~(15%)	40	Fresh	23:52:10	17.96	-	$3.6L_{40}$
6	3.6~(15%)	40	Recycled	19:24:40	13.11	red. 27%	$3.6L_{40}R$
7	7.2 (30%)	30	Fresh	22:22:20	2.63	-	$7.2L_{-}30$
8	7.2(30%)	35	Fresh	24:00:00	5.97	-	$7.2L_35$
9	7.2 (30%)	40	Fresh	18:58:00	15.84	-	$7.2L_{40}$
10	14.4 (60%)	40	Fresh	24:00:00	13.67	-	$14.4L_{40}$

Table 3.3: Tank 4, tests performed, ramp procedure.



Figure 3.16: Tank 4: Tank 4, filling level of 3.6 L, $T_{in} = 20^{\circ}C$, $T_{target} = 30^{\circ}C$, $35^{\circ}C$, $40^{\circ}C$: (a) canister mass variation; (b) fuel temperature profiles.



Figure 3.17: Tank 4, filling level of 3.6 L, 7.2 L and 14.4 L, $T_{in} = 20^{\circ}C$, $T_{target} = 40^{\circ}C$: (a) canister mass variation; (b) fuel temperature profiles.

in Figure 3.15. From Figure 3.15(b) it is possible to notice the thermal delay of liquid fuel with respect to the vapor dome to be very little compared to the one with respect to the external environment. "Recycled" fuel test has been conducted with an aged fuel, the same already used in the "fresh" fuel test, to compare the fuel evaporated quantity after a cycle of increasing and decreasing temperature, in the same initial and external conditions. Results are compared in Figure 3.15(a): the mass adsorbed by the canister in the fresh fuel test is 17.96 g, instead in the aged fuel test it is reduced, as expected, and equal to 13.11 g, with a reduction of 27%. Similar tests were performed for lower target temperatures, 30 °C and 35 °C, where results gave a lower reduction in terms of vapor mass stored in the canister, respectively of 24% and 20%, as shown in Table 3.3.

Figure 3.16(a) shows a comparison between tests performed at different target tem-



Figure 3.18: Tank 4, filling level of 3.6 L, CARB test cycle, 72 h: (a) canister mass variation; (b) comparison between the three test days.

peratures. As expected, there is a significant increment in the fuel evaporation with temperature, due to the fuel saturation pressure variation with the temperature itself and also to the specific volume variation of the vapors inside the fuel tank, that escape to the canister (the so-called "breathe"). The increment in percentage of the canister mass variation recorded for the tests with a temperature increase of 5 °C is equal to 68% with respect to the case with $T_{target} = 30$ °C, while it is 55% with respect to the case with $T_{target} = 35$ °C.

Other tests have been conducted to have a comparison on the evaporation results with the same target temperature (40 °C) but with different filling levels (respectively of 3.6 L, 7.0 L and 14.4 L, that correspond to 15%, 29.2% and 60% of the tank normal volumetric capacity). Results are shown in Figure 3.17. Here again it is possible to see how the evaporation varies as the filling level and, therefore, the headspace volume changes. In halving the filling level, there is an increment of the canister final mass variation of 15.8% with respect to the 60% filling case, and there is an increment of 13.4% with respect to the 30% filling case. Moreover, the transitional phase is seen to be faster as the filling level decreases, and this can be also noted on the temperature trends (Figure 3.17(b)). This is due to the thermal inertia reduction, because of the fuel mass reduction itself. This is a further confirmation of the strong influence of the temperature on the evaporation dynamics.

Finally, in Figure 3.18 the results of a variable type test are presented, which has been

performed on the prototype tank with a filling level of 3.6 L. A CARB diurnal temperature profile has been applied for 3 consecutive times. Figure 3.18(a) shows the typical trend of the canister mass variation during a diurnal test, already seen in 3.1.2, while the effects of fuel aging during the test can be noticed in Figure 3.18(b).

3.2 0D Tank Evaporation Model

3.2.1 System of equations

A 0D fuel evaporation model has been developed in this research activity, in order to predict the fuel quantity evaporated from a gasoline fuel tank under different environmental thermal conditions. A schematic representation of the fuel tank is given in Figure 3.19: the tank internal volume is divided in two control volumes, which correspond to the liquid fuel and the vapor dome or ullage space.

The liquid volume V_U is occupied by liquid fuel m_L , while the vapor dome V_U is filled with air m_a and fuel vapor m_f , initially in equilibrium conditions with its liquid phase. \dot{m}_{VL} is the fuel mass flow rate that evaporates and passes from the liquid to the vapor volume. Temperature is considered uniform in the entire system (this is an acceptable approximation, after having seen from experimental results that the difference between liquid and vapor temperatures is negligible). The tank system can interact with the external by:

- liquid fuel mass, from filling line (\dot{m}_{FILL}) and through the engine supply and return (if present) lines $(\dot{m}_{sup/ret})$;
- vapor fuel mass exiting from the vapor dome (\dot{m}_{fX}) and entering the carbon canister;
- air mass entering and exiting from the vapor dome through the vent line (\dot{m}_{aX}) and eventually through the filling line $(\dot{m}_{a,FILL})$;
- radial heat from tank underbody (\dot{Q}_R) ;
- convective heat from the environment (Q_C) ;



Figure 3.19: Schematic representation of a fuel tank.

• heat generated by the fuel pump (\dot{Q}_{pump}) .

The objective of this analysis is to evaluate the fuel evaporation under parking conditions, therefore the effects of the fuel sloshing will not be considered. Furthermore, \dot{m}_{FILL} and $\dot{m}_{a,FILL}$ are equal to 0, since there is no refueling, and so is $\dot{m}_{sup/ret}$ and \dot{Q}_{pump} , since the engine is turned off.

The following system has been built by using a semi-empirical approach and by considering the fuel as a pseudo-single component (as done by [91]), with its own properties (density, specific heat, latent heat of vaporization, REID vapor pressure). Fuel vapor pressure inside the fuel tank has been considered equal to the saturation fuel pressure, hence the system is in a quasi-steady equilibrium, which is mainly influenced by the system temperature variation. This hypothesis can be made by considering that the heating/cooling of the tank is a much slower process than the evaporation one. Therefore, with the hypothesis of ideal gas, the fuel vapor partial pressure can be written as:

$$P_f = \frac{m_f \ R \ T}{W_f \ V_U} = P_{sat}(T) \tag{3.1}$$

where W_f is the fuel vapor molar mass. The equation that relates saturation pressure with temperature will be described later in 3.2.2. Vapor dome air partial pressure can be written as:

$$P_a = \frac{m_a R T}{W_a \left(V_U + V_L \alpha \frac{T}{273 K}\right)} \tag{3.2}$$

where air dissolved at equilibrium in the fuel is considered by adding an effective volumetric term, in which α represents the solubility of air in fuel ($\alpha = 0.185$, according to [62]). Then, according to Dalton's Law, the total pressure can be written as:

$$P_{tot} = P_f + P_a \tag{3.3}$$

The total pressure is set as a constant and equal to the atmospheric pressure for a standard gasoline tank, while if the tank can withstand overpressures, this value is set to the maximum pressure value guaranteed by the equipped relief valve. This hypothesis is in accordance with what found in the experimental activity, that is the canister and the vent system pressure losses are negligible for the flow rate involved in this phenomenon.

Mass balances on air, liquid and vapor fuel are following:

$$\frac{dm_a}{dt} = -\dot{m}_{aX} \tag{3.4}$$

$$\frac{dm_L}{dt} = -\dot{m}_{VL} \tag{3.5}$$

$$\frac{dm_f}{dt} = -\dot{m}_{fX} + \dot{m}_{VL} \tag{3.6}$$

where \dot{m}_{VL} is considered positive if the fuel is evaporating.

The energy conservation for the liquid can be written in terms of temperature as follows:

$$\frac{dT}{dt} = \frac{\dot{Q} - \Delta H_{vap} \cdot \dot{m}_{VL}}{\Sigma_i m_i c_i} \tag{3.7}$$

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where $\Sigma_i m_i c_i$ is the sum of the thermal capacities of liquid fuel, vapor and tank walls, while \dot{Q} is equal to:

$$\dot{Q} = \dot{Q}_{pump} + \dot{Q}_C + \dot{Q}_R = 0 + \frac{T_{env} - T}{R_C} + \sigma \frac{T_{ub}^4 - T^4}{R_R}$$
(3.8)

being R_C and R_R the convective and radial resistances of the system, respectively.

Finally, the vapor flow exiting the tank can be assumed to have the same concentration of the vapor mixture inside the tank itself, hence:

$$\dot{m}_{fX} = \frac{P_f}{P_a} \dot{m}_{aX} \tag{3.9}$$

Equations 3.1 to 3.9 can be combined in a system of 4 differential algebraic equations (DAE), as follows:

$$\frac{dm_L}{dt} = -\frac{dm_f}{dt} + \frac{dm_a}{dt} \cdot \frac{P_{sat}(T)}{P_{tot} - P_{sat}(T)}$$
(3.10a)

$$P_{tot} = \frac{m_a \ R \ T}{W_a \ V_U \ \left(1 + \frac{\alpha \ V_L/V_U}{273 \ K} \ T\right)} + P_{sat}(T)$$
(3.10b)

$$\frac{m_f \ R \ T}{W_f \ V_U} = P_{sat}(T) \tag{3.10c}$$

$$\frac{dT}{dt} = \frac{\frac{T_{env} - T}{R_C} + \sigma \frac{T_{ub}^4 - T^4}{R_R} + \Delta H_{vap} \cdot \frac{dm_L}{dt}}{m_L c_L + m_{tank} c_{tank} + m_f c_{p,v} + m_a c_{p,a}}$$
(3.10d)

which can be rearranged in a system of 2 ordinary differential equations (ODE) that can be solved for m_L and T:

$$\frac{dm_L}{dt} = \frac{-A(T) \cdot B(T)}{\Delta H_{vap} \cdot A(T) + C(m_L, T)}$$
(3.11a)

$$\frac{dT}{dt} = \frac{B(T)}{\Delta H_{vap} \cdot A(T) + C(m_L, T)}$$
(3.11b)

where A(T), B(T) and $C(m_L, T)$ are:

$$A(T) = \frac{V_U}{R T^2} \cdot \frac{P_{sat}(T)}{P_{tot} - P_{sat}(T)} \cdot \left[T \ \frac{dP_{sat}(T)}{dT} \left(W_f \ \left(\frac{P_t ot}{P_{sat}(T)} - 1 \right) + W_a \ \left(1 + \frac{\alpha \ V_L/V_U}{273.15 \ K} \ T \right) \right) - (W_f - W_a) \left(P_{tot} - P_{sat}(T) \right) \right]$$
(3.12a)

$$B(T) = \frac{T_{env} - T}{R_C} + \sigma \frac{T_{ub}^4 - T^4}{R_R}$$
(3.12b)

$$C(m_L, T) = m_L c_L + m_{tank} c_{tank} + \frac{W_f V_U}{R T} c_{p,v} + \frac{W_f V_U}{R T} \left(1 + \frac{\alpha V_L / V_U}{273.15 K} T \right) (P_{tot} - P_{sat}(T)) c_{p,a}$$
(3.12c)

The system of equations 3.11 and 3.12 represents a 0D model of the fuel evaporation inside the tank. In this model, the canister filter has been considered as a simple container, without fuel adsorption properties, therefore its mass variation has been evaluated as difference between the initial fuel liquid and vapor quantity and the one evaluated for each timestep.

3.2.2 Saturation Pressure

Saturation pressure can be determined by various equations. The most simple relation is the one given by Reddy in [127] (equation 2.61). However, this approach has proved not to be effective, since the constants were evaluated on a limited number of gasoline types, which currently are no longer used.

Therefore, another approach has been tested, which is the one presented by Lavoie et

al. [62] and presented in equation 2.22. It involves the use of a new variable, which is the mass fraction evaporated Z, which represents a kind of aging factor of the gasoline: the more fuel vapor has been evaporated from liquid gasoline, the less will evaporate from the same fuel batch (as described in 2.2). However, this approach requires to know several fuel properties, along with the RVP, which are the focal pressure and temperature and the experimental relation between the fuel boiling point and Z itself, which are parameters that cannot be easily found in literature for every gasoline mixture. Furthermore, Z has to be evaluated in the system as a variable, along with m_L and T, thus requiring a higher computational effort [139].

A simpler approach has then used, presented by Campbell [140]:

$$P_{sat}(T) = exp\left[A1_C - A2_C \cdot ln(RVP) - \frac{B1_C - B2_C \cdot ln(RVP)}{T + C_C}\right]$$
(3.13)

where the constants $A1_C$, $A2_C$, $B1_C$, $B2_C$ and C_C have been evaluated by averaging more than 70 commercial gasolines used worldwide⁴.

A future development will be to introduce a more detailed composition of the gasoline, by considering the saturation pressure of the gasoline hydrocarbon components.

3.2.3 Model Resolution and Discussion

The system has been coded and solved in MATLAB[®] environment⁵. MATLAB[®] (MA-Trix LABoratory) is a proprietary multi-paradigm programming language and numeric computing environment developed by MathWorks. MATLAB allows matrix manipulations, plotting of functions and data, implementation of algorithms, creation of user interfaces, and interfacing with programs written in other languages. The MATLAB application is built around the MATLAB programming language. Common usage of the MATLAB application involves using the "Command Window" as an interactive mathematical shell

⁴If P_{sat} is in Pa and T is in K, $A1_C = 9.7309$, $A2_C = -0.9658$, $B1_C = 2986.1$, $B2_C = 9.9$ and $C_C = 0$. The average percent variation by using these values is 1.06%

 $^{^5\}mathrm{However},$ the code can also be solved by the open source software GNU-Octave


Figure 3.20: Tank 4, filling level of 3.6 L, $T_{in} = 20 \ ^{\circ}C$, $T_{target} = 40 \ ^{\circ}C$, comparison between exp. results and model: (a) liquid temperature; (b) canister mass variation.



Figure 3.21: Tank 4, filling level of 7.2 *L*, $T_{in} = 20 \ ^{\circ}C$, $T_{target} = 35 \ ^{\circ}C$, comparison between exp. results and model: (a) liquid temperature; (b) canister mass variation.

or executing text files containing MATLAB code. MATLAB supports several types of variables (numeric and alphanumeric), structure data types and programming with functions.

The code is reported in Appendix C. Several fuel and tank properties are needed (geometry, density, heat capacity, fuel RVP, etc.), as well as initial conditions of liquid fuel mass and temperature and boundary conditions such as total pressure and environmental temperatures. In this section, some results will be presented and compared with experimental results previously obtained.

Figure 3.20 shows a comparison between experimental data and model results for the ramp test case on the tank 4 with a filling level of 3.6 L and a target temperature of 40 $^{\circ}C$



Figure 3.22: Tank 2, filling level of 22 *L*, $T_{in} = 20 \ ^{\circ}C$, $T_{target} = 35 \ ^{\circ}C$, comparison between exp. results and model: (a) liquid temperature; (b) canister mass variation.



Figure 3.23: Tank 4, filling level of 3.6 L, CARB test cycle comparison between exp. results and model: (a) liquid temperature; (b) canister mass variation.

(the worst case among those previously analyzed in terms of evaporative emissions). Other results for the *ramp* have been presented in Figure 3.21 and 3.22, respectively for the tank 4 filled with 7.2 L and with a target temperature of 35 °C and for the tank 2 (HDPE tank) filled with 22 L and with a target temperature of 35 °C. A good level of agreement has been found for both temperature and canister mass variation. A slightly difference is shown in the latter test (tank 2, Figure 3.22(b)), because of a small decrement of fuel vapors in the canister filter, which has already been discussed.

On the other hand, Figure 3.23(b) shows the results of the model for the first 24 h of the *variable* test. The model shows a similar level of agreement for the rising ramp, where the estimated and the measured curves of canister mass variation are pretty close. However, when the temperature decreases, after 12 h, the two profiles are quite different: the measured mass slightly decreases, due to the natural purging (or back-purging) caused by the tank cooldown, while the estimated quantity drastically decreases until it reaches the value of 0 after 24 h. This is due to the absence of the adsorption/desorption behavior of the canister in the evaporation model: as said, the carbon canister is assumed to be a container at atmospheric pressure, therefore, during the back-purge phase, it opposes no resistance to the vapor backflow, as a real canister does, and the whole fuel vapor returns in the tank and condensates. To simulate this behavior, the model needs to be coupled with a canister adsorption/desorption model, which is the object of the next chapter of this work.

Chapter 4

Canister adsorption model

The carbon canister filter is the main component of the EVAP system, the one that effectively prevents the fuel vapors to go outside the vehicle and into the environment as hydrocarbon VOCs.

As said, adsorption is an exothermic process in which a component in its fluid phase (adsorbate) is attracted on the surface of a solid material (adsorbent). This process is highly dependent on temperature conditions, and in general, adsorption performances decrease with increasing temperature; therefore, the process intrinsically decreases its performance. Adsorption capacity is strongly dependent on the overall surface area since the phenomenon is mainly due to unbalanced molecular forces on solid surfaces. A carbon canister performance parameter is the butane working capacity (BWC), which is the quantity of n-butane a canister can adsorb before it is saturated. According to GTR-19 [37], the BWC shall be determined by loading the canister with 40 g/h of n-butane, in mixture with nitrogen at 50% vol., until the quantity of n-butane that escapes from the canister reaches 2.0 g (the so-called 2 grams of breakthrough), and then purging it with 300 bed volumes of nitrogen at 25 L/min. This process needs to be performed after several loading and purging cycles in order to analyze the performance of an aged canister. Canister aging consists of a performance decrease in storing fuel vapors, mainly due to micropores filling with high boiling hydrocarbons, which can remain trapped even after the purging phase and consequently reduce the effective volume of storage available in

the pores [141]. This process continues until the canister reaches a certain stabilization in performance, and therefore its BWC can be considered stable and repeatable. A similar analysis can be performed for determining the gasoline working capacity (GWC), by using specific gasoline fuel vapors instead of n-butane.

In this chapter, a carbon canister filter, made for European applications, has been tested to study adsorption and desorption phenomena by analyzing its behavior during loading and purging phases. The experimental activity has been made in collaboration with Stellantis N.V. at the Pomigliano Technical Center. Hydrocarbons stored quantity in the canister has been dynamically measured as it has been filled and purged with standard n-butane and nitrogen mixture fluxes, by means of a precision weight scale. Since these processes are exothermic and endothermic, respectively, the carbon bed temperature measurement has also been carried out. Results have then been used for calibrating a theoretical 1D model for the canister adsorption developed at the Center for Automotive Research of the Ohio State University, in Columbus (OH), which will be reported later in the chapter. Finally, a DFSS (Design for Six Sigma) process has been executed on the canister model to accurately calibrate model parameters.

4.1 Experimental activity

4.1.1 Setup

The experimental activity has been performed on a 1.0 L carbon canister (Figure 4.1(a)), specifically designed for European applications (i.e. not suitable for ORVR systems). The sampled canister has a U-shape geometry, with two main chambers filled with wood-based carbon pellets of type BAX 1100, which has a theoretical BWC of 110 g/L (grams of n-butane adsorbed in a liter of carbons) and an apparent density¹ of $320 \div 370 \ kg/m^3$. The canister has a built-in liquid separator of 0.12 L for preventing the liquid fuel to go inside the carbon chamber (this would cause a drastic collapse of the adsorption and

¹The apparent density is the density of the activated carbons by also considering the void volume due to their porous structure.



Figure 4.1: Carbon canister filter: (a) sampled canister; (b) schematic representation.

desorption performance of the activated carbons) and an internal plate supported by a system of springs that keeps the activated carbon pellets compressed. Figure 4.1(b) shows a schematic representation of the canister filter. The canister is positioned in the vehicle vertically, as pictured in the scheme, to guarantee the liquid separator functioning. During the loading phase (Figure 4.2(a)), when the PCV is closed and the fuel tank is put in communication with the canister, fuel vapor flow from the tank enters the canister through port T, passes through the separator and then in the carbon bed, through the "U" path, in which fuel vapor is adsorbed from the activated carbons, while clean air exits in the atmosphere through port A. During the purging phase (Figure 4.2(b)), the PCV puts the canister in communication with the engine intake manifold, hence, thanks to the depression during the intake phase, air coming from atmosphere passes through port A^2 and purges the carbons before being sucked in the intake manifold, through port E, and in the engine cylinder where the desorbed fuel vapors are burned along with the fresh charge.

To analyze the thermal behavior of the adsorption and desorption phenomena, four K-type thermocouples (appendix B, device 1) have been installed inside the carbon bed, two of them in each chamber, as seen in Figure 4.1(b), respectively at 70 mm and at 140 mm from the topmost section of the canister. Thermocouples order (T1 to T4)

²Before entering the canister through port A, air passes through an air filter.



Figure 4.2: Vapor fluxes through canister filter: (a) loading flow path; (b) purging flow path.

follows the loading flow path. Another thermocouple, named *skin* thermocouple, has been placed on the external plastic wall at the back of the canister, in correspondence with thermocouple T1, to analyze the difference in temperature increasing between various parts of the same section and to estimate the carbon bed heat capacity. A leakage test has been performed on the canister filter to ensure the canister watertight after the installation of the thermocouples. This test has been repeated several times during the experimental activity. The canister is then positioned on a metallic support for better stability and ease of installation on the test bench, and to ensure that the skin thermocouple does not touch the ground when the canister is positioned on the bench.

Tests have been conducted on a test bench designed for this type of applications, represented in Figure 4.3. The bench is equipped with two precision weight scales that dynamically measure the weight variation of the sampled canister and of the spare canister (appendix B, device 5 and 6, respectively), that will be described later. The bench is equipped with a filling system that can provide n-butane and nitrogen at various mixing levels and mass flow. The bench is controlled via PC, which also records weight scales and thermocouples measurements. An ambient thermocouple measures the environmental temperature, while the test laboratory is provided with several HC detectors which stop



Figure 4.3: Canister test bench: (a) sampled canister positioned on the bottom floor weight scale, and connected with the spare canister positioned on the top floor weight scale; (b) detail of the sampled canister and thermocouple connections.

the test if they reveal unsafe values of unburned hydrocarbons in the environment. A detailed explanation of the experimental setup for both loading and purging phases is given below:

- The sampled canister is tested for leakages, to ensure the watertight of the canister wall, and pre-weighed by an external weight scale (which is the "spare" scale described in 3.1.1; appendix B, device 4).
- 2. The canister is placed on the bottom weight scale of the test bench (Figure 4.3(a)). For the loading test, port T is connected to the inlet pipe, which provides the loading flux. Port A is connected through a vent system to the spare canister, also called *auxiliary* canister, which is a small cylinder filled with activated carbons, placed on



Figure 4.4: Test bench setup: (a) loading phase; (b) purging phase.

the top weight scale. Port E is closed (Figure 4.3(b)). Thermocouples T1 to T4 and T_{skin} are connected to the measuring system. Cables and pipes are fixed in their positions to avoid their tensions to affect the test results.

- 3. The loading test starts (Figure 4.4(a)): a constant flow of 40 g/h of n-butane mixed with nitrogen at 50% vol. fills the sampled canister and n-butane is adsorbed by the carbons, thus increasing the canister mass and carbon bed temperature. The measuring system records the canister weight variation and thermal changes, along with environmental temperature and spare canister weight changes, with a frequency of 0.1 Hz.
- 4. After some time (generally, 2.5 to 3 hours, part of n-butane starts to flow through the auxiliary canister and to be adsorbed in here: when the system detects an increase of 2.0 g of the spare canister weight, the main canister is considered saturated and the test is stopped. The spare canister outlet is connected to an exhaust line and remaining vapors (mainly nitrogen) are disposed in order not to create a pressure increase at the canister outlet. This process is in line with what prescribed from the UN GTR no. 19 [37] regarding the butane working capacity measurement.
- 5. The canister is disconnected from the system and weighed on the spare scale to measure its weight increase, to have a static measurement of the canister weight gain, without the weight of pipes and thermocouple connections. Since adsorption

Canister			
activated carbons type canister bed volume	BAX 1100 1.0 <i>L</i>		
Loading		Purging	
n-butane constant flow nitrogen vol. flow rate initial temperature environmental temperature	$\begin{array}{c} 40 \ g/h \\ 0.5 \\ \sim 20 \ ^{\circ}C \\ \sim 20 \ ^{\circ}C \end{array}$	cooling down time nitrogen constant flux purging flow volume	$\sim 2 h$ 25 L/min 3000 BV (3000 L)

Table 4.1: Carbon canister filter: general testing conditions.

is an exothermic process, at the end of the loading test the internal temperature is higher than the environmental one, therefore the canister is cooled down for about 2 hours, until thermocouple T4 measures the environmental temperature.

- 6. The canister is then reconnected to the test bench for the purging test. Port A is connected to the inlet pipe, which provides the purging flux. Port E is connected to the exhaust line and port T is closed. Thermocouples connections and pipes disposition follow the same measures previously described for the loading test. In the purging phase of the test, the auxiliary canister is excluded.
- 7. The purging test starts (Figure 4.4(b)): nitrogen purges the sampled canister with a constant flow of 25 *L/min*, until the purging volume equals the 3000 bed volumes, which means that, for a 1.0 *L* canister, the purging test lasts 2 hours. It has been decided to use a higher level of purging with respect to the standard regulations (UN GTR [37]), which require a purging level of 300 *BV*, to better analyze the purging behavior and the canister mass variation during a longer time, since, as shown below, a nitrogen flow of 300 *BV* only purges about 60 % of the adsorbed n-butane quantity³.
- 8. The canister is weighed on the spare scale and test results are post-processed.

³The objective of this activity is to analyze the behavior of a full canister purging, hence a longer purging phase than the regulations prescribe. The target of the regulations is to set a purging period to standardize the definition of butane working capacity and to be closer to a common canister purging phase on a real on-road vehicle.

A complete test cycle lasts about 7 hours. The loading/purging test conditions are summarized in Table 4.1.

4.1.2 Results and Discussion

An example of data acquired during a loading test is shown in Figure 4.5. Figure 4.5(a) represents the canister mass variation due to n-butane adsorption during time⁴. The plot shows a linear increment of the canister mass for almost 2.5 h, then the curve slope slightly decreases until the test is interrupted at 2.75 h, when the spare canister has loaded 2.0 g of n-butane and the main canister is considered saturated.

In Figure 4.5(b) internal temperatures, recorded from the four thermocouples placed inside the carbon bed (see Figure 4.1(b) for thermocouples position), are compared each other and with the environmental temperature, during time. Since adsorption is an exothermic process, when the carbon bed near the thermocouple begins to adsorb fuel vapor, temperature increases rapidly, as seen from data recorded by thermocouples T1and T_2 , then, it slowly decreases until it reaches environmental values. The internal temperature variation allows to follow the adsorption path in the canister bed, while the canister mass gain only gives a total amount of adsorbed hydrocarbons during time. In particular, the shape of the temperature curve suggests the presence of two adsorption phases: a high-rate adsorption phase, in which the carbon bed section rapidly adsorbs a certain amount of fuel vapor and thus releases energy, and a low-rate adsorption phase, in which the carbon bed begins to cool down because of thermal exchange with the environment. Moreover, the temperature rise delay between thermocouples shows that each carbon bed section begins the adsorption only when the previous one has completed its first adsorption phase. This is due to a slow diffusion of the fuel vapor through the carbon bed [28] and to the very low n-butane flow rate at the inlet (port T). Temperatures recorded from thermocouples T3 and T4 are slightly different from the first ones: there is a small increment of temperature after 1 hour, and before the higher increment that

 $^{^4\}mathrm{Values}$ are non-dimensionalized with respect to the final mass value, because of agreements with Stellantis N.V.



Figure 4.5: Canister loading: (a) canister mass variation; (b) internal temperature variation.



Figure 4.6: Canister purging: (a) canister mass variation; (b) internal temperature variation.

characterizes the beginning of the adsorption. This behavior is due to the thermal exchange between the two canister sections: since T3 and T4 are at the same height of T2 and T1respectively, they also record the temperature increase of the first chamber of the canister.

Results of the purging test are shown in Figure 4.6. Unlike the loading, during the purging test most of the fuel vapor is desorbed in the first minutes of the test, and 90% of n-butane is purged in less than an hour, as can be seen in Figure $4.6(a)^5$. The dot on the curve in Figure 4.6(a) represents the quantity of desorbed vapor after 300 BV of purging flux, i.e. after 12 minutes of purging, which corresponds to the 56% of the total desorbed

 $^{^5\}mathrm{Values}$ are non-dimensionalized with respect to the final mass value, because of agreements with Stellantis N.V.



Figure 4.7: Internal and skin temperature comparison: (a) loading and (b) purging.

quantity of n-butane. After 2 hours, the canister mass trend is almost constant, and the canister can be considered purged.

As seen in Figure 4.6(b), temperatures recorded from the four thermocouples decrease almost at the same time, showing a different behavior with respect to the loading phase: when the fuel vapor is adsorbed, its quantity in the vapor flux is reduced, therefore the next section of the carbon bed is not interested in adsorption until the previous one begins to be saturated; on the other hand the purging flux affects all the sections of the carbon bed at once, therefore the desorption effects are recorded from all the thermocouples at the same time. Then, after this phase, the temperature gradually rises with a certain delay between the sections in which thermocouples are installed, starting from T4, which is the thermocouple that is closer to the inlet port of the purging flux (port A). This delay suggests that the desorption is gradually completed through the carbon bed, being the section near the port E the last one to complete the process. The purging process can also be influenced by a re-adsorption of butane, which has been purged from the first sections (e.g. near T4) and adsorbed from the last ones (e.g. near T1). This can be detected as a small temperature increase recorded by thermocouples 1 and 2 in the very first minutes of the test.

Temperature recorded by the skin thermocouple has been compared with the internal temperature variation recorded by T1, in Figure 4.7, for both loading and purging test phases. The two thermal profiles are similar, except for a scale factor that is obviously



Figure 4.8: Canister aging: total mass gain after canister breakthrough (non-dimensionalized with respect to the first value) and total loading time.



Figure 4.9: Canister aging: thermal profiles recorded by T1 (a) and T4 (b) for tests 1, 4 and 7.

due to the heat exchange with the environment: there is almost no delay between the two peaks (for loading) or valleys (for purging), and this suggests a constant-like behavior of the adsorption and desorption through the section. Therefore, the two phenomena can be described as they have a linear behavior that follows the flow path.

A series of 8 complete cycles (loading and purging) have been performed on the sampled canister. In Figure 4.8 the total adsorbed quantities, after the loading test, non-dimensionalized with respect to the value of the first loading, are compared to each other: it is possible to see a reduction of the canister adsorption capacity with the loading

cycles. This phenomenon can be explained by considering the "aging" of the carbons inside the canister filter: as described before, the micropores of the carbon bed are easily filled with high boiling hydrocarbons, which tend to remain trapped in these pores even during a high purging phase, as the one applied during the experiments. Therefore, the effective canister capacity is reduced for every cycle, until the adsorption performance stabilize. Even if 8 tests are few to determine a canister stabilization in loading performance, it is possible to see a principle of an asymptotic trend from data acquired. Figure 4.8 also reports the loading times, i.e. the time of each loading test until the 2.0 q of breakthrough are reached; as expected, a similar reduction trend is shown for the times. The same trend is confirmed by looking at the temperature profiles in Figure 4.9. Thermocouple T1 records a decrease of the temperature peak with the loading tests (Figure 4.9(a)), due to a reduction in the adsorption performance, and a less energetic second phase of adsorption, characterized by a reduced temperature. Moreover, subsequent thermocouples record an advance in time of the temperature rising with the loading tests; in particular, for thermocouple T4, where this effect is more visible (Figure 4.9(b)), there is a significant advance of the temperature peak and, thus, of the beginning of the adsorption phase in the section near the thermocouple (of about 0.4 h between test 1 and 7): since the carbon bed has a reduced adsorption capacity, the various sections of the canister are reached early, by the loading flux.

Other tests have been performed with this sampled canister, by using certified gasoline of type E10. The canister has been connected to the prototype fuel tank, described in 3.1.2. The tank has been filled with a predetermined quantity of fuel, placed inside the Mini-SHED (by following the procedure described in 3.1.1, points 1 to 4) and connected to the sampled canister, which is put inside the Mini-SHED, alongside the tank (representation of the test bench is given in Figure 4.10). Mini-SHED temperature is changed, by following the *ramp* and the *variable* test approaches. Canister internal and skin temperatures are recorded, along with liquid fuel temperature and tank vapor dome temperature⁶.

⁶Canister mass variation has attempted to be recorded. Since the Mini-SHED is an explosion risk environment, the precision weight scale used for the previous described applications cannot be used in this case. Therefore, an ATEX load cell (appendix B, device 7) has been adopted. However, for long-time tests, the load cell output has proven not to be reliable, since some mass variations have been recorded which cannot be caused by fuel vapor adsorption. Hence, canister mass variation data have not been reported.



Figure 4.10: Canister loading test with gasoline type E10: (a) test bench; (b) schematic representation.



Figure 4.11: Canister loading test with gasoline type E10, internal canister temperatures: (a) filling of 3.6 L, $T_{target} = 40 \ ^{\circ}C$; (b) filling of 7.2 L, $T_{target} = 40 \ ^{\circ}C$.

Figure 4.11 shows two examples of results obtained by this experimental setup, obtained by the *ramp* approach. Thermocouple T1 records a substantial increment of temperature in the first section of the canister, as the liquid fuel temperature rises till 40 °C, as a consequence of the adsorption process. On the other hand, temperature profiles recorded by thermocouples T2 and T3 follow the Mini-SHED temperature, meaning that the rest of the canister bed is not interested in adsorption. Thermocouple T4 records a small increment of temperature, that deviates from the T2 and T3: this is probably due to the fact that the temperature of the canister bed in the section near T4 is influenced by



Figure 4.12: Canister loading test with gasoline type E10, internal canister temperatures: filling of 3.6 L, CARB cycle.

the temperature in the section near T1, given the canister geometry and thermocouple disposition. A small difference in the peaks reached by thermocouple T1 in the cases of tank filling 3.6 L and 7.2 L is noted: this behavior confirms the higher level of fuel evaporation inside a fuel tank with a greater vapor space.

Finally, Figure 4.12 reports the results obtained by following the variable approach. It is possible to note an increment of the temperature recorded by thermocouple T1 with respect to the environmental temperature (which is followed by thermocouples T3 and T4), in the first day of the test, which means that only this section of the canister is interested by the adsorption. This increment is also recorded in the second day of the test, however, in this case, an higher temperature peak is recorded from thermocouple T2: while the first canister bed section continues to be filled by the fuel vapors, the second section starts to be interested by the vapors adsorption. During the third day, only thermocouple T2records a temperature increment, which means that the first section has been saturated. Of course, even if the test last 72 h and the canister has a small bed volume (1.0 L), the canister filter has not reached the saturation (indeed, only half of the canister has been interested by fuel adsorption) because the fuel tank (and then the fuel vapor quantity) is much smaller than a common tank for automotive applications.

4.2 1D Canister Adsorption Model

A 1D non-adiabatic, non-isothermal adsorption model has been developed, for analyzing and simulating the adsorption phenomena and for predicting the adsorption level and the canister saturation and breakthrough. Fuel vapor adsorption on active carbons has been evaluated by means of the adsorption isotherm theory. Then mass transport and thermal transport equations have been derived from the conservation of mass and energy, respectively. Geometric properties have also considered in canister modeling, since one of the aims of the project is to provide an instrument that can contribute for a better canister filter designing. Finally, the model has been implemented and solved in MATLAB(R)environment. The following model is partly derived from [121].

4.2.1 Adsotption Isotherm

An adsorption isotherm is a relation that describes the equilibrium conditions of an adsorbate-adsorbent system. As seen in 2.3, during the years many types of adsorption isotherms have been derived, but, in general, all of them describe an equilibrium relation between the quantity of the fluid (i.e. the *adsorbate*) which is adsorbed by a liquid or a solid (i.e. the *adsorbent*) and the quantity which has not yet been adsorbed, at a particular temperature (since the phenomenon has proved to be particularly sensitive to the temperature conditions). In particular, the adsorption isotherm theory adopted for deriving this adsorption model, which is the *potential theory* of adsorption, relates the adsorbed quantity of the vapor (i.e. the fuel vapor, or butane) adsorbed by the adsorbent (i.e. the activated carbons inside the canister filter) and the partial pressure of the non-adsorbed vapor in equilibrium with its adsorbed phase, by considering an adsorption potential (ε) which is function of the distance from the adsorbent surface. By considering equipotential surfaces, the adsorbent surface ($\varepsilon = f(V)$, equation 2.49).

Starting from the hypotheses described in 2.3.3, it is possible to derive an expression

of the adsorption potential, also called differential free energy of adsorption:

$$\varepsilon = RT \ln\left(\frac{P_{sat}(T)}{P_f}\right) = RT \ln\left(\frac{P_{sat}(T)}{P_{tot}} \cdot \frac{1}{Y_f}\right)$$
(4.1)

in which P_f is the partial pressure of the vapor adsorbate, in equilibrium with its adsorbed phase, P_{sat} is the saturation vapor pressure at the temperature T and $Y_f = P_f/P_{tot}$ is the vapor molar fraction (f at the subscript stands for fuel vapor). The Dubinin-Asthakov equation relates the differential free energy of adsorption with the adsorbed volume:

$$v = \frac{V}{V_0} = \exp\left[-\left(\frac{\varepsilon}{E}\right)^n\right] \tag{4.2}$$

where v is the relative volume of adsorbed fuel, and V_0 , E and n are calibration parameters dependent on the particular pair of adsorbate-adsorbent. In particular, V_0 is the maximum adsorbable volume of fuel, as liquid, per mass of carbon (measured in m^3/kg_C), since the adsorbed phase can be considered as having the same density of the liquid phase of the fuel. This parameter can be evaluated by the working capacity of the activated carbons (butane or gasoline working capacities: *BWC*, *GWC*), which is the mass of adsorbable fuel per volume of carbons (measured in kg/m_C^3):

$$V_0 \cdot \rho_L = WC/\rho_{app} \tag{4.3}$$

where ρ_L and ρ_{app} are the density of the fuel as liquid and the apparent density of the carbons, respectively. Hence, the mass of the adsorbed fuel vapor per mass of carbons (kg/kg_C) , can be derived as follows:

$$\bar{m} = V \cdot \rho_L = v \ V_0 \cdot \rho_L = v \ WC/\rho_{app} \tag{4.4}$$

By combining equations 4.1, 4.2 and 4.4, it possible to obtain the following relation between the adsorbed mass and the vapor molar fraction (i.e. the partial pressure of fuel in equilibrium with its adsorbed phase):

$$\bar{m} = \frac{WC}{\rho_{app}} \cdot \exp\left[-\left(\frac{RT}{E} \cdot \ln\left(\frac{P_{sat}(T)}{P_{tot}} \cdot \frac{1}{Y_f}\right)\right)^n\right]$$
(4.5)

A modification of equation 4.2 has been proposed by Lavoie and coworkers (equation 2.55), which has been rearranged here to have comparable measure units for the free energy of adsorption:

$$v = \begin{cases} A^* exp\left[-\left(\frac{\varepsilon}{E_1}\right)^n\right] & \varepsilon \ge E^* \\ B^* \left(1 + \frac{E_0}{\varepsilon}\right) & \varepsilon < E^* \end{cases}$$
(4.6a)

$$A^* = v^* \cdot \exp\left[\left(\frac{E^*}{E_1}\right)^n\right] \tag{4.6b}$$

$$B^* = \frac{v^*}{1 + \frac{E_0}{E^*}} \tag{4.6c}$$

where E_0 , E_1 (which is the equivalent of E for the first equation), E^* and v^* are calibration parameters determined by fitting experimental data obtained from butane adsorption on activated carbons at different temperatures and partial pressures. Thus, equation 4.5 becomes:

$$\bar{m} = \begin{cases} A^* \frac{WC}{\rho_{app}} \cdot \exp\left[-\left(\frac{1}{E_1} \cdot RT \ln\left(\frac{P_{sat}(T)}{P_{tot}} \cdot \frac{1}{Y_f}\right)\right)^n\right] & Y_f \le \frac{P_{sat}(T)}{P_{tot}} \cdot \exp\left(-\frac{E^*}{RT}\right) \\ B^* \frac{WC}{\rho_{app}} \cdot \left[1 + E_0 / \left(RT \ln\left(\frac{P_{sat}(T)}{P_{tot}} \cdot \frac{1}{Y_f}\right)\right)\right] & Y_f > \frac{P_{sat}(T)}{P_{tot}} \cdot \exp\left(-\frac{E^*}{RT}\right) \end{cases}$$
(4.7)

The differences between equation 4.2 and 4.6a can be visualized in Figure 4.13. Both the equations have been implemented in the adsorption model, although the second approach has proven to give better results [121].



Figure 4.13: Differential free energy of adsorption vs relative volume of adsorbed fuel: comparison between Dubinin-Asthakov and Lavoie equations.

4.2.2 Mass Transport Equation

As seen, experimental observations suggest that the adsorption behavior in a carbon bed of a canister filter can be described by using a 1D approach, with a good approximation. Hence, it is possible to consider a control volume of cylindrical form, with ∂x as height and the canister bed cross-sectional area $A_C(x)$ as basis. For this volume, the quantity of adsorbed vapors can change in time because of convective and diffusive fluxes, as represented by the continuity of moles below:

$$\frac{\partial \left(A_C(x) \cdot \bar{n}\right)}{\partial t} = -\frac{\partial \left(\dot{N}_{conv} + \dot{N}_{diff}\right)}{\partial x} \tag{4.8}$$

where $\bar{n} \ (mol/m_C^3)$ is the number of moles adsorbed by a unit volume of carbons, while \dot{N}_{conv} and \dot{N}_{diff} are respectively the convective and diffusive molar fluxes (mol/s) of fuel vapor. If the fuel vapor flow is in mixture with an inert (e.g. air, nitrogen), it is possible to evaluate the convective term of the equation by relating the fuel flux with the inert one, \dot{N}_a , which is defined by initial conditions and remains constant across the bed (since it

does not take part in the adsorption):

$$\dot{N}_{conv} = \dot{N}_a \cdot \frac{Y_f}{Y_a} = \dot{N}_a \cdot \frac{Y_f}{1 - Y_f} \tag{4.9}$$

The diffusive factor can be expressed as:

$$\dot{N}_{diff} = -A_C(x)D_f \frac{\partial n_f}{\partial x}$$
(4.10)

where D_f is the fuel vapor phase diffusion coefficient⁷ and n_f is the molar concentration of the fuel vapor in the gas phase (mol/m^3) , which can be written as the total gas phase concentration n_{tot} times the vapor molar fraction Y_f . For the ideal gas law, n_{tot} is equal to P_{tot}/RT , hence, its variation with x is little since it only depends on the variation of the absolute temperature, thus, it can be removed from the differential term. Moreover, by considering the two components (fuel vapor and air/inert) as ideal gases, the fuel vapor diffusion coefficient can be written in terms of the inert self-diffusion coefficient $D_f = D_a \sqrt{W_a/W_f}$ (being W_f and W_a the molar mass of the fuel and the inert, respectively). Therefore:

$$\dot{N}_{diff} = -A_C(x) \ D_a \sqrt{\frac{W_a}{W_f}} \ \frac{P_{tot}}{RT} \ \frac{\partial Y_f}{\partial x}$$

$$(4.11)$$

Equation 4.8 then becomes:

$$A_C(x) \cdot \frac{\partial \bar{n}}{\partial t} = -\frac{\partial}{\partial x} \left[\dot{N}_a \ \frac{Y_f}{1 - Y_f} - A_C(x) \ D_a \sqrt{\frac{W_a}{W_f}} \ \frac{P_{tot}}{RT} \ \frac{\partial Y_f}{\partial x} \right]$$
(4.12)

Finally, by replacing \dot{N}_a with \dot{m}_a/W_a (\dot{m}_a being the inert mass flow) and changing the moles of adsorbed fuel per unit volume with the mass per unit mass of carbons (i.e.

⁷Diffusion in the gas phase is prevalent with respect to the one in the adsorbed phase, which is neglected in this model.

multiplying all the terms by W_f/ρ_{app}), the mass transport equation can be written as:

$$A_C(x)\frac{\partial \bar{m}}{\partial t} = \frac{\partial}{\partial x} \left[D_a \; \frac{P_{tot} \cdot W_a}{R \cdot \rho_{app}} \; \sqrt{\frac{W_f}{W_a}} \; A_C(x) \; \frac{1}{T} \; \frac{\partial Y_f}{\partial x} \; + \frac{\dot{m}_a}{\rho_{app}} \; \frac{W_f}{W_a} \; \left(1 - \frac{1}{1 - Y_f}\right) \right]$$
(4.13)

4.2.3 Thermal Transport Equation

Considering the same element of the canister bed, the conservation of energy is the follow:

$$\frac{\partial E}{\partial t} = -\frac{\partial Q_c}{\partial x} - \frac{\partial Q_k}{\partial x} - \frac{\partial Q_l}{\partial x}$$
(4.14)

where $E(J/m_C \text{ joule per meter of carbon bed})$ is the total energy in the canister bed element, while Q_c and $Q_k(W)$ are energy fluxes due to convection and conduction⁸, and $Q_l(W)$ is the energy lost through the canister plastic wall and into the environment.

The energy convective flux is the sum of the enthalpies of the gas species, fuel vapor and inert:

$$Q_{c} = \dot{m}_{f}h_{f} + \dot{m}_{a}h_{a} = \dot{m}_{a}\left(\frac{\dot{m}_{f}}{\dot{m}_{a}}h_{f} + h_{a}\right) = \dot{m}_{a}\left(\frac{W_{f}}{W_{a}} \cdot \frac{Y_{f}}{1 - Y_{f}}h_{f} + h_{a}\right) = \frac{\dot{m}_{a}}{W_{a}\left(1 - Y_{f}\right)}\left(W_{f}h_{f}Y_{f} + W_{a}h_{a}\left(1 - Y_{f}\right)\right)$$

$$(4.15)$$

The conduction term is expressed as:

$$Q_k = -A_C(x) \cdot k_C \frac{\partial T}{\partial x}$$
(4.16)

where k_C is the thermal conductivity of the carbon bed.

 $^{^{8}\}mathrm{The}$ energy flux due to diffusion is expected to be small compared with the conduction term, and hence it is neglected

The loss term Q_l represents the heat lost to the environment through the perimeter $P_C(x)$ of the canister section:

$$\frac{\partial Q_l}{\partial x} = P_C(x) \cdot U_{ext} \cdot (T - T_{env}) \tag{4.17}$$

where U_{ext} is the overall heat transfer coefficient between the carbon bed and the external environment⁹.

The internal energy E is the sum of the specific energies of carbons (e_c) , plastic wall (e_p) , fuel (e_f) and inert vapors (e_a) , evaluated with respect to the mass of carbons, as well as adsorbed fuel (E_s) :

$$\frac{\partial E}{\partial t} = \frac{\partial}{\partial t} \left\{ \rho_{app} \cdot A_C(x) \cdot \left[e_c + m_p e_p + m_f e_f + m_a e_a + E_s\left(\bar{m}, T\right) \right] \right\} =
= \frac{\partial}{\partial t} \left\{ \rho_{app} \cdot A_C(x) \cdot \left[c_{v,c} T + m_p c_{p,p} T_p + m_f c_{v,f} T + m_a c_{v,a} T + E_s\left(\bar{m}, T\right) \right] \right\}$$
(4.19)

where m_p , m_f and m_a are the masses of plastic, fuel vapor and inert per unit mass of carbons (kg/kg_C) , while E_s is the specific energy of the adsorbed phase, evaluated per unit mass of carbons (J/kg_C) . This quantity can be determined by considering the heat of adsorption of the fuel vapor (ΔH_A) , which is defined as the differential change in specific enthalpy of the vapor going from the adsorbed state to the vapor state. By applying the energy conservation principle on the fuel vapor during its desorption, considering the volume of the liquid phase negligible, and by applying the ideal gas law, it is possible to

$$U_{ext} = \frac{1}{\frac{1}{U_C} + \frac{\sqrt{A_C(x)}}{F_q \cdot k_C}}$$
(4.18)

 $^{{}^{9}}U_{ext}$ can be expressed as the composition of the conductive heat transfer coefficient, inside the canister, and the convective one, outside the canister (U_C) , as follows:

where F_g is a geometric factor that depends on the shape of the carbon bed section (for squared sections, $F_g = 3$).

derive the internal energy change as:

$$de_f = dh - P \ dv = \Delta H_A - P \left(v_{vap} - v_{liq} \right) = \Delta H_A - P v_{vap} = \Delta H_A - \frac{RT}{W_f}$$
(4.20)

The heat of adsorption can also be considered as the sum of the heat of vaporization (ΔH_{vap}^{10}) and the differential free energy of adsorption ($\varepsilon(v)^{11}$). Therefore, the differential energy of the adsorbed fuel, with respect to the mass adsorbed, is:

$$\frac{dE_s}{d\bar{m}} = c_{v,f}T - \left(\Delta H_A - \frac{RT}{W_f}\right) = c_{p,f}T - \Delta H_A = c_{p,f}T - \Delta H_{vap}(T) - \frac{\varepsilon(v)}{W_f}$$
(4.21)

and its integral form is:

$$E_s = (c_{p,f}T - \Delta H_{vap}(T)) \cdot \bar{m} - \int \frac{\varepsilon(v)}{W_f} d\bar{m}$$
(4.22)

Then, equation 4.19 becomes¹²:

$$\frac{1}{\rho_{app}A_{C}(x)} \cdot \frac{\partial E}{\partial t} = \frac{\partial}{\partial t} \left[c_{v,c}T + m_{p}c_{p,p}T_{p} + (c_{p,f}T - \Delta H_{vap}(T)) \cdot \bar{m} - \int \frac{\varepsilon(v)}{W_{f}} d\bar{m} \right] = \\ = \left[c_{v,c} + m_{p}c_{p,p}\frac{\partial T_{p}}{\partial T} + \bar{m} \cdot \left(c_{p,f} - \frac{\partial \Delta H_{vap}}{\partial T} \right) \right] \cdot \frac{\partial T}{\partial t} + \left[c_{p,f}T - \Delta H_{vap}(T) - \frac{\varepsilon(v)}{W_{f}} \right] \cdot \frac{\partial \bar{m}}{\partial t}$$

$$(4.23)$$

 $^{^{10}}$ Which can be valuated by the Clausius-Clapeyron relation or from known values in literature (e.g. [142]).

¹¹Obtained by inverting equation 4.1 or 4.6a

¹²The internal energies of the vapor components $(m_f c_{v,f} T \text{ and } m_a c_{v,a} T)$ is negligible compared to the other factors, and then it has been removed from the equation, for reducing the computational effort.

Finally, the thermal transport equation can be derived:

$$\begin{bmatrix} c_{v,c} + m_p c_{p,p} \frac{\partial T_p}{\partial T} + \bar{m} \cdot \left(c_{p,f} - \frac{\partial \Delta H_{vap}}{\partial T} \right) \end{bmatrix} \cdot \frac{\partial T}{\partial t} + \\ \begin{bmatrix} c_{p,f} T - \Delta H_{vap}(T) - \frac{\varepsilon(v)}{W_f} \end{bmatrix} \cdot \frac{\partial \bar{m}}{\partial t} = \\ = -\frac{1}{A_C(x)} \cdot \frac{\partial}{\partial x} \left[\frac{\dot{m}_a T}{\rho_{app} W_a (1 - Y_f)} \left(c_{p,f} W_f Y_f + c_{p,a} W_a (1 - Y_f) \right) + \\ -A_C(x) \frac{k_C}{\rho_{app}} \frac{\partial T}{\partial x} \right] - \frac{P_C(x) \cdot U_{ext} \cdot (T - T_{env})}{\rho_{app} A_C(x)} \end{aligned}$$
(4.24)

The thermal inertia of the plastic wall with respect to the carbon bed, $\partial T_p/\partial T$, is determined experimentally by averaging the relation between the plastic wall temperature and the internal carbon bed temperature, during time, evaluated in the same canister section (therefore, the need of a *skin* thermocouple on the canister wall). The heat transfer coefficient U_{ext} (or U_C , see 9) can be also determined experimentally by solving equation 4.24 in the canister cooldown phase after the loading experiment: in this condition, there is no adsorption $(\partial \bar{m}/\partial t = 0)$ or flow, hence, the loss term is prevalent on the others $(Q_c, Q_k << Q_l)$:

$$\frac{\partial T}{\partial t} = -\frac{\left(P_C(x) \cdot U_{ext}\right) / \left(\rho_{app} A_C(x)\right)}{c_{v,c} + m_p c_{p,p} \frac{\partial T_p}{\partial T} + \bar{m} \cdot \left(c_{p,f} - \frac{\partial \Delta H_{vap}}{\partial T}\right)} \cdot \left(T - T_{env}\right)$$
(4.25)

4.2.4 Model Implementation

The coupled system of 1D partial differential equations (pde) 4.13 and 4.24 has been implemented in MATLAB® environment¹³. The two transport equations have been

¹³With some future modifications, the model can also be executed on GNU Octave, however, the computational speed and result accuracy obtrained in MATLAB environment are not guaranteed.

rearranged as follows:

$$a(\bar{m},T)\frac{\partial\bar{m}}{\partial t} + b(\bar{m},T)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[\alpha(\bar{m},T)\bar{m} + \gamma(\bar{m},T)\frac{\partial\bar{m}}{\partial x} \right] + \frac{\partial}{\partial x} \left[\beta(\bar{m},T)T + \delta(\bar{m},T)\frac{\partial T}{\partial x} \right] + S(\bar{m},T)$$

$$(4.26)$$

where the coefficients determined for the mass and the temperature equations are listed below:

$$a_m(\bar{m},T) = A_C(x) \tag{4.27a}$$

$$b_m(\bar{m},T) = 0 \tag{4.27b}$$

$$\alpha_m(\bar{m},T) = 0 \tag{4.27c}$$

$$\beta_m(\bar{m}, T) = \frac{\dot{m}_a}{\rho_{app}} \frac{W_f}{W_a} \left(1 - \frac{1}{1 - Y_f(\bar{m}, T)} \right) \cdot \frac{1}{T}$$
(4.27d)

$$\gamma_m(\bar{m},T) = D_a \frac{P_{tot} \cdot W_a}{R \cdot \rho_{app}} \sqrt{\frac{W_f}{W_a}} A_C(x) \frac{1}{T} \frac{\partial Y_f(\bar{m},T)}{\partial \bar{m}}$$
(4.27e)

$$\delta_m(\bar{m},T) = D_a \frac{P_{tot} \cdot W_a}{R \cdot \rho_{app}} \sqrt{\frac{W_f}{W_a}} A_C(x) \frac{1}{T} \frac{\partial Y_f(\bar{m},T)}{\partial T}$$
(4.27f)

$$S_m(\bar{m},T) = 0 \tag{4.27g}$$

$$a_T(\bar{m},T) = A_C(x) \cdot \left(c_{p,f}T - \Delta H_{vap}(T) - \frac{\varepsilon(\bar{m})}{W_f} \right)$$
(4.28a)

$$b_T(\bar{m},T) = A_C(x) \cdot \left[c_{v,c} + m_p c_{p,p} \frac{\partial T_p}{\partial T} + \bar{m} \cdot \left(c_{p,f} - \frac{\partial \delta h_{vap}(T)}{\partial T} \right) \right]$$
(4.28b)

$$\alpha_T(\bar{m}, T) = 0 \tag{4.28c}$$

$$\beta_T(\bar{m},T) = \frac{\dot{m}_a c_{p,f} W_f}{\rho_{app} W_a} \cdot \left(1 - \frac{1}{1 - Y_f}\right) - \frac{\dot{m}_a}{\rho_{app}} c_{p,a}$$
(4.28d)

$$\gamma_T(\bar{m}, T) = 0 \tag{4.28e}$$

$$\delta_T(\bar{m},T) = A_C(x) \cdot \frac{k_C}{\rho_{app}} \tag{4.28f}$$

$$S_T(\bar{m}, T) = -\frac{P_C(x) \cdot U_{ext} \cdot (T - T_{env})}{\rho_{app} A_C(x)}$$

$$(4.28g)$$

where $Y_f(\bar{m}, T)$ is evaluated from equation 4.1:

$$Y_f(\bar{m}, T) = \frac{P_{sat}(T)}{P_{tot}} \cdot \exp\left(-\frac{1}{RT} \cdot \varepsilon(\bar{m})\right)$$
(4.29)

and the adsorption potential $\varepsilon(\bar{m})$ is derived as a function of \bar{m} by combining equation 4.4 with equation 4.2 (or with equation 4.6a):

$$\varepsilon(\bar{m}) = E \left[ln \left(\frac{WC}{\rho_{app}\bar{m}} \right) \right]^{\frac{1}{n}}$$
(4.30a)

$$\varepsilon(\bar{m}) = \begin{cases} E_1 \left[ln \left(\frac{A^* \cdot WC}{\bar{m}\rho_{app}} \right) \right]^{\frac{1}{n}} & \bar{m} \le \bar{m}^* \\ E_0 / \left(\frac{\bar{m} \cdot \rho_{app}}{B^* \cdot WC} - 1 \right) & \bar{m} > \bar{m}^* \end{cases}$$
(4.30b)

where \bar{m}^* is derived from 4.4, by replacing v with v^* .

The boundary conditions considered are of the first type on the left (at the beginning of the carbon bed, with respect to the flow direction, x = 0), since the fuel molar fraction and the temperature of the flows are known, while they are of the second type of the right (at the end of the carbon bed, x = L), being the adsorbed mass and temperature variations through x equal to 0 at the end of the canister). Initial conditions are given as uniform on the whole carbon bed, since before the test it can be considered uniformely purged and in thermal equilibrium with the environment.

$$B.C.: \begin{cases} \bar{m}(0,t) = \bar{m}_0(t) = \bar{m}_0; & T(0,t) = T_0(t) = T_0 \\ \frac{\partial \bar{m}}{\partial x}(L,t) = 0; & \frac{\partial T}{\partial x}(L,t) = 0 \end{cases}$$
(4.31a)

$$I.C.: \ \bar{m}(x,0) = \bar{m}_{init}(x) = \bar{m}_{init} \ ; \ T(x,0) = T_{init}(x) = T_{init}$$
(4.31b)

The system has been numerically solved by discretizing the two partial differential equations in a series of algebraic equations. Starting from equation 4.26, the various terms are discretized as follows, by adopting the implicit (backward Euler) method:

$$a(\bar{m},T)\frac{\partial\bar{m}}{\partial t}\Big|_{i,n+1} = a_{i,n+1} \cdot \frac{\bar{m}_{i,n+1} - \bar{m}_{i,n}}{\Delta t}$$
(4.32a)

$$b(\bar{m},T)\frac{\partial T}{\partial t}\Big|_{i,n+1} = b_{i,n+1} \cdot \frac{T_{i,n+1} - T_{i,n}}{\Delta t}$$
(4.32b)

$$\frac{\partial}{\partial x} \left[\alpha(\bar{m}, T) \cdot \bar{m} \right] \Big|_{i,n+1} = \frac{\alpha_{i+1,n+1} \bar{m}_{i+1,n+1} - \alpha_{i-1,n+1} \bar{m}_{i-1,n+1}}{2\Delta x}$$
(4.32c)

$$\left. \frac{\partial}{\partial x} \left[\beta(\bar{m}, T) \cdot T \right] \right|_{i,n+1} = \frac{\beta_{i+1,n+1} T_{i+1,n+1} - \beta_{i-1,n+1} T_{i-1,n+1}}{2\Delta x}$$
(4.32d)

$$\frac{\partial}{\partial x} \left[\gamma \cdot \frac{\partial \bar{m}}{\partial x} \right] \Big|_{i,n+1} = \gamma_{i,n+1} \frac{\bar{m}_{i+1,n+1} - 2\bar{m}_{i,n+1} + \bar{m}_{i-1,n+1}}{(\Delta x)^2} + \frac{\gamma_{i+1,n+1} - \gamma_{i-1,n+1} + \bar{m}_{i+1,n+1} - \bar{m}_{i-1,n+1}}{(\Delta x)^2}$$

$$(4.32e)$$

$$\frac{\partial}{\partial x} \left[\delta \cdot \frac{\partial T}{\partial x} \right] \Big|_{i,n+1} = \delta_{i,n+1} \frac{\Delta x}{T_{i+1,n+1} - 2T_{i,n+1} + T_{i-1,n+1}}_{(\Delta x)^2} + \frac{\delta_{i+1,n+1} - \delta_{i-1,n+1}}{\Delta x}$$
(4.32f)

$$\Delta x \qquad 2\Delta x \qquad (4.32g)$$

where, for each parameter, $c_{i,n} = c(\bar{m}_{i,n}, T_{i,n})$. Subscripts *i* (that goes from 1 to *N*) and *n*



Figure 4.14: Geometric interpretation of the Newton-Raphson method [143].

(that goes from 0 to τ) represent the *i*-th spatial node of the spatial mesh and the *n*-th time step, respectively. By replacing equations 4.32 into equations 4.26 for both mass and temperature (and by discretizing the equations for the boudary conditions 4.31a), it is possible to obtain a system of 2N algebraic equations, in the implicit form $f_i(\bar{m}, T) = 0$, where N is the number of nodes in which the spatial mesh is divided. The system is solved by the Newton-Raphson method, which is an iterative method for solving non-linear equations and systems. The iteration is briefly described below (Figure 4.14, [143]):

- 1. Start with a guess for the root vector, $[\phi] = [\phi]^0$, where $[\phi]$ is composed by the unknown values of \bar{m} and T for each node;
- 2. derive the Jacobian matrix $[J] = [\partial f_i / \partial \phi_j]$ by determining the partial derivatives of the functions $f_i(\bar{m}, T)$ with respect to the variables φ_i ;
- 3. determine the next approximation of the root vector by solving the equation $[J]^{(n)} \left([\phi]^{(n+1)} [\phi]^{(n)} \right) = [f]^{(n)};$
- 4. update the solution $[\phi]^{(n+1)} = [\phi]^{(n)} + \omega \left([\phi]^{(n+1)} [\phi]^{(n)} \right);$
- 5. repeat steps 3 and 4 until convergence is reached (i.e. the residual must be: $R_2 = \sqrt{\sum_{i=1}^{2N} (f_i)^2} < \epsilon$).



Figure 4.15: Algorithm of the canister model.

 ω is the relaxation factor, which is usually between 0 and 1: for values of ω smaller than 1, the solution between the successive iterations is changed by only a fraction of the predicted change. This helps to stabilize the convergence, but, on the other hand, in general more iterations will be required for the convergence.

A representation of the algorithm of the model is given in Figure 4.15. Starting from a guess of the solution, which is given by the solution of the previous time step (for the first timestep, it is the initial condition), the system is solved and the residual is evaluated. If the residual respects the convergence condition (i.e. $R_2 < \epsilon$), the solution found is saved and the code passes to a new timestep to re-execute the process, otherwise, the solution is used as a new guess to solve the system until the convergence condition is respected (a minimum number of iterations can be given to the system, to avoid inexact solutions). Two sub-routines have been added to the code, which allow for dynamic modifications of two factors that can influence the convergence. The first one is the timestep reduction: if the iteration process does not reach the convergence condition after a predetermined number of iterations, the timestep is halved and the iteration starts from the previous guess. Then, when the number of iterations needed for convergence is less than half

the maximum allowable number of iterations, for a predetermined number of steps, the timestep is doubled, until it reaches a maximum value. This sub-routine allows for a better resolution of the system for critical timesteps (such as the first ones, when there is an high gradient of adsorbed mass between the first node and the next ones), while allowing to speed up the simulation under normal circumstances. The second sub-routine checks for a convergence issue: since in the system there are some logarithmic dependencies between variables (as the one expressed in equation 4.30), during the research of a solution for the specific time step, the iteration can reach negative values for one or more variables, and this generates an error that interrupts the simulation. Hence, the relaxation factor is added, to avoid this error, but since, as said, a low relaxation factor (less than 0.5) significantly slows down the simulation, a variable relaxation factor has been introduced. In normal conditions, the simulation runs with the higher value of relaxation (the default value is 1, but it can be changed) and checks for negative values of the solution; when the check is positive, the relaxation factor is reduced and the iteration starts from the previous guess (if the relaxation factor reaches a minimum value, the timestep is reduced and the iterations starts again).

4.2.5 Results and discussion

To be solved, the model needs various parameters, that regard the fuel and the air/inert gas characteristics, as well as active carbons thermal and adsorption properties and some calibration parameters for the adsorption isotherm relation. Table 4.2 reports a complete list of parameters needed for the model, along with a brief description and the value initially adopted for the case analyzed, which is the case proposed in the experimental activity reported previous in this chapter.

In Figure 4.16, results of the simulation have been compared to the experimental data presented in 4.1.2: the model predicts well the canister mass gain for the first 1.5 h, then, the adsorption rate of simulated canister begins to decrease, as the carbon bed becomes to be completely filled by the adsorbate, almost 45 minutes before the real canister. From Figure 4.16(a), it can be noted that, after 3 h, the simulated canister has adsorbed only the 70% of what has been loaded on the real canister after 2.75 h (at its breakthrough

Field	Symbol	Name	Current value	Unit measure
general	$\mid R$	universal gas constant	8.314	$J/(mol \ K)$
adsorbate (butane)	$ \begin{vmatrix} \rho_L \\ W_f \\ P_{sat}(T) \\ c_{p,f} \\ \Delta H_{vap} \end{vmatrix} $	liquid density vapor molar mass saturation vapor pressure vapor specific heat capacity (isobaric) specific heat of vaporization	$ \begin{array}{c} 604 \\ 58.12 \cdot 10^{-3} \\ \text{tabular } (T) \\ 1732 \\ \text{tabular } (T) \end{array} $	$\begin{array}{c} Kg/m^3\\ kg/mol\\ Pa\\ J/(kg\;K)\\ J/kg \end{array}$
inert (nitrogen)	$\left \begin{array}{c} W_a \\ c_{p,a} \\ D_a \end{array}\right $	molar mass specific heat capacity (isobaric) self-diffusion coefficient	$28.0134 \cdot 10^{-3} \\ 1040 \\ 1.5$	$ \begin{array}{c} kg/mol\\ J/(kg\ K)\\ m^2/s \end{array} $
canister	$ \begin{vmatrix} L_C \\ P_C(x) \\ A_C(x) \\ V_C \\ WC \\ \rho_{app} \\ c_{v,c} \\ k_C \\ U_C \\ m_p \\ c_{p,p} \\ dT_p/dT \end{vmatrix} $	carbon bed length carbon bed cross-sectional perimeter carbon bed cross-sectional area carbon bed volume working capacity (with butane) apparent carbon density carbon specific heat capacity thermal conductivity of carbon bed convective heat transfer coefficient mass of plastic wall per mass of carbon plastic wall specific heat capacity wall/carbon temperature change ratio	$\begin{array}{c} 0.387 \\ \text{tabular } (x) \\ \text{tabular } (x) \\ 1.0 \cdot 10^{-3} \\ 110 \\ 363 \\ 700 \\ 0.13 \\ 13 \\ 0.5 \\ 1900 \\ 0.34 \end{array}$	$\begin{array}{c} m \\ m \\ m^2 \\ m^3 \\ Kg/m_c^3 \\ Kg_c/m_c^3 \\ J/(kg \; K) \\ W/(m \; K) \\ W/(m \; K) \\ W/(m^2 \; K) \\ kg/kg_c \\ J/(kg \; K) \\ K/K \end{array}$
adsorption isotherm	$\begin{vmatrix} E_0 \\ E_1 \\ n \\ E^* \\ v^* \end{vmatrix}$	adsorption isotherm parameter adsorption isotherm parameter adsorption isotherm exponent adsorption isotherm parameter (treshold) adsorption isotherm parameter (treshold)	$\begin{array}{c} 48.153 \\ 8.18 \cdot 10^3 \\ 1.2 \\ 385 \\ 0.9 \end{array}$	J/mol J/mol m^3/m^3
mesh definition	$\left \begin{array}{c} \Delta x \\ \Delta t \\ \tau \end{array}\right $	distance between mesh nodes timestep (max. value) simulation time	$0.004 \\ 0.5 \\ 3$	$egin{array}{c} m \ s \ h \end{array}$
convergence parameters	$\left \begin{array}{c} i_{max} \\ \epsilon \end{array} \right $	maximum number of iterations allowable convergence criterion $(R_2 < \epsilon)$	$25 \\ 10^{-10}$	_
initial conditions	$\begin{vmatrix} \bar{m}_{init}(x) \\ T_{init}(x) \end{vmatrix}$	initial adsorbed mass in carbon bed initial temperature in carbon bed	tabular (x) tabular (x)	$\frac{kg/kg_c}{K}$
boundary conditions	$ \begin{vmatrix} \dot{m}_{f,left} \\ Y_{f,left} \\ T_{left} \\ P_{tot} \\ T_{env} \end{vmatrix} $	inlet adsorbate mass flow inlet molar fraction of adsorbate temperature of the inlet flux flow pressure environmental temperature	$\begin{array}{c} 40/(3.6\cdot10^6)\\ 0.5\\ 20+273.15\\ 101325\\ 20+273.15\end{array}$	kg/s mol/mol K Pa K

 Table 4.2: Parameters for canister adsorption model.



Figure 4.16: Canister loading, model results, comparison with experimental data: (a) canister mass variation; (b) internal temperature variation.

condition). From Figure 4.16(b), it is also possible to notice that the carbon sections of the simulated canister increase their temperature before the ones in the real canister,

hence, the saturation is reached more quickly than it should have¹⁴. This behavior is probably due to a wrong set of calibration parameters, particularly, of the adsorption isotherm, which have been initially taken from literature, since a direct evaluation of these parameters would have required an equipment that was not available in the test facility. Therefore, an indirect approach has been adopted for parameters calibration, which has been developed by using an optimization method, which is described in the next section.

4.2.6 DFSS optimization

DFSS stands for Design For Six Sigma, which is a business process management methodology for the development and optimization of a product or a process, at the lowest possible cost [144]. It was derived by Dr. Genichi Taguchi with the aim of developing a product or a process that is characterized by solutions (the final product/process) that are as less influenced by uncontrollable variations (raw material properties variation, external weather conditions, etc.) as possible. In a production process, or in a simulation model, it is possible to distinguish the various parts (or terms) in three groups: the *signals* are the intended outputs of the system, that is the final product or the results of a simulation; the *design parameters* are the inputs of the process, i.e. what is required to obtain the targets of the process (raw materials, machines, personnel, or model type, input and calibration parameters, computing power, etc.); the *noises* are composed by the elements of disturbance which can affect the final product, and were not included in the design process. Differently from the classical optimization models, the DFSS model is a "method to learn" about the relations among parameters and their influence on the whole system. A complete DFSS approach consists of five phases, identified by the acronym *IDDOV*:

¹⁴Simulated thermocouples T1 and T2 record a temperature increase slightly before the real thermal variation recorded in the experimental test. This is probably due to the internal geometry of the canister itself: after the liquid separator, the flow passes through a small cylinder inserted in the carbon bed, with openings on its side surface. Thus, the carbon section near T1 begins the adsorption phase before its simulated equivalent, since it is reached by a part of the vapors that has not passed through the first centimeters of the carbon bed. This behavior cannot be emulated by a 1D model, since at least another spatial dimension is required. Nevertheless, it is possible to notice that the time delay between the thermal increase recorded by T1 and T2 is smaller than the real one, and this confirms the fact that the simulated adsorption is faster and less effective that the real case.

- *Identify* the problem, by defining what is the purpose of the activity. In this phase, a distinction is made between what is "in-scope", i.e. what are the needs to reach, and "out-of-scope", i.e. what influences the process but will not be changed/optimized. Then, a plan is developed on how to satisfy the targets, based on the previous identifications.
- *Define* the customers and the customers' requirements, which in general are different from the ones the engineer thinks the customer has. Then, these requirements are converted in functional requirements (through a process named Quality Function Deployment, QFD), that are specific, countable ways to ensure the customers' needs, and with which the needs are uniquely defined.
- Develop the concepts as well as generate concept alternatives and select the best strategy. In this phase, the system is deeply analyzed, therefore internal contradictions are resolved and the functional elements for optimization are determined. This is the main phase of the project, in which there is the greater opportunity of development and where the main part of the resources allocated to the project are spent.
- Optimize the process to develop a "robust" product/process¹⁵. This is done by defining the scope of the optimization and identifying the response function of the process/system, which is the function to be optimized. Then, design and noise parameters are defined, which are respectively the input parameters to vary and the uncontrollable parameters that have more effect on the system. The system is tested by varying the parameters values according to specific strategies, that will help to identify the sensitivity of these parameters on the response function, and how the system robustness to noise factors is affected by changing these parameters. An optimal design is then built by choosing the parameters values that increase the response function value and the robustness of the system.
- Verify that the product/process has reached the functional requirement predicted,

¹⁵Robusness is defined as "the state of performance where the technology, product, or process is minimally sensitive to factors causing variability at the lower cost" [144].
by testing the optimal configuration derived in the previous phase.

For this application, the IOV reduction method has been used, that is identify the problem and parameters (already done in the previous sections), optimize the calibration parameters system and verify the system results. The value to be optimized is the difference between the simulated and the experimental adsorbed quantity in the canister. Therefore, the approach named *Nominal the Best* has been adopted, which is used when there is a single value that represents the optimal output of the system.

Several parameters have been chosen as design parameters, to be optimized, which are the adsorption isotherm parameters $(E_0, E_1, n, E^* \text{ and } v^*)$ and the canister thermal properties $(k_C, c_{v,c}, c_{p,p}, U_C, m_p \text{ and } dT_p/dT)$. Parameters that represent the external noises are the working capacity (WC), being dependent on the canister filter and thus not controlled, and the initial and boundary temperatures $(T_{init}, T_{left} \text{ and } T_{env})$, being dependent on external uncontrolled conditions. Table 4.3 lists the values of the noise parameters adopted for this analysis. Values have been chosen among the plausible values for these parameters: a batch-to-batch variation on the activated carbons can lead to a variation on the (butane) working capacity, while during the operating conditions on the gasoline vehicle, the external temperature can significantly change. These values are divided in two configurations, which have a low-response (N1) and a high-response (N2) on the optimization function: a lower working capacity leads to a lower value of fuel adsorbed quantity, while adsorption performance decreases with the temperature.

The DFSS optimization process consists of varying the parameters values in a predetermined way, that allows for obtaining information about the influence they have on the response function without executing the experiments/simulations for all their possible combinations. To be effective, however, the number of parameters and also the number

Table 4.3: Noise	parameters val	ues.
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	Noise	N1	N2	Unit
1	WC	100	120	kg/m_c^3
2	T_{init}	35	20	$^{\circ}C$
3	T_{left}	45	20	$^{\circ}C$
4	T_{amb}	35	20	$^{\circ}C$

of values for each parameter must be chosen within a set of predetermined quantities: this allows for building an orthogonal array of experimental/simulation cases, that defines the minimum number of cases to execute, by varying the parameters values, to obtaining the data required for understanding the mutual influences the parameters have on the response function¹⁶. Examples of standard orthogonal arrays are:

- L4 (2^3) : 4 cases to study 3 parameters with 2 values each (complete set of cases: 8);
- L16 (2¹⁵): 15 cases to study 11 parameters with 2 values each (complete set of cases: 32768);
- L18 (2¹ 3⁷): 18 cases to study 1 parameter with 2 values and 7 parameters with 3 values each (complete set of cases: 354294);
- L36 (2¹¹ 3¹²): 36 cases to study 11 parameters with 2 values and 12 parameters with 3 values each (complete set of cases: 1088391168);

Since eleven parameters have been chosen, the optimization phase has been divided in two parts, one executing with the pattern L4 (3 parameters) and the other with the pattern L18 (8 parameters). The second optimization has been executed by fixing the first 3 parameters at their best value obtained by the first optimization. Table 4.4 lists the parameters values for both the two phases. Initial values are highlighted in bold.

Test performed in the first phase are summarized in Table 4.5. Each test has been performed with the combination of values of the parameters shown in column "P values", and each test has been performed for the low-response and the high-response noise configurations. \bar{y} is the average of the tests N1 and N2, while the signal to noise ratio (S/N, measured in decibels) represents how the response varies relative to the nominal or value, under the two different noise conditions: the higher it is, the better the response of the model to noises, when evaluated with this set of parameters. Through a series of transformations, it is possible to derive how \bar{y} and S/N change with respect to the

 $^{^{16}\}mathrm{It}$ is not necessary to have a number of parameters that match exactly these numbers, but this certainly allows for a better analysis and optimal case prediction

	N°	Parameter	P1	P2	P3	Unit
	А	E_0	24.076	48.153		J/mol
1 st	В	E^*	385	770		J/mol
	С	v^*	0.7	0.9		m^{3}/m^{3}
	А	$c_{p,p}$	1900	2100		$\int J/(kg \ K)$
	В	E_1	5453	8180	12270	J/mol
	С	n	1.1	1.2	1.3	_
0m d	D	dT_p/dT	0.17	0.34	0.50	K/K
200	Е	U_C	1.3	13	65	$W/(m^2 K)$
	F	k_C	0.07	0.13	0.26	W/(m K)
	G	$c_{v,c}$	600	700	800	J/(kg K)
	Η	m_p	0.35	0.5	0.65	kg/kg_c

 Table 4.4:
 Design parameters values.

Table 4.5: First optimization cycle: tests results. Values are reported in percentage with respectto the experimental value.

	P v	value	es	N1	N2	\bar{y}	S/N
Test	A	В	С	$m_{ads}(\%)$	$m_{ads}(\%)$	$m_{ads}(\%)$	(dB)
1	1	1	1	38.9	57.1	48.0	11.27
2	1	2	2	52.7	75.6	64.2	11.78
3	2	1	2	51.4	73.0	62.2	12.04
4	2	2	1	40.9	59.4	50.1	11.51
current	2	1	2	51.4	73.0	62.2	12.04
BE	2	2	2	53.5	75.8	64.3	12.04



Figure 4.17: Factorial effects, first phase: (a) Signal to Noise ratio; (b) avg. adsorbed mass.

parameter values change. This is reported in Figure 4.17, where the effects of the parameters are compared. Condition 2 for parameters A and C (i.e. E_0 and v^*) brings to a better S/N ratio and thus to a more robust configuration, while condition 2 for parameter B (i.e. E^*) results in a S/N which is slightly under the average, being its contribution almost negligible. Regarding \bar{y} , the contribution of parameter A changing can be neglected, while the variations of parameters B and C significantly affect the target value.

Before choosing the best set of parameter values for optimizing the response function, it is important to underline that this analysis helped to a better understanding about how the model works and how it is influenced by these parameters. In particular, the response value (which is the quantity of fuel adsorbed), is less dependent on the parameter E_0 , which characterizes the second part of the adsorption isotherm adopted in the model (equation 4.6a), while it helps the robustness the system. On the other hand, the other two parameters, that represent the position of the threshold point in the adsorption isotherm

	P •	value	es						N1	N2	$ \bar{y}$	S/N
Test	A	В	С	D	Е	F	G	Η	$m_{ads}(\%)$	$m_{ads}(\%)$	$m_{ads}(\%)$	(dB)
1	1	1	1	1	1	1	1	1	32.4	49.5	41.0	10.38
2	1	1	2	2	2	2	2	2	38.1	62.2	50.1	9.12
3	1	1	3	3	3	3	3	3	38.4	64.6	51.5	8.58
4	1	2	1	1	2	2	3	3	51.9	74.6	63.2	11.76
5	1	2	2	2	3	3	1	1	53.2	77.9	65.6	11.33
6	1	2	3	3	1	1	2	2	44.3	61.2	52.7	12.76
7	1	3	1	2	1	3	2	3	55.7	72.9	64.3	14.37
8	1	3	2	3	2	1	3	1	62.0	81.9	71.9	14.06
9	1	3	3	1	3	2	1	2	66.0	88.7	77.4	13.57
10	2	1	1	3	3	2	2	1	39.3	63.0	51.1	9.45
11	2	1	2	1	1	3	3	2	32.3	52.1	42.2	9.36
12	2	1	3	2	2	1	1	3	36.4	59.2	47.8	9.20
13	2	2	1	2	3	1	3	2	51.1	72.3	61.7	12.16
14	2	2	2	3	1	2	1	3	44.8	62.5	53.7	12.55
15	2	2	3	1	2	3	2	1	54.0	78.8	66.4	11.40
16	2	3	1	3	2	3	1	2	62.9	85.2	74.1	13.36
17	2	3	2	1	3	1	2	3	63.3	83.9	73.6	14.00
18	2	3	3	2	1	2	3	1	56.9	73.8	65.3	14.68
current	1	2	2	2	2	2	2	2	53.5	75.8	64.3	11.57
BE	1	3	3	1	3	3	1	1	66.1	89.3	77.7	13.40

Table 4.6: Second optimization cycle: tests results. Values are reported in percentage with respect to the experimental value.



Figure 4.18: Factorial effects, second phase: (a) Signal to Noise ratio; (b) avg. adsorbed mass.

graph in Figure 4.13, have a greater influence on the target value, and one of them (v^*) also has an influence on the robustness. Finally, the second values of the three parameters have been chosen for obtaining the best configuration (Best Engineering, BE) of this first phase: Table 4.5 also reports the results for the current case (which is the starting case, with no modifications on parameters) and the BE: both the average value of the adsorbed mass and the S/N ratio have been incremented, confirming the expectations.

Same considerations can be made for the second phase of the optimization, which results have been reported in Table 4.6. As can be seen in Figure 4.18, the variation on the values of many parameters produces an opposite trend on S/N and \bar{y} values. However, the influence of most of them on the robustness of the model can be considered negligible if compared to the one exerted by parameter B: as expected, the main parameter of the adsorption isotherm, E_1 , has a strong influence on S/N as well as \bar{y} . On the other hand, comes unexpected the influence of U_C : a higher convective heat transfer coefficient helps to cool down the carbon bed and, thus, improves the adsorption, but it is interesting that this effect prevails on the heat capacity or the thermal conductivity of the carbons.



Figure 4.19: Canister loading, model results, comparison with experimental data: (a) canister mass variation; (b) internal temperature variation.

Finally, the BE case has been derived (by selecting the parameters highlighted in Figure 4.18(a)). Results of the simulation executed with this combination of parameters are reported in Figure 4.19. It is possible to see a notable increment in the prediction of adsorbed mass of butane on the active carbons, which was indeed the target of the DFSS activity performed: after 3 h of simulation, the adsorbed mass on the simulated canister

reaches the 90% of the real one, with an increment of 20% with respect to the initial case. However, the temperature profiles obtained by the simulation are, again, far from the temperatures recorded by the experimental apparatus, even if the time delay between the rise of the simulated temperatures is increased and now it is comparable to the time delay between the real temperatures rise. Having seen these results, future developments of the model can include a DFSS optimization on the temperature values (e.g. by comparing the peak values recorded by the thermocouples and/or the time at which they occur).

Chapter 5

Refueling model

As said in chapter 1, for a gasoline filled vehicle, refueling is the most critical phase in terms of evaporative emissions, since the fuel tank ullage space is occupied by a mixture of air and fuel vapor in equilibrium with liquid gasoline, much of which is expelled from the tank in few seconds during refueling, generating a high fuel vapor flow. *Stage II* and ORVR are the two most adopted techniques to limit the problem, the second one being a better solution in terms of efficiency, with respect to the first one, but with higher costs for the vehicle producer and without an opportunity for retrofitting. In this chapter, an experimental/modeling activity is presented, which focused on a ORVR-type tank.

During the years, with the development of the CFD approach and the rise of the computational power, the 3D CFD simulation has become the standard procedure for designing a fuel tank and, in particular, the receptacle and filler pipe, along with the vent system. This technique is mainly used for studying the liquid fuel motion and detecting the pressure developed in the fuel tank vapor dome and in the other fuel system components. An over-pressure can indeed be the cause of some problems for the user experience: the nozzle of the fuel dispenser can interrupt the fuel delivery way before the fuel tank has reached its maximum capacity, or the fuel can exit the receptacle if it does not flow correctly through the filling line, that is a serious safety issue. However, the problem has not been well analyzed from the perspective of the evaporative emissions, since this would imply to simulate the whole refueling process, which requires a long CFD simulation and

a very high computational effort.

Target of this activity is to implement a simplified tool for evaluating the fuel vapor exiting the tank during refueling, without increasing the computational demand of the simulation by adding further equations to include the evaporation physics. In this activity, the Reddy simplified correlation has been adopted for estimating the quantity of vapor loss during the refueling phase of an automotive fuel tank for U.S. applications (equipped with ORVR system). Simulation has been performed by using a commercial CFD code (SimericsMP+[®]), and results have been compared with experimental data acquired by executing refueling tests in the VT Mini-SHED at the Stellantis N.V. laboratories.

5.1 Experimental Activity

5.1.1 Setup

Experimental refueling tests have been performed on an automotive gasoline fuel tank for U.S. applications, provided by Stellantis N.V. The tank is realized in multi-layer high-density polyethylene (HDPE) by blow molding, it has a nominal capacity of 55 Lof liquid fuel and a minimum vapor dome volume of 12.1 L. A ventilation system inside the fuel tank consists of two roll-over values (ROV) and a fill limit vent value (FLVV): vapors from the tank dome enter the values and go through the vent system until reaching the carbon canister filter. A floating system at the bottom of the FLVV closes the valve when the liquid fuel level reaches a predetermined value, letting the vapor dome pressure increase, which triggers the automatic interruption system present in the refueling nozzle, and then causing the refueling to stop. The tank is placed on a supporting frame to ensure a correct horizontal position and to give stability to the filling line and the receptacle (Figure 5.1(a)). The ventilation system is connected to a carbon canister filter designed for the NAFTA market (i.e. suitable for ORVR applications), which has a volume of carbons of 1.8 L, distributed in 3 chambers. The canister is placed on a weight scale built with a load cell specifically made for ATEX applications (appendix B, device 7). ATEX instrumentation is needed as a measuring system placed inside the Mini-SHED, since it is



Figure 5.1: Refueling test: (a) fuel tank within its supporting frame; (b) canister filter placed on a weight scale made from a load cell.

an explosion risk environment (Figure 5.1(b)).

Before entering in the Mini-SHED, this setup has been tested for refueling in an open environment, for safety reasons. A fuel dispenser provides a fixed flow rate of fuel (for these preliminary tests, a E5-type recycled fuel has been adopted), until the fuel tank is completely filled. During the test, canister mass variation has been recorded by an acquisition system controlled via software. After the test, the fuel tank is emptied and the fuel is re-placed in the fuel dispenser. Results of this activity will be briefly discussed in the next section. This preliminary activity was useful to a better definition of the experimental setup and procedure of the tests performed in the Mini-SHED, which is represented in Figure 5.2 and described below:

- 1. The sampled fuel tank is emptied and placed inside the Mini-SHED. The Mini-SHED itself is modified, by opening a side gate and placing an extendable pipe that allows for fuel nozzle positioning in the tank receptacle.
- 2. The canister filter is purged by compressed air at 25L/min for a reasonable time to consider the canister fully emptied. The canister is then pre-weighed on an external weighing scale (appendix B, device 4), to have an accurate measurement of its mass in stationary conditions, without measuring the pipes weight.



Figure 5.2: Refueling test: (a) fuel tank and measure equipment placed in the Mini-SHED; (b) schematic representation of the refueling test bench.

- 3. The canister is placed inside the Mini-SHED, on the load cell, and connected to the tank vent pipe. The volumetric flow rate exiting the tank is measured by a turbine flow meter (appendix B, device 8) placed upstream the canister.
- 4. The fuel dispenser is emptied and filled with a batch of certified fresh fuel (E10 type). The fuel dispenser can provide fuel at different flow rates, to simulate the fuel rates of the various regulations in force in different countries (for instance, the tests performed have been done by using a fuel flow rate of 37.8 L/min, and fractions

of this rate, which corresponds to $10 \ gal/min$, the U.S. standard for refueling). The dispenser is also equipped with a heat system, to provide fuel at a desired temperature.

- 5. The Mini-SHED chamber is pre-conditioned, to reach a desired level of temperature, which is kept constant during the whole test. The temperature of the fuel coming from the dispenser is set to the same Mini-SHED temperature. This has been done in order not to have thermal influences on the evaporation process and to evaluate the sole effects of fuel sloshing and vapor pushed out from fresh fuel.
- 6. The nozzle of the fuel dispenser is placed in the tank receptacle, then, the nozzle is triggered, even if the pump of the fuel dispenser is not activated. During the preliminary activity, it has been found that activating the fuel pump first and then pulling the nozzle trigger would affect the canister mass variation measurement, generating a leap caused by the trigger activation.
- 7. The fuel dispenser pump is activated and the test begins. Volumetric flow rate coming outside the fuel tank is recorded by the flowmeter at a rate of 10 Hz, along with the canister mass variation, recorded by the load cell. During the test, the Mini-SHED FID detector is also activated, which controls if fuel vapors escape the canister filter. This data allows for confirming the initial hypothesis of the test, which states that all the fuel vapors flowing outside the tank are adsorbed and captured in the canister filter, hence, the canister mass variation corresponds to the fuel vapor quantity that escapes the tank.
- 8. The test finished when the fuel volume reaches the nominal maximum filling of the tank and the gas nozzle stops the first time. Then, the canister is weighed on the external weight scale to evaluate the mass difference with the previous weighing and, thus, the total fuel vapor mass produced, measured in stationary conditions. Then the canister is purged and the fuel tank is emptied, to be ready for a next test.



Figure 5.3: Preliminary refueling tests, consecutive loading at: (a) 9.5 L/min, 19 L/min and 38 L/min; (b) 38 L/min, 19 L/min and 9.5 L/min.

5.1.2 Results and Discussion

Even if the preliminary tests were not conducted under rigorous initial and boundary conditions, some results obtained by these experiments are worth to be discussed. Figure 5.3 shows the canister mass variation during time obtained by six tests under different boundary conditions. In particular, Figure 5.3(a) shows results for three consecutive tests (i.e. without purging the canister between the tests) performed by refueling the tank with 9.5 L/min (≈ 2.5 gal/min), 19 L/min (≈ 5 gal/min) and 38 L/min (≈ 10 gal/min), respectively, while Figure 5.3(b) shows the results of another series of consecutive tests performed by inverting the order of the previous one. It is possible to notice that a higher speed refueling produces more fuel vapor at the end of the refueling process. Considering the fuel mass adsorbed by the canister at the end of the refueling at 38 L/min, the difference between the value recorded when this is the first test of the series (i.e canister fully purged) and when it is the last test (i.e canister already loaded) is of almost 10 q(20% of the purged canister case), and the same is for the case at 9.5 L/min of refueling. This means that the refueling performance of a canister significantly drops if it is already partially loaded. However, these considerations must be proven by further, more rigorous tests and, in any case, it would be difficult to make two or more consecutive refuelings without canister purging, for a real gasoline vehicle.

Inside the Mini-SHED, two refueling tests have been performed, to test the repeatability

Tank type	Gasoline, U.S.
Tank nominal capacity	55 L
Tank vapor dome	12.1 L
Canister filter carbons volume	1.8 L
Initial temperature	$20 \ ^{\circ}C$
Ambient temperature	$20 \ ^{\circ}C$
Inlet fuel temperature	$20 \ ^{\circ}C$
Inlet fuel vol. flow	$38 \ L/min$

 Table 5.1: Refueling experimental test conditions.



Figure 5.4: Refueling tests inside the Mini-SHED, at 38 L/min: (a) volumetric flow rate exiting the tank; (b) canister mass gain.

of the procedure¹. Table 5.1 summarizes the experimental test conditions, while Figure 5.4 reports the results recorded during the two tests, for the volumetric flow of vapors exiting the fuel tank and fuel vapors quantity adsorbed in the canister, respectively. The adsorbed mass is comparable between the two tests (Figure 5.4(b)), the second test recording only 1.2 g of adsorbed mass more than the first one. Regarding the volumetric flow (Figure 5.4(a)), after a first transitory phase, the value is stabilized on a constant level, which is approximately equal to the loading flow rate (38 L/min), as expected. Then, when the nozzle stops to deliver the fuel (~ 80 s), the flow rate drops until 0 in around 5 s.

¹Unfortunately, due to the difficulty in acquiring fresh certified fuel, these were the only two tests performed with the conditions described in 5.1.1.

5.2 3D CFD Refueling Model

5.2.1 Model Development

The numerical description of the tank refueling has been realized with a three-dimensional CFD approach, by using the commercial CFD software SimericsMP+[®] (V 5.0.9).

SimericsMP+[®] is a collection of core 3D CFD capabilities and physical modules that enables accurate virtual testing for multi-purpose applications involving single phase or multiphase flow, turbulence, cavitation/aeration, heat and mass transfer, particle and fluid-structure interaction. It includes several features such as streamlined setup procedures, automated mesh/re-mesh for key components especially moving components, and customized data reduction [145]. It is the evolution of PumpLinx[®], which was a CFD software specifically designed for analysis and performance prediction of fluid pumps, motors, compressors, turbines, valves, and complete fluid systems with rotating/sliding components, with a particular attention on the cavitation phenomena. The software has been used for years by the Fluid Power Research Group (FPRG) at the Department of Industrial Engineering of the University of Naples Federico II, which has also contributed for its development. The main features of this software are a rapid learning curve, the ease in creating computational models, and a built-in mesh generator (named Binary Tree Meshing) that divides the control volume in hexahedral cells to improve numerical efficiency and accuracy [146].

The multi-phase flow has been described by using a homogeneous approach of the Eulerian multi-fluid model, which requires the solution of mass, momentum and turbulence equations for each phase. Instead, the homogeneous approach averages the phase governing equations and solves a set of mixture transport equations, while the volume fractions of each phase are solved as follows [146]:

$$\frac{\partial \left(\alpha_{q} \ \rho_{q}\right)}{\partial t} + \nabla \cdot \left(\alpha_{q} \rho_{q} \vec{V}\right) = \sum_{p=1}^{n} \left(\dot{m}_{pq} - \dot{m}_{qp}\right) + S_{q}$$
(5.1)

in which, for the total mass conservation, the sum of phase volume fractions α_q must be

equal to 1. On the other side, the momentum equation is:

$$\frac{\partial \left(\rho \vec{V}\right)}{\partial t} + \nabla \cdot \left(\rho \ \vec{V} \ \vec{V}\right) = -\nabla P + \nabla \cdot \left(\Gamma \ \nabla \vec{V}\right) + \rho \vec{B}_f S_{\vec{V}}
+ \nabla \cdot \sum_{q=1}^n \left(\alpha_q \rho_q \left(\vec{V}_q - \vec{V}\right) \left(\vec{V}_q - \vec{V}\right)\right)
+ \sum_{q=1}^n \left(\sum_{p>q}^n \left(\dot{m}_{pq} \left(\vec{V}_p - \vec{V}\right) - \dot{m}_{qp} \left(\vec{V}_q - \vec{V}\right)\right)\right)$$
(5.2)

The terms ρ , α , \vec{V} , S and Γ represent density, volume fraction, velocity, source term and diffusion coefficient, respectively, for the mixture, the *q*-th and the *p*-th phase, while \dot{m}_{pq} is the mass transfer from the *p*-th phase to the *q*-th phase.

A standard $k - \epsilon$ model has been adopted for considering the turbulence phenomena in the simulation:

$$\frac{\partial \left(\rho k\right)}{\partial t} + \nabla \cdot \left(\rho \vec{V} k\right) = \nabla \cdot \left[\left(\mu + \frac{\mu_t}{\sigma_k}\right) \nabla k\right] + G_k - \rho \epsilon + S_k$$
(5.3a)

$$\frac{\partial(\rho\epsilon)}{\partial t} + \nabla \cdot \left(\rho \vec{V} \ \epsilon\right) = \nabla \cdot \left[\left(\mu + \frac{\mu_t}{\sigma_\epsilon}\right) \nabla \epsilon\right] + C_{1\epsilon} \frac{\epsilon}{k} G_k - C_{2\epsilon} \rho \frac{\epsilon^2}{k} + S_\epsilon$$
(5.3b)

where k is the turbulence kinetic energy, ϵ is the turbulence dissipation rate, G_k is the turbulent production term from stress and strain; $C_{1\epsilon} = 1.44$ and $C_{2\epsilon} = 1.92$ are empirical constants, $\sigma_k = 1.0$ and $\sigma_{\epsilon} = 1.3$ are turbulent Prandtl numbers. In equations (5.1) to

(5.3b), the mixture density, velocity and viscosity are evaluated as follows:

$$\rho = \sum_{q=1}^{n} \alpha_q \rho_q \tag{5.4a}$$

$$\vec{V} = \frac{1}{\rho} \sum_{q=1}^{n} \alpha_q \rho_q \vec{V}_q \tag{5.4b}$$

$$\mu = \sum_{q=1}^{n} \alpha_q \mu_q \tag{5.4c}$$

while the turbulent viscosity μ_t is directly evaluated as:

$$\mu_t = \rho C_\mu \frac{k}{\epsilon^2} \tag{5.5}$$

being $C_{\mu} = 0.09$.

The fluid volume for the simulation has been obtained from the CAD geometry of the gasoline fuel tank described above, along with the fuel filling line and the ventilation hoses. The computational domain has been discretized by a hexahedral mesh grid (Figure 5.5, cell base size: 2 to 8 mm), with a variable cell size approach: a finer mesh grid has been used for describing the receptacle volume, because of its complex geometry and fluid dynamics, and the inner part of the ventilation system. Various refinement levels were adopted in the fuel tank volume near the inlet port and the ventilation valve. The final mesh counts 1.43 million cells.

The inlet check value at the end of the filling hose has been described as a circumferential value, by assigning a moment of inertia and torsion properties of the value spring, and its opening solved each timestep based on instantaneous force/torque balance (Figure 5.6(a)). Since the value is rotating during the simulation, a small cylinder-shape volume has been introduced around the moving surface, in which a cylindrical mesh grid is deformed to match the value motion².

 $^{^2 {\}rm The}$ deforming mesh was built with the help of the circumferential valve template provided by Simerics®.



Figure 5.5: Fuel tank computational mesh, realized in Simerics $MP + \mathbb{R}$.



Figure 5.6: Details of the fuel tank mesh: (a) inlet check valve; (b) fill limit vent valve (simplified).



Figure 5.7: Carbon canister filter: dimensionless pressure loss vs. volumetric flow rate.

The FLVV geometry has been edited and simplified in order to decrease the complexity of the fluid domain (Figure 5.6(b)): the floating closure system has not been considered, and the valve inner vents have been simplified. Furthermore, since most of the fuel vapor passes through this valve, during the refueling, the two ROVs have not been modeled. The canister filter pressure drop has been considered by adding a small cylinder of porous media at the end of the vent hose. The pressure loss has been taken into account by adding a source term in the momentum equation:

$$\vec{F} = -C_l \beta \vec{V} - C_d \rho \beta^2 \left| \vec{V} \right| \vec{V}$$
(5.6)

where β is the porosity of the carbon bed, while C_l and C_d are the linear and quadratic drag coefficients, respectively, which are empirical constants obtained from a $\Delta P - Q$ curve, derived by an experimental flow test executed on the specific canister filter (Figure 5.7). A small cylinder volume is placed upstream the receptacle, in order to emulate the inner volume of the gas station refueling nozzle.

No relevant thermal gradients have been expected during the refueling process analyzed, because the reference experimental activity was executed in a constant temperature environment and the whole process lasts less than 100 s. Therefore, the thermal equations have not been solved.

Phase 1	Gasoline
Conditions Density Dyn. Viscosity	$ \begin{array}{ l l l l l l l l l l l l l l l l l l l$
Phase 2	Air
Conditions Mol. Weight Temperature	ideal gas $28.97 \cdot 10^{-3} \ kg/mol$ $20 \ ^{\circ}C$

 Table 5.2:
 Simulated fluid properties.



Figure 5.8: Fuel tank nozzle and receptacle, inlet boundary condition.

Two phases have been simulated, respectively gasoline and air; fluid properties are summarized in Table 5.2. The constant temperature condition also allows for considering a constant density and viscosity for liquid gasoline, while air has been considered as an ideal gas. Initially, the fuel tank is almost filled with air (a small quantity of gasoline is present at the bottom of the tank). At the beginning of the nozzle (Figure 5.8), a constant volumetric flow rate of gasoline (38 L/min) is set as boundary condition, while, at the end of the porous cylinder representing the carbon canister, a static pressure equal to 1.013 bar is imposed.

The estimated fuel vapor mass stored in the carbon canister has been derived from the vapor volumetric flow (\dot{V}) by considering the fuel vapor acting as an ideal gas:

$$P_f \dot{V} = \frac{\dot{m}_f}{W_f} R T \tag{5.7}$$

where P_f is the fuel vapor partial pressure inside the tank, which is generally evaluated as a fraction of the saturation vapor pressure ($P_f = r \cdot P_{sat}$). However, before the refueling operation, the air/fuel vapor mixture inside the fuel tank can be considered saturated of fuel vapor, therefore r can be set to 1.

Since gasoline is a mixture of hundreds of different components that have different evaporation rates, its saturation vapor pressure is generally hard to evaluate. For a first approximation of this value, the simplified equation proposed by Reddy [127] can be used, which relates the RVP and fuel temperature (T) with the saturation pressure (equation 2.61).

5.2.2 Model Resolution and Discussion

The computational mesh, that counts 1.43 million cells, has been solved in parallel in SimericsMP+[®] environment, on a workstation with 16 cores and 128*GB* of RAM (64bit architecture). The model has been solved under transient conditions, with a frequency of 1000 Hz.

Gasoline fuel filling is shown in Figure 5.9 at 0, 10, 20, and 30 s. Results (Figure 5.10) are given in terms of vapor flow exiting the fuel tank and estimated fuel vapor mass stored in the carbon canister. As seen in Figure 5.10(a), the trend of the predicted volumetric flow exiting the tank departs from experimental data during the first transitional phase of the test, then it estimates quite well the constant trend. Figure 5.10(b), on the other hand, shows a quite good correlation between experimental data and simulation results, only slightly overestimating the fuel mass loading in the canister.

For this type of simulation, computational time is the real issue: on average, the simulation took about 10 h per second of simulated time. Therefore, as seen in Figures 5.9 and 5.10, the simulation is still incomplete. However, first results show the validity of the applied method for estimating the canister mass variation during the refueling process. The application of this tool can give a good prediction of the fuel vapor quantity to be stored in an ORVR canister filter. Thus, this approach can be used in fuel tank and carbon canister design in order to significantly reduce evaporative emissions, with only a



Figure 5.9: Fuel tank filling with time.

limited increase of computational effort compared to a standard (i.e. without evaporative emissions evaluation) tank filling CFD simulation.

Future works will be the completion of the simulation and model validation with other tank geometries and systems, as well as further simplifications of the CFD domain, in order to reduce the computational effort. Finally, the implementation of different equations for vapor partial pressure evaluation will be considered, in order to improve the fuel vapor quantity estimation.



Figure 5.10: Model results: (a) volumetric flow rate exiting the fuel tank; (b) canister mass variation.

Conclusions

Unburned hydrocarbon evaporation from a vehicle gasoline-filled fuel tank represents a significant source of air pollutants, in the form of VOCs, which represent a serious treat to human health and environment. Because of this, vehicle evaporative emissions have been regulated and restricted since the late 1960s, and new restrictions are added every year, especially in the last decade, when urban air pollution and global warming have become among the most important items of discussion for almost every industrialized country. Optimistic estimations affirm that the global energy production must rely on non-renewable sources for at least 30 to 50 years, and this also includes transportation sector. Even if technology and research for electric vehicles is making great progresses in the last years, it is not possible to think to perform a complete electrification of the whole transportation sector in few years, since this will only shift the problem of pollutant emissions towards other fields, which are energy production and batteries making and disposal. Therefore, a gradual transition is needed and it is the most adopted strategy from almost all the countries: the hybrid vehicle has become a suitable compromise for vehicle manufacturers (that must comply with new and more stringent regulations), customers (that are moved by the cost of the product, driving autonomy and recharging/refueling operation times), oil and gas companies (that can continue to remain on the energy market), governments (which are charged to reduce pollutant emissions), new research applications in the vehicle electrification (e.g. batteries life cycle, new materials and recharging strategies for batteries, etc.), urban pollution (that is reduced thanks to a better usage of petrol), and of course human health and environmental conditions (for obvious reasons).

It has been seen that, for an hybrid vehicle, while tailpipe emissions are naturally reduced, evaporative emissions represent a serious problem. Therefore, a deeply research analysis about the most cost-effective and most used strategy for reducing these emissions, which is the EVAP system, is needed. This analysis, exposed in this elaborate, has been performed with the specific intent of making available simple and effective instruments that help to understand the fuel evaporation and carbon adsorption-desorption phenomena, in order to design more efficient fuel tanks and canister filters in terms of reducing hydrocarbon emissions in the environment.

After a brief introduction to the problem and an exhaustive analysis of what has been done in literature regarding the EVAP system modeling, virtual, semi-empirical models have been developed for three of the most important aspects that regard vehicle evaporative emissions, that are: fuel evaporation inside the fuel tank due to diurnal temperature changes (DBLs), fuel vapor storage inside the canister filter by adsorption on activated carbons, and estimation of fuel vapor production during refueling operations. For all of them, an experimental analysis has been performed, that helped to set, calibrate and validate the correspondent model.

A 0D, lumped parameters model has been developed for fuel evaporation inside a vehicle fuel tank. This model gives information about the hydrocarbons quantity escaping a gasoline fuel tank due to environment temperature variations, by considering the fuel tank geometry and properties (internal volume, external surface, thermal properties, etc.), the gasoline properties (fuel vapor pressure, density, thermal conductivity, etc.) and the tank filling level (more specifically, the ullage space volume): experimental results show a strong dependence of fuel vapors emitted from both the temperature variation and the vapor headspace volume, as expected. Model estimations have been compared with experimental results, and a good agreement has been found for most of the tests that involves a thermal variation of the tank system from an initial temperature to a constant value (ramp simulation). The comparison with the evaporation quantity recorded during a 24 h diurnal cycle test gives a fairly good agreement of the model results, however, the model lacks to correctly predict the amount of fuel vapors desorbed from the canister filter during the fuel tank cooldown, since a desorption sub-model of the canister has not been implemented. Future works should be the implementation of the canister behavior to correctly estimate the canister filling level during diurnal temperature variation, and an

implementation of more accurate relations to estimate the fuel vapor pressure, that can also consider substantial variations of gasoline composition.

It has been shown that internal temperature recording is an important step for a deeper characterization of the adsorption and desorption behavior of the carbon canister. In fact, with this information, it has been possible to follow the adsorption and desorption "path" inside the carbon bed. In particular the following information can be deduced: for a specific carbon bed section, the adsorption happens in two steps, the first that releases more energy than the second; across the carbon bed, adsorption shows a stratified behavior, the bed filled per layers; during desorption, part of the fuel vapor purged from the first sections of the carbon bed invested by the nitrogen flux can be re-adsorbed from the next sections, determining a small temperature increase. A 1D transient model has been developed to simulate the adsorption behavior of a common canister filter, that considers both the adsorbed quantity of fuel vapors and carbon bed thermal variation, since, as known, adsorption is a strong exothermic process and it is also influenced by temperature levels. The model has then been tested with experimental data, and a DFSS optimization strategy has been performed to calibrate the model in order to better predict the adsorbed fuel mass trend during time. However, the model still lacks in temperature prediction. Future activities could be a further optimization of the thermal parameters of the model to match the thermal behavior and/or a 2D or 3D description of the carbon bed, since a 1D modeling has been found as an upper limit for a deeper characterization of the canister behavior.

Refueling operation has been studied on a fuel tank and EVAP system specifically designed for ORVR applications. Since refueling is the most critical situation in terms of hydrocarbon release quantity, its containment is crucial for reducing the evaporative emission contribution of a gasoline vehicle. The problem has been analyzed by means of experimental activities and, then, with a 3D CFD simulation. First simulation data have been compared with experimental results, showing that a fairly good agreement can be reached by applying a simplified method for fuel vapor estimation to a complex simulation that is already performed by many manufacturers for solving other types of problems (tank headspace pressure variations, gas nozzle premature shut-off, etc.), with a minimum increase of the computational effort required for the "standard" refueling CFD simulations (which already requires very high computational effort and time). Future works could study the validity of this approach on other fuel tank configurations, and the implementation of different equations for vapor partial pressure evaluation, in order to improve the estimation of the fuel vapor quantity lost during refueling operations.

Appendix A

Volume method for adsorption equilibrium measurement

A closed recirculating apparatus is used, in which a known volume of hydrocarbon gas is introduced. Adsorbed quantity is evaluated by difference between initial condition and equilibrium condition [147–156].

- 1. A known amount of activated carbons is inserted in the system: the bed column temperature is maintained under control by a jacket, a constant temperature bath or similar systems, in which temperature is maintained constant, at the desired level (isothermal).
- 2. Void is created inside the system (by void pumps).
- 3. A hydrocarbon gas is introduced in the system; initial pressure, temperature, volume and composition are measured before introducing (or at the first instant).
- 4. The gas is recirculated by a sealed gas compressor.
- 5. A pressure sensor and a volume regulator are used; Wilson and Danner [156] used a differential pressure cell and a manometer for pressure measurement and a volumetric micrometer for volume regulation; Danner and Wenzel [157] used a mercury manometer in which mercury level on the circuit side is brought to the

same level to yield the circuit volume constant, while the pressure is evaluated by reading the mercury level on the other side of the manometer.

- 6. The test lasts until equilibrium between gas and adsorbed phases is reached; various methods are used to evaluate if the equilibrium is established:
 - (a) a differential thermal conductivity detector continuously compares the thermal conductivities of the flux entering and leaving the carbon bed: once there is no difference, equilibrium is reached;
 - (b) a gas chromatography periodically evaluates the gas composition.

Adsorbed quantity (mol) is evaluated by difference from initial to equilibrium condition (by indirect measurement from P, V, T and gas composition by gas chromatography); data are expressed in ads. volume on mass of carbons or number of moles on mass of carbons vs vapor pressure (i. e. measured pressure), at various temperatures (established by constant temperature baths, etc.).

Appendix B

Measuring devices properties

'	Table B.1	: Pi	roperties of	the measu	ring devic	es used	in this	experin	mental	activity.	Uncertai	nties
(on devices	3, 4	are determ	nined with	respect t	o the n	ominal	value 1	NV, m	easured	by the d	evice
((in grams).											

N.	Туре	Model	Full scale and Resolution	Uncertainty
1	K-type thermocouple	G. SENSOR ASTC-K-3	$ -200 \div 1350 \ ^{\circ}C$ -	$ \begin{array}{c} 0.58 \ ^{\circ}C \\ (\text{until } 100 \ ^{\circ}C) \end{array} $
2	pressure transducer	Keller PR-23SX	$ \begin{vmatrix} 0 \div 1000 \ mbar \\ 0.1 \ mbar \end{vmatrix} $	3.057 mbar
3	weighing scale	Mettler Toledo XP2004S	$ \begin{array}{c c} 0 \div 2300 \ g \\ 0.0001 \ g \end{array} $	$\begin{array}{c} (0.12 + 0.012 \cdot NV[g]) \ mg \\ (\max \ 28 \ mg) \end{array}$
4	weighing scale	Sartorius SIWSBBP-1-6-H	$\begin{vmatrix} 0 \div 6100 \ g \\ 0.01 \ g \end{vmatrix}$	$ \begin{array}{c c} (0.15 + 0.0011 \cdot NV[g]) \ mg \\ (\max \ 14 \ mg) \end{array} $
5	weighing scale	Sartorius BP4100S	$\begin{vmatrix} 0 \div 4100 \ g \\ 0.01 \ g \end{vmatrix}$	$0.61 \ g \ (\mathrm{max})$
6	weighing scale	Sartorius BP4100S	$\begin{array}{c} 0 \div 3100 \ g \\ 0.01 \ g \end{array}$	$0.51 \ g \ (\max)$
7	load cell	$\left \begin{array}{c} \text{HBM} \\ \text{SP4MC3MR}/5 \text{ kg} \end{array}\right.$	$0 \div 50 N$	$650 \ \mu N \ (\text{max})$
8	turbine flow meter	BAGGI BFA/DI182	$ \begin{vmatrix} 0 \div 100 \ L \\ 0.01 \ L/min \end{vmatrix} $	$< 0.01 \cdot NV$

Appendix C

Evaporation Model: Computational Code

C.1 Main code

```
restoredefaultpath;
 1
 2
   close all;
 3
   clear; clc
 4
                       % set: 0 if solved with MATLAB
 5
   solver=0;
6
                       %
                              1 if solved with OCTAVE
 7
 8
   f_folder='functions_evap_model'; % folder from which the functions are taken
9
   if ~exist(f_folder,'dir')
       error(['folder "',f_folder,'" does not exist'])
10
11
   end
12
   addpath(genpath(f_folder)) % add function folder to the matlab path
13
14 %% INPUTS
15 if solver; pkg load io; end
16
17 |% exp_data=readmatrix("proto_7L_20to35.xlsx"); % exp. data (from excel file)
18
19
   exp_data_container='data_proto';
20 exp_data_input='ramp_3_6L_40';
21
   exp_data=load(exp_data_container,exp_data_input);
22
   exp_data=exp_data.(exp_data_input);
23
24 ext_T_input=0;
                       % type of input temperature:
25
                       % 0: constant env. temperature
26
                       % 1: CARB diurnal test env. temperature
```

```
27
                      % 2: assigned env. temperature (from data)
28
                      % 3: assigned internal temperature (from data)
29
30
   use_h_amb=0;
                      % use constant h or not
31
                      % 0: use constant h_amb
32
                      % 1: use theoretical heat exchange, natural convection
33
34 % fuel_type='E5';
35
   fuel_type='E10';
36
37 % tank_type='R520_gas';
38 % tank_type='R520_hyb';
39
   tank_type='Proto';
40
41 % initial conditions
                              %[m^3]....fuel volume (liquid)
42 V_L=0.0036;
43 A_L=0.12;
                              %[m^2].....fuel liquid interface
                              %[degC].....initial temperature value
44 T_init_C=20;
                              %[degC].....constant external temperature
45 T_env_const_C=40;
                              %[Pa].....overpressure of a relief valve
46 Dp_valve=0;
47
48 % simulation time
49 N_d=1.0;
                              %[d].....number of days of simulation
50 Dt=1.0;
                              %[s].....simulation timestep
51
52 % INITIALIZATION
53 % input elaboration
54 fuelP=fuel_properties(fuel_type);
55 tankP=tank_properties(tank_type);
56 airP=air_properties();
57 heatEX=heat_exchange(use_h_amb,tankP);
58 P=structEdit(fuelP,tankP,airP,heatEX);
59 P.V_L=V_L:
60 P.A_L=A_L;
61 P.p_int=P.p_amb+Dp_valve;
                                      %[Pa].....internal total pressure
62
   P.V_U=P.V_int-P.V_L:
                                      %[m^3]....ullage volume
63
64 P=structEdit(P);
                             %[s].....time array
65
   int_t=(0:Dt:24*3600*N_d)';
66
   switch ext_T_input
67
       case 0
68
           T_env=[0 T_env_const_C+273.15; int_t(end) T_env_const_C+273.15];
69
       case 1
70
           T_env_CARB_F=dlmread('CARB_summer_cycle_F.txt'); %[degF] ext_T_input=1
71
           T_env_CARB_C(:,1)=T_env_CARB_F(:,1);
```

```
72
            T_env_CARB_C(:,2)=(T_env_CARB_F(:,2)-32).*5./9;
 73
            T_env_CARB(:, 1) = T_env_CARB_F(:, 1);
 74
            T_env_CARB(:,2)=(T_env_CARB_F(:,2)-32).*5./9+273.15;
 75
            T_env_d(:,1)=T_env_CARB(:,1)*3600;
 76
            T_env_d(:,2)=T_env_CARB(:,2);
 77
            T_env=[];
 78
            for i=1:ceil(N_d)
 79
                T_env=[T_env; T_env_d(:,1)+(i-1)*24*3600];
 80
            end
 81
            T_{env}(:,2) = repmat(T_{env}d(:,2), ceil(N_d), 1);
 82
            T_env(end+1,1)=ceil(N_d)*24*3600;
 83
            T_env(end,2)=T_env(1,2);
 84
        case 2
 85
            T_env_data(:,1)=exp_data.time*3600;
 86
            T_env_data(:,2)=movmean(exp_data.T_shed,20)+273.15;
 87
            T_env=T_env_data;
 88
        case 3
 89
            T_int_data(:,1)=exp_data.time*1000;
 90
            T_int_data(:,2)=movmean(exp_data.T_lig,20)+273.15;
 91
            T_int=T_int_data;
 92
    %
              T_int(:,1)=int_t;
 93 %
              T_int(:,2)=interp1(T_int_data(:,1),T_int_data(:,2),int_t,'spline');
 94
    end
 95
 96 % initial conditions elaboration
                                            %[K].....INITIAL VALUE T
 97 | T_0=T_init_C+273.15;
98 if ext_T_input==1; T_0=T_env(1,2); end %[K]....if CARB cycle
                                            %[kg/m^3].....air density at t=0
99 ro_a_0=P.p_int*P.W_a/(T_0*P.R);
                                            %[-].....INITIAL VALUE Z
100 Z_0=0;
101
    p_sat_0=P_sat(T_0,P);
                                            %[Pa].....INITIAL fuel pressure
102 p_f_0=p_sat_0*1.00;
103
    m_vU_0=p_f_0*P.V_U*P.W_f/(P.R*T_0);
                                            %[kg].....INITIAL VALUE m_vU
    m_aU_0=(P.p_int-p_f_0)*(P.W_a*(P.V_U+P.alpha*(T_0/273)*P.V_L)/(P.R*T_0));...
104
105
                                            %[kg].....INITIAL VALUE m_aU
                                            %[kg].....INITIAL VALUE m_L
106 m_L_0=P.ro_L*P.V_L;
107
108 % initialization variables
109 m_L=zeros(length(int_t),1);
    if ext_T_input~=3; T=zeros(length(int_t),1); end
111 Z=zeros(length(int_t),1);
112 m_vU=zeros(length(int_t),1);
113 m_aU=zeros(length(int_t),1);
114 p_f_eq=zeros(length(int_t),1);
115 p_f=zeros(length(int_t),1);
116 delta_p=zeros(length(int_t),1);
```

```
m_VL=zeros(length(int_t),1);
117
118
    m_C=zeros(length(int_t),1);
119
120 %% SYSTEM RESOLUTION
121
    tic
122
    options = odeset('RelTol', 1e-10, 'AbsTol', 1e-10);
123
    % options = odeset();
124
    if ext_T_input~=3
125
        x_0 = [m_L_0; T_0];
126
         [t,xa]=ode45(@(t,x) odesys(t,x,P,T_env),int_t,x_0,options);
127
        m_L(:,1)=(xa(:,1));
                                     %[kg]
128
        T(:,1)=(xa(:,2));
                                     %[K]
129
        for i=1:length(T)
130
             m_vU(i,1)=((P.W_f*P.V_U)/(P.R*T(i)))*P_sat(T(i),P);
131
             m_aU(i,1)=((P.W_a*P.V_U)/(P.R*T(i)))*(1+((P.alpha*(P.V_L/P.V_U))/...
132
                 273.15)*T(i))*(P.p_int-P_sat(T(i),P));
133
        end
134
        m_vU_0_new=m_vU(1);
135
         m_aU_0_new=m_aU(1);
136
    else
137
        x_0=m_L_0;
138
         [t,xa]=ode45(@(t,x) odesys_alt(t,x,P,T_int),int_t,x_0,options);
139
        m_L(:,1)=(xa(:,1));
                                     %[kg]
140
        T(:,1)=T_{int}(:,1);
                                   %[K]
141
        for i=1:length(T)
142
             m_vU(i,1)=((P.W_f*P.V_U)/(P.R*T(i)))*P_sat(T(i),P);
143
             m_aU(i,1)=((P.W_a*P.V_U)/(P.R*T(i)))*(1+((P.alpha*(P.V_L/P.V_U))/...
144
                 273.15)*T(i))*(P.p_int-P_sat(T(i),P));
145
         end
146
        m_vU_0_new=m_vU(1);
147
        m_aU_0_new=m_aU(1);
148
    end
149
150
    for i=1:length(int_t)
151
         p_f(i) = m_vU(i) * T(i) * P.R/(P.W_f*P.V_U);
152
         delta_p(i)=p_f_eq(i)-p_f(i);
153
        m_C(i)=m_L_0-m_L(i)-m_vU(i)+m_vU_0_new;
                                                     %[kg]....ads. mass
154
    end
155
    toc
156
157
    %% PLOTS
                                 %[h]....number of hours between each x—tick
158
    x_tick=3;
159 t_h=int_t./3600;
                                 %[h].....time array (hours)
160
161 if exist('exp_data','var')
```

```
162
         down_factor=1;
163
         if size(exp_data,1)>100; down_factor=10; end
164
         exp_T(:,1)=downsample(exp_data.time,down_factor);
         exp_T(:,2)=downsample(exp_data.T_liq,down_factor);
166
         exp_m(:,1)=downsample(exp_data.time,down_factor);
167
         exp_m(:,2)=downsample(exp_data.D_mass,down_factor);
168
    end
169
170 % figure for temperature
171
    figure; hold on
172 plot(t_h,T-273.15, '-', 'LineWidth',2, 'color', [0, 0.4470, 0.7410]);
173 |leg_temp={'T_{model}'};
174
    if exist('exp_data','var')
175
         plot(exp_T(:,1),exp_T(:,2),'-.','LineWidth',2,'color',...
176
             [0.8500, 0.3250, 0.0980]);
177
         leg_temp(end+1)={'T_{exp}}';
178
    end
179
    plot(T_env(:,1)./3600,T_env(:,2)-273.15,'---','LineWidth',2,'Color',[0 0.5 0]);
180 leg_temp(end+1)={'T_{env}}';
181 grid on
182
    set(gca, 'FontSize',14);
183 |xlim([0 N_d*24]); ylim([15 45]); xticks(0:N_d*3:N_d*24); yticks(15:5:45)
184 |xlabel('time (h)', 'FontSize', 18);
    ylabel(['Temperature (' char(176) 'C)'], 'FontSize', 18)
185
186 legend(leg_temp,'location','southeast')
187 title('Temperatures', 'FontSize', 20);
188
    set(gcf,'units','pixels','position',[300, 300, 600, 400]);
189
190 | saveas(gcf,'tank_MODEL_temperature.fig')
191
    saveas(gcf, 'tank_MODEL_temperature.png')
192
193 % figure for mass
194
    figure; hold on
195 |plot(t_h,m_C*1000,'-','LineWidth',2,'color',[0, 0.4470, 0.7410]);
196 leg_mass={'m_{model}'};
197
    if exist('exp_data','var')
198
         plot(exp_m(:,1),exp_m(:,2),'-.','LineWidth',2,'color',...
199
             [0.8500, 0.3250, 0.0980]);
         leg_mass(end+1) = { 'm_{exp} ' };
200
201 end
202 grid on
203 set(gca, 'FontSize', 14);
204 |xlim([0 N_d*24]); ylim([0 20]); xticks(0:N_d*3:N_d*24); yticks(0:4:20)
205 xlabel('time (h)', 'FontSize', 18);
206 ylabel('\Delta mass (g)', 'FontSize', 18)
```

```
207 legend(leg_mass,'location','southeast')
208 title('Canister mass variaion','FontSize',20);
209 set(gcf,'units','pixels','position',[300, 300, 600, 400]);
210
211 saveas(gcf,'tank_MODEL_mass.fig')
212 saveas(gcf,'tank_MODEL_mass.png')
213
214 fprintf('final canister mass: %f g\n',m_C(end)*1000);
```

C.2 Initialization functions

```
function [fuelProp] = fuel_properties(fuel_type)
1
2
   %FUEL_PROPERTIES based on fuel type
3
       E5 or E10
   %
   switch fuel_type
4
5
       case 'E5'
6
           % FUEL: E5 (5% ethanol, 95% gasoline)
           fuelProp.A=94.4;
                                          %[K].....eq.flash vaporization: slope
7
                                           %[1/K].....air solubility in fuel (vol.)
8
           fuelProp.alpha=0.185;
9
           fuelProp.c_L=2018;
                                           %[J/(kg*K)].fuel specific heat (liquid)
10
           fuelProp.Dh_vap=513000;
                                          %[J/kg]....latent heat of vaporization
11
                                           %[m/s].....mass transfer coefficient
           fuelProp.h_D=0.1;
                                           %[Pa].....fuel focal pressure
12
           fuelProp.p_foc=483*10^6;
13
           fuelProp.ro_L=750;
                                          %[kg/m^3]...fuel density (liquid)
                                           %[Pa].....REID vapour pressure
14
           fuelProp.RVP=67*10^3;
                                           %[K].....fuel focal temperature
15
           fuelProp.T_foc=1667;
                                           %[K].....T in REID conditions
16
           fuelProp.T_RVP=37.8+273.15;
17
                                          %[kg/mol]...fuel molar mass
           fuelProp.W_f=57*10^-3;
18
           fuelProp.c_p_v=1000;
                                          %[J/(kg*K)].vapor specific heat capacity
19
       case 'E10'
20
           % FUEL: E10 (10% ethanol, 90% gasoline)
21
           fuelProp.A=94.4;
                                          %[K].....eq.flash vaporization: slope
22
           fuelProp.alpha=0.185;
                                          %[1/K].....air solubility in fuel (vol.)
23
           fuelProp.c_L=2047;
                                          %[J/(kg*K)].fuel specific heat (liquid)
                                           %[J/kg]....latent heat of vaporization
24
           fuelProp.Dh_vap=459000;
                                           %[m/s]....mass transfer coefficient
           fuelProp.h_D=0.1;
26
           fuelProp.p_foc=483*10^6;
                                          %[Pa].....fuel focal pressure
27
           fuelProp.ro_L=750;
                                          %[kg/m^3]...fuel density (liquid)
28
           fuelProp.RVP=67*10^3;
                                           %[Pa].....REID vapour pressure
29
           fuelProp.T_foc=1667;
                                           %[K].....fuel focal temperature
30
           fuelProp.T_RVP=37.8+273.15;
                                          %[K].....T in REID conditions
31
                                           %[kg/mol]...fuel molar mass
           fuelProp.W_f=61*10^-3;
32
           fuelProp.c_p_v=1600;
                                          %[J/(kg*K)].vapor specific heat capacity
```
33 **end**

34 **end**

L	<pre>function [tankProp] = tank_properties(ta</pre>	ank_type)
2	%TANK_PROPERTIES based on tank type	
	<pre>% Renegade 520 gasoline, Renegade 520</pre>	hybrid, Prototype tank
	<pre>switch tank_type</pre>	
	<pre>case 'R520_gas'</pre>	
	% HDPE	
	<pre>tankProp.V_int=0.0675;</pre>	<pre>%[m^3]total tank internal volume</pre>
	<pre>tankProp.V_tank=0.0082;</pre>	<pre>%[m^3]tank tare volume</pre>
	<pre>tankProp.A_tank=1.49;</pre>	<pre>%[m^2]external tank area</pre>
)	<pre>tankProp.c_tank=2250;</pre>	<pre>%[J/(kg*K)]tank specific heat</pre>
	<pre>tankProp.ro_tank=950;</pre>	<pre>%[kg/m^3]tank density</pre>
	case 'R520_hyb'	
	% STAINLESS STEEL AISI 316L	
	<pre>tankProp.V_int=0.04128;</pre>	<pre>%[m^3]total tank internal volume</pre>
į.	<pre>tankProp.V_tank=0.0018;</pre>	<pre>%[m^3]tank tare volume</pre>
	<pre>tankProp.A_tank=0.677;</pre>	<pre>%[m^2]external tank area</pre>
	<pre>tankProp.c_tank=470;</pre>	%[J/(kg∗K)]tank specific heat
	<pre>tankProp.ro_tank=7900;</pre>	<pre>%[kg/m^3]tank density</pre>
	case 'Proto'	
	% STAINLESS STEEL AISI 304	
	<pre>tankProp.V_int=0.024;</pre>	<pre>%[m^3]total tank internal volume</pre>
	<pre>tankProp.V_tank=0.000788;</pre>	<pre>%[m^3]tank tare volume</pre>
	<pre>tankProp.A_tank=0.5308;</pre>	<pre>%[m^2]external tank area</pre>
	<pre>tankProp.c_tank=500;</pre>	%[J/(kg*K)]tank specific heat
	<pre>tankProp.ro_tank=7900;</pre>	<pre>%[kg/m^3]tank density</pre>
	end	
7	end	

```
1
  tunction [airProp] = air_properties()
2
  % AIR_PROPERTIES
3 % other constants have been included in this list for simplicity
4 airProp.gamma=1.4;
                                %[1].....specific heat ratio (air)
5 airProp.R=8.315;
                            %[J/(mol*K)]....univ. gas constant
6 airProp.sigma_SB=5.67*10^(-8); %[W/(m^2*K^4)]..Stefan-Boltzmann constant
7
  airProp.W_a=28.9647*10^—3; %[kg/mol].....air molar mass
8 airProp.c_p_a=1006;
                       %[J/(kg*K)]....air specific heat capacity
  airProp.p_amb=101325;
9
                             %[Pa].....environmental pressure
10 end
```

1 function [heatExchange] = heat_exchange(use_h_amb,tankP)

```
2 % HEAT_EXCHANGE
```

3 heatExchange.h_amb=6; %[W/(m^2*K)].unitary convective thermal conductance

```
4 heatExchange.Q_pump=0;
                                %[W].....heat flux from pump (joule effect)
5
   heatExchange.R_rad=1000000; %[1/(m^2)]...radial resistance (tank and ub.)
6
   heatExchange.R_conv=dlmread("R_conv.txt"); % prev. evaluated conv. resistance
7
   if use_h_amb==0
                                % conv. resistance evaluated if constant h is used
8
       heatExchange.R_conv=(1/(heatExchange.h_amb*tankP.A_tank))*...
9
           ones(size(heatExchange.R_conv,1), size(heatExchange.R_conv,2));
10
           %[K/W].....convective resistance (outside the tank)
11
   end
12
   heatExchange.T_var=(15:0.1:45)+273.15;
13
   end
```

```
1
   function s = structEdit(varargin)
2
   s = struct;
3
   for i=1:nargin
4
        temp_s = varargin{i};
5
        names = fieldnames(temp_s);
6
        for j = 1:numel(names)
7
            if isfield(s,names{j})
8
                error('overlap_struct')
9
            else
                s.(names{j}) = temp_s.(names{j});
11
            end
12
        end
13
   end
14
   [~, order] = sort(lower(fieldnames(s)));
   s = orderfields(s, order);
15
16
   end
```

C.3 Calculation functions

C.3.1 Main functions

```
1
  function f=odesys(t,x,P,T_env)
2
  T_amb=interp1(T_env(:,1),T_env(:,2),t);
  % variables: x(1)=m_L; x(2)=T;
3
4
  A = P.V_U/(P.R*x(2)^2)*(P_sat(x(2), P)/(P.p_int-P_sat(x(2), P)))*(x(2)*...
5
       dP_sat_dT(x(2),P)*(P.W_f*(P.p_int/P_sat(x(2),P)-1)+P.W_a*(1+((P.alpha*...
6
       (P.V_L/P.V_U))/273.15)*x(2)))-(P.W_f-P.W_a)*(P.p_int-P_sat(x(2),P)));
7
  B = P.Q_pump+(T_amb-x(2))/(interp2(P.T_var, P.T_var, P.R_conv, x(2), T_amb))+\dots
8
       P.sigma_SB*((T_amb.^4-x(2)^4)/P.R_rad);
9
  C = (x(1)*P.c_L+P.ro_tank*P.V_tank*P.c_tank+(P.W_f*P.V_U)/(P.R*x(2))*...
       P_sat(x(2), P)*P.c_p_v+(P.W_a*P.V_U)/(P.R*x(2))*(1+((P.alpha*...)))
```

```
11 (P.V_L/P.V_U))/273.15)*x(2))*(P.p_int-P_sat(x(2),P))*P.c_p_a);
12
13 f = [ (-A*B)/(P.Dh_vap*A+C);
14 B/(P.Dh_vap*A+C)
15 ];
16 end
```

```
function f=odesys_alt(t,~,P,T_int)
1
2 T_i=interp1(T_int(:,1),T_int(:,2),t);
3 dT_i_dt=interp1(T_int(:,1),gradient(T_int(:,2))./gradient(T_int(:,1)),t);
  % variables: x=m_L;
4
5
  A = P.V_U/(P.R*T_i^2)*(P_sat(T_i,P)/(P.p_int_P_sat(T_i,P)))*(T_i*...
       dP_sat_dT(T_i,P)*(P.W_f*(P.p_int/P_sat(T_i,P)-1)+P.W_a*(1+((P.alpha*...
6
7
       (P.V_L/P.V_U))/273.15)*T_i))-(P.W_f-P.W_a)*(P.p_int-P_sat(T_i,P)));
8
9
  f =
          —A*dT_i_dt;
  end
```

C.3.2 Sub-functions

```
function val = P_sat(T,P)
1
2
   %P_SAT saturation pressure of gasoline
   P_sat_mode=1; % swith between equations for evaluating evaporation pressure
3
4
   switch P_sat_mode
5
       case 0
6
                   % Reddy
7
           A = 25.61:
8
           B = 2789.78;
9
           val = A * T * P.RVP * exp(-B/T);
                   % Campbell
10
       case 1
11
           A1=9.4947;
12
           A2=-0.9658;
13
           B1=2917.76;
14
           B2=9.9001;
15
           C=273.15;
16
           A1_bar = A1 + log(1000) * (1 + A2); %for conversion from kPa to Pa
17
           B1_bar = B1 + B2 * log(1000);
                                                %for conversion from kPa to Pa
           C_{bar} = C - 273.15;
18
                                                %for conversion from kPa to Pa
19
           val = exp(A1_bar_A2*log(P.RVP)-(B1_bar_B2*log(P.RVP))/(T+C_bar));
20
       case 2
                   % Lavoie
21
           val = P.p_foc *exp((log(P.RVP/P.p_foc) *(1/T-1/P.T_foc))/ ...
22
                (1/(P.T_RVP+P.A*(Z-P.Z_RVP))-(1/P.T_foc)));
23
   end
```

24 end

```
function val = dP_sat_dT(T,P)
1
2
   % P_SAT saturation pressure of gasoline
3
   P_sat_mode=1; % swith between equations for evaluating evaporation pressure
4
5
   switch P_sat_mode
6
       case 0
                    % Reddy
7
           A = 25.61;
8
           B = 2789.78;
9
           val = A * P.RVP * exp(-B/T) * (1 + B/T);
10
       case 1
                   % Campbell
11
           A1=9.4947;
12
           A2=-0.9658;
13
           B1=2917.76;
14
           B2=9.9001;
15
           C=273.15;
16
           A1_bar = A1 + log(1000) * (1 + A2);
17
           B1_bar = B1 + B2 * log(1000);
18
           C_{bar} = C - 273.15;
19
           val = \exp(A1\_bar\_A2*log(P.RVP)-(B1\_bar\_B2*log(P.RVP))/(T+C\_bar)) * \dots
20
                (B1_bar_B2*log(P.RVP))/((T+C_bar)^2);
21
       case 2
                    % Lavoie
22
            val = (-1/T^2) * P.p_foc * (log(P.RVP/P.p_foc)/(1/(P.T_RVP+P.A*...)))
23
                (Z-P.Z_RVP))-(1/P.T_foc))) * exp((log(P.RVP/P.p_foc) * ...
24
                (1/T-1/P.T_foc))/(1/(P.T_RVP+P.A*(Z-P.Z_RVP))-(1/P.T_foc)));
25
   end
26
   end
```

Appendix D

Adsorption Model: Computational Code

D.1 Main code

```
restoredefaultpath; clear; close all; clc;
1
2
3 f_folder='functions_canisterModel'; % folder from which the functions are taken
                                        % add function folder to the matlab path
4 \quad \text{addpath(genpath(f_folder))}
5 % properties
6 meshP = mesh_def();
                                                % define mesh parameters
7
   convP = convergence_par();
                                               % define convergence parameters
8 fuelP = fuel_properties();
                                               % define fuel properties
9 airP = air_properties();
                                               % define air/inert properties
10 canP = canister_properties();
                                               % define canister properties
11 funP = function_properties();
                                               % define adsorption parameters
12 % other properties
13
   [~,can_geometry] = canister_properties();
14 [~,fuelP_sat_table] = fuel_properties();
15 % addings
16 | canP.P_x = interp1(canP.P_cross(1,:),canP.P_cross(2,:),meshP.x_nodes);
17 | canP.A_x = interp1(canP.A_cross(1,:),canP.A_cross(2,:),meshP.x_nodes);
18 % input parameters
19 IC = initial_conditions();
                                                % define initial conditions
20 BC = boundary_conditions();
                                                % define boundary conditions
21 % Constants
22
   c = constants();
                               % regrouping of constants for a faster calculation
23 % grouping variables
24 |v = structEdit(fuelP,airP,canP,funP,BC,c); % regrouping of variables/properties
25
26 plot_seconds=0;
                               % after how many seconds do you want to plot ...
```

```
27
                               % another line on the graph? if equal to 0, ...
28
                               % there will be no graph during the simulation
29 if plot_seconds ~= 0
30
       plot_every_n=floor(plot_seconds/meshP.t_step_max);
31
   end
32 %% printing data
33
   diary([mfilename,'_',datestr(now,'yyyy.mm.dd','local'),'_',...
34
       datestr(now, 'hh.MM', 'local'), '.log'])
                                                          % create log file
35 | for_printing=['Simulation: Canister loading\n'... % print information
36
                 'Length = %4.3f m;\t Dx = %3.1f mm;\n'...
37
                 'Time = %4.2f h;\t Dt = %3.1f s;\n'];
38 fprintf(for_printing,canP.length,meshP.x_step*1000,meshP.n_hours,...
39
       meshP.t_step_max)
40 if meshP.var_t_step
       fprintf('Variable time step: min. Dt = %3.1f s;\n',meshP.t_step_min)
41
42 end
43 % BC values (array ?)
44
   fprintf(['left BC mass = ',num2str(BC.m_left),' [kg/kgC];\n',])
   fprintf(['left BC temperature = ',num2str(BC.T_left),' [K];\n'])
45
46
47 total_time=tic;
48 %% Inizialization (editing input parameters)
49 t_steps=zeros(meshP.n_ts,1);
50
51 m_sol=zeros(meshP.n_ts,meshP.n_nodes);
                                             % preallocation for solution
52 T_sol=zeros(meshP.n_ts,meshP.n_nodes);
                                             % preallocation for solution
53 Res=zeros(meshP.n_ts,convP.it_max);
                                             % preallocation for residuals
54 relax_view=zeros(meshP.n_ts,1);
                                              % preallocation for relaxation
55 oh=zeros(1,meshP.n_nodes);
56
   m=oh; T=oh; m_s=oh; T_s=oh; m_n=oh; T_n=oh; % various preallocations
57
   clear oh
58
59 ts_time=0;
                               % timestep time initialization
60 cv=0;
                               % counter: number of timesteps after Dt decrease ...
61
                               % before Dt increment
62
   j=0;
                               % initialization of iteration counter j
63 if meshP.var_t_step
64
       Dt_now=meshP.t_step_min; % initialize Dt as min. value
65
   else
66
                                 % initialize Dt as max. value
       Dt_now=meshP.t_step_max;
67 end
68
   relax=convP.relax_init; % relaxation factor initialized as max. value
69 Res_j=1;
                               % residual of the timestep initialized as 1
70
71 if convP.variable_relax
```

```
72
         k=ones(meshP.n_ts,1); % counter: for each timestep how many times ...
 73
                                 % there is need to reduce the relaxation factor
 74
         n_col=length(convP.relax_min:convP.relax_sub:convP.relax_init);
 75
    else
 76
         n_col=1;
 77
    end
 78
    if convP.record_it
                                 % preallocation for data recording ...
 79
                                 % guess [x], evaluated [x_s] and updated [x_n] ...
 80
                                 % values for each timestep, iteration, ...
 81
                                 % spatial node and relaxation factor reduction event
 82
        m_it=cell(meshP.n_ts,n_col);
                                         T_it=cell(meshP.n_ts,convP.it_max);
 83
        m_s_it=cell(meshP.n_ts,n_col); T_s_it=cell(meshP.n_ts,convP.it_max);
 84
         m_n_it=cell(meshP.n_ts,n_col); T_n_it=cell(meshP.n_ts,convP.it_max);
 85
         fun_it=cell(meshP.n_ts,n_col);
 86
    end
 87
    clearvars n_col
88
    if convP.w
 89
         lastwarn('');
                         warning('off','MATLAB:nearlySingularMatrix')
 90 end
 91
    %% initial conditions
 92
    m_sol(1,:)=IC.m_in(meshP.x_nodes); %[kg/kgC].values of m for the first timestep
    T_sol(1,:)=IC.T_in(meshP.x_nodes); %[K].....values of T for the first timestep
 93
 94
 95
    if convP.record_it
 96
        m_it{1,1}(1,:)=m_sol(1,:);
                                         T_it{1,1}(1,:)=T_sol(1,:);
        m_s_it{1,1}(1,:)=m_sol(1,:);
                                         T_s_it{1,1}(1,:)=T_sol(1,:);
 98
        m_n_it{1,1}(1,:)=m_sol(1,:);
                                         T_n_it{1,1}(1,:)=T_sol(1,:);
    end
99
100
101
    if plot_seconds \sim= 0
102
         % 2D figure. results: mass and temperature vs space (parameter: time)
103
         f2d=figure('Units','normalized','Position',[0.051 0.5 0.9 0.42]);
104
         colors=jet(length(0:meshP.t_step_max*plot_every_n:3600*meshP.n_hours));
105
         index_Dtmax=1;
106
         subplot(1,2,1)
107
         plot(meshP.x_nodes,m_sol(1,:),'color',colors(index_Dtmax,:)); hold on;
108
         title('ads. mass (x)'); xlabel('x [m]');xlim([0 canP.length]);
109
         xticks(0:0.05:canP.length); ylabel('m [kg/kgC]');
110
         grid on
111
         subplot(1,2,2)
112
         plot(meshP.x_nodes,T_sol(1,:)-273.15,'color',colors(index_Dtmax,:)); hold on;
113
         title('Temperature (x)'); xlabel('x [m]');xlim([0 canP.length]);
114
         xticks(0:0.05:canP.length); ylabel('T [degC]');
115
         grid on
116
         drawnow
```

```
117
    end
118
119
    %% starting iteration for each timestep (t=1 means initial conditions)
120
     % while t_steps(end)<3600*meshP.n_hours</pre>
121
     v.f_alt_count=0;
122
     for t=2:meshP.n_ts
123
         ts_time=tic;
                                      % stopwatch for each timestep
124
         relax=convP.relax_init;
                                      % relaxation factor reset as max. value
125
         Res_j=1;
                                      % residual of the timestep reset to 1
126
127
         m=m_sol(t-1,:);
                                      % guess / previous timestep for m
128
         T=T_sol(t-1,:);
                                      % guess / previous timestep for T
129
         i=0;
130
         while j<=convP.it_max</pre>
131
             j=j+1;
132
             t_step_now=t_steps(t-1,1)+Dt_now;
133
             t_steps(t,1)=t_step_now;
134
135
             % fun and Jac evaluation to solve the system for this timestep:
136
              \text{S} \operatorname{Jac}(x) * (x_s - x) = \operatorname{fun}(x) 
137
             fun=function_can(meshP.n_nodes, meshP.x_step, meshP.x_step_end,...
                 Dt_now, m, m_sol(t-1,:), BC.m_left, BC.Jm_right, T, T_sol(t-1,:),...
138
139
                 BC.T_left, BC.JT_right, v);
140
             Jac=jacobian_can(meshP.n_nodes, meshP.x_step, meshP.x_step_end,...
141
                 Dt_now, m, m_sol(t-1,:), BC.m_left, BC.Jm_right, T, T_sol(t-1,:),...
142
                 BC.T_left, BC.JT_right, v);
143
144
                                                            % unite m and T in one array
             phi=[m,T]';
145
             phi_s=phi+Jac\(-fun);
                                                            % system resolution
146
             m_s=phi_s(1:meshP.n_nodes)';
                                                            % estimation for mass
147
             T_s=phi_s(meshP.n_nodes+1:2*meshP.n_nodes)';% estimation for temperature
148
             m_n=m+relax*(m_s—m);
                                                            % new value for mass
149
             T_n=T+relax*(T_s—T);
                                                            % new value for temperature
150
151
             if convP.record_it
152
                 % record previous, estimated and new values for mass, temperature
153
                 % and function (horizontal arrays in space) for each iteration (j),
154
                 % each restart for relax. value change (k(t)) and each timestep (t)
155
                 m_it{t,k(t)}(j,:)=m;
                                               T_{it}{t,k(t)}(j,:)=T;
156
                 m_s_it{t,k(t)}(j,:)=m_s;
                                               T_s_it{t,k(t)}(j,:)=T_s;
157
                 m_n_it{t,k(t)}(j,:)=m_n;
                                               T_n_{it{t,k(t)}(j,:)=T_n;
158
                 fun_it{t,k(t)}(j,:)=fun;
159
             end
160
161
             if convP.w
```

162	<pre>[msg,msgID]=lastwarn; warning('on','MATLAB:nearlySingularMatrix')</pre>
163	end
164	<pre>if (convP.w && strcmp(msgID,'MATLAB:nearlySingularMatrix')) </pre>
165	(convP.variable_relax && (any(m_n <= 0) any(m_n >= canP.m_sat)
166	any(T_n <= max(abs(fuelP.T_min)))))
167	j==convP.it_max
168	<pre>fprintf(['Timestep n: %04d (',datestr(seconds(t_step_now),</pre>
169	'HH:MM:SS'),') — relax: %1.2f — Num.iterations: %02d'],
170	t-1,relax,j)
171	if convP.variable_relax && relax > convP.relax_min &&
172	j < convP.it_max
173	<pre>relax=relax_convP.relax_sub; % reduce relaxation factor</pre>
174	k(t)=k(t)+1; % k counter updated
175	<pre>if (convP.w && strcmp(msgID,'MATLAB:nearlySingularMatrix'))</pre>
176	<pre>fprintf(' (matrix warning)\n')</pre>
177	else
178	<pre>fprintf('\n')</pre>
179	end
180	else
181	if meshP.var_t_step
182	if Dt_now > meshP.t_step_min
183	Dt_now=Dt_now/2; % Dt reduced
184	k(t)=1; % k counter reset
185	if j==convP.it_max
186	fprintf('\n>>> Max. number of iterations reached (%d)
	: Dt reduced, new Dt: %.3T s.\n',CONVP.1t_max,
107	DT_NOW)
107	for intf() have belayation factor is belay the minimum
100	value (% 2f), Dt reduced new Dt, % 2f c \n'
	convP rolay min Dt now)
180	
190	relax=convP relax init: % relax factor reset
191	cv=0:
192	if convP.record it
193	<pre>m_it(t.:)={[]}: T_it(t.:)={[]}:</pre>
194	<pre>m_s_it(t,:)={[]}; T_s_it(t,:)={[]};</pre>
195	<pre>m_n_it(t,:)={[]}; T_n_it(t,:)={[]};</pre>
196	fun_it(t,:)={[]};
197	end
198	else
199	<pre>fprintf('\n');</pre>
200	error(['Dt value is below the minimum value (',
201	<pre>num2str(meshP.t_step_min,'%.3f'),' s).'])</pre>
202	end

```
203
                     else
204
                         fprintf('\n');
205
                         error('Max. number of iteration reached w/o convergence.')
206
                     end
207
                 end
208
                                              % residual value reset
                 Res_j=1;
209
                 Res(t,:)=1;
                                              % residual value history reset
210
                 m=m_sol(t-1,:);
                                             % m value reset to previous value
211
                 T=T_sol(t-1,:);
                                             % m value reset to previous value
212
                 j=0;
213
                 continue
214
             end
215
             f_Res=function_can(meshP.n_nodes, meshP.x_step, meshP.x_step_end, ...
216
                 Dt_now, m_n, m_sol(t-1,:), BC.m_left, BC.Jm_right, T_n, ...
217
                 T_sol(t-1,:), BC.T_left, BC.JT_right, v);
                                        % residual for j iteration of this timestep
218
             Res_j=sum(f_Res.*f_Res);
219
                                         % record residual value
             Res(t,j)=Res_j;
220
             if Res_j > convP.convergence || j<3</pre>
221
                 % when the convergence criterion is not respected,
222
                 % the guess is updated to the new value, and the loop continues
223
                 m=m_n;
224
                 T=T_n;
225
             else
226
                 break
227
             end
228
         end
                                     % record of relaxation factor
229
         relax_view(t,1)=relax;
230
                                     % solution of m recorded
         m_sol(t,:)=m_n;
231
         T_sol(t,:)=T_n;
                                     % solution of T recorded
232
233
         if plot_seconds~=0 && mod(t_step_now,plot_every_n*meshP.t_step_max)==0
234
             index_Dtmax=index_Dtmax+1;
235
    %
               figure(f2d);
                                     % figure recall: ads. mass and temperature
236
                                     % evolution in space, during time
237
             subplot(1,2,1)
238
             plot(meshP.x_nodes,m_sol(t,:),'color',colors(index_Dtmax,:));
239
             hold on; title('ads. mass (x)'); xlabel('x (m)'); xlim([0 canP.length]);
240
             xticks(0:0.05:canP.length); ylabel('m (kg/kgC)');
241
             subplot(1,2,2)
242
             plot(meshP.x_nodes,T_sol(t,:)-273.15, 'color', colors(index_Dtmax,:));
243
             hold on; title('Temperature (x)');xlabel('x (m)');xlim([0 canP.length]);
244
             xticks(0:0.05:canP.length); ylabel('T (degC)');
245
             drawnow
246
         end
247
```

```
248
         ts_time_end=toc(ts_time); % end of stopwatch for this timestep
249
         fprintf(['END of Timestep n: %04d (',datestr(seconds(t_step_now),'HH:MM:SS'),
            ') — Dt: %02.3f s — relax: %.2f — Num.iterations: %02d — it.time: %.3f s
            .\n'],t-1,Dt_now,relax,j,ts_time_end);
250
251
         if j<convP.it_max/2</pre>
252
             cv=cv+1;
253
        end
254
         if meshP.var_t_step && cv>=2^meshP.incr_f
255
             if j<convP.it_max/2 && Dt_now<meshP.t_step_max ...</pre>
256
                    && mod(t_step_now,Dt_now*2)==0
257
                Dt_now=Dt_now*2;
258
                 fprintf('>>> Dt increased, new Dt: %.1f s.\n',Dt_now)
259
                 cv=0:
260
             elseif Dt_now==meshP.t_step_max
261
                 cv=0:
262
             end
263
         end
264
         if t_step_now==meshP.n_hours*3600
265
             break
266
         end
267
    end
268
    %% post-processing results
269
    SOL.m=m_sol(1:t,:);
270 SOL.T=T_sol(1:t,:);
271 SOL.t_steps=t_steps(1:t,:);
272
273 %% figure 3D
274 ind=find(mod(SOL.t_steps,meshP.t_step_max)==0);
    f3d=figure('Units','normalized','Position',[0.05 0.05 0.9 0.37]);
275
276 colormap('jet')
277
    subplot(1,2,1)
278
    surf(meshP.x_nodes,SOL.t_steps(ind),SOL.m(ind,:),'LineStyle',':')
279 title('ads. mass (x,t)')
280 |xlabel('x (m)');xlim([0 canP.length]);xticks(0:0.05:canP.length);
281
    ylabel('time (s)');ylim([0 3600*meshP.n_hours]);
282 yticks(0:1800:3600*meshP.n_hours);
283 zlabel('m (g/gC)');
284
    subplot(1,2,2)
285 surf(meshP.x_nodes,SOL.t_steps(ind),SOL.T(ind,:),'LineStyle',':')
286 |title('Temperature (x,t)')
287
    xlabel('x (m)');xlim([0 canP.length]);xticks(0:0.05:canP.length);
288 ylabel('time (s)');ylim([0 3600*meshP.n_hours]);
289 yticks(0:1800:3600*meshP.n_hours);
```

```
290 zlabel('T (K)');
```

```
291
292
    %%
293
    rmpath(genpath(f_folder))
294
295
     [time.h,time.m,time.s]=hms(duration(0,0,toc(total_time)));
296
    fprintf('Simulation time: %2.0f hr, %2.0f min, %2.1f sec.\n',...
297
         time.h,time.m,time.s);
298
299
    diary off
300
301
    % catch ME
302
    %
           fprintf(['ERROR: ',ME.message,'\n'])
303
    %
           diary off
304
        if convP.w
             lastwarn('')
306
             warning('off','MATLAB:nearlySingularMatrix')
307
         end
308
    %
           restoredefaultpath
    % end
309
311
    %%
312
    function s = structEdit(varargin)
313
    s = struct;
314
    for i=1:nargin
315
        temp_s = varargin{i};
316
         names = fieldnames(temp_s);
317
        for j = 1:numel(names)
318
             if isfield(s,names{j})
319
                 error('overlap_struct')
320
             else
321
                 s.(names{j}) = temp_s.(names{j});
322
             end
323
         end
324
    end
     [~, order] = sort(lower(fieldnames(s)));
     s = orderfields(s, order);
326
327
    end
```

D.2 Initialization functions

```
1 function val = mesh_def()
2 % MESH_DEF definition of mesh parameters
3 val.x_step = 0.004; %[m].....distance between one node to another
```

```
val.x_geom_end=0;
4
 5
                       %[h]..number of hours of the simulation
 6
   val.n_hours=3;
 7
   val.t_step_max=0.5; %[s]..time interval
8
   val.var_t_step=1;
                      %[-]..activate variable time step iteration (1: ON; 0: OFF)
   val.decr_factor=3; %[-]..for evaluating the minimum timestep allowed: ...
9
10
                               % t_step_min=t_step_max/2^decr_factor
11
   val.incr_f=4;
                       %[-]..increase factor: after how many timesteps Dt is ...
12
                               % increased (doubled)? after 2^i_f timesteps, ...
13
                               % if the num. of iterations is less than it_max/2
14
15 % DO NOT EDIT AFTER THIS POINT
16
   len=canister_properties().length;
17
   val.x_nodes=0:val.x_step:len;
                                          %[m]..spatial nodes array
18
   if val.x_nodes(end)<len</pre>
19
       if val.x_geom_end
20
           val.x_nodes(end+1)=len;
21
       end
22
   end
23
   val.x_step_end=val.x_nodes(end)-val.x_nodes(end-1);
24
   val.n_nodes = length(val.x_nodes); %[-]..number of canister spatial nodes
25
26 if val.var_t_step
27
       val.t_step_min=val.t_step_max/2^val.decr_factor; %[s]..minimum time interval
28
       val.n_ts=length(0:val.t_step_min:3600*val.n_hours); % number of timesteps
29
   else
30
       val.n_ts=length(0:val.t_step_max:3600*val.n_hours); % number of timesteps
31
   end
32
   end
```

```
1
   function val = convergence_par()
2
   %CONVERGENCE_PAR definition of convergence parameters
   val.convergence = le-10; %[-]..convergence criterion (residual needs to be ...
3
4
                                    % less than this value)
5
   val.variable_relax = 1;
                             %[-]..activate/deactivate loop for variable relaxation
                             %[-]..max. relaxation factor
6
   val.relax_init = 1.0;
7
                              %[-]..subtraction factor for relaxation value ...
   val.relax_sub = 0.05;
                                    % (used in loop for variable relaxation)
8
9
                             %[-]..min. relaxation factor allowable (generally ...
   val.relax_min = 0.7;
                                    % taken equal to the subtraction factor)
10
   val.it_max = 25;
                              %[-]..max. number of iterations
11
                             %[-]..activate/deactivate recording of mass and ...
12
   val.record_it = 1;
13
                                    % temperature for each iteration ...
14
                                    % (WARNING: if "it" is too high and "Dx" and ...
15
                                    % "Dt" is too low, this leads to a memory error)
```

```
16 val.w = 0;
                             %[-]..activate/disable check on warnings about ...
17
                                   % bad scaled matrix:
18
                                   % 0: warnings activated (nothing changes);
19
                                   % 1: warnings disabled
20 end
   function [val,fuelProp_sat_table] = fuel_properties()
1
2
   %FUEL_PROPERTIES definition of fuel properties
3 % n—butane
4 fuelProp_sat_table=getfield(load('butane_sat'),'sat_table');
   fuelProp_sat=table2array(fuelProp_sat_table(:,[1 2 6 7]));
5
6 poly_deg_p_sat=4;
   poly_deg_Dh_vap=4;
7
   [val.p_sat,~,val.p_mu]=polyfit(fuelProp_sat(:,1),fuelProp_sat(:,2),...
8
9
       poly_deg_p_sat);
10 val.p_sat_d1=polyder(val.p_sat);
   val.p_sat_d2=polyder(val.p_sat_d1);
11
12 val.Cp_vap=1732;
13 [val.Dh_vap,~,val.Dh_mu]=polyfit(fuelProp_sat(:,1),fuelProp_sat(:,4),...
14
       poly_deg_Dh_vap);
15 val.Dh_vap_d1=polyder(val.Dh_vap);
16
   val.Dh_vap_d2=polyder(val.Dh_vap_d1);
17
18 val.MW_vap=58.12e-3;
                               %[kg/mol]..fuel molar mass (n—butane)
   val.T_min=fuelProp_sat(1,1);
19
20 val.rho_liq=604;
                               %[kg/m^3]..n—butane density as liquid (25 C,Patm)...
21
                                   % (considered constant with temperature)
22
   end
```

```
function val = air_properties()
1
2
   %AIR_PROPERTIES definition of air/inert properties
3
   % AIR
4 % val.Cp_a = 1006;
                                %[J/(kg*K)]....specific heat of air
5 % val.MW_a=28.96*10^-3;
                                %[kg/mol].....molecular weight of air
6 % NITROGEN
7
   val.Cp_a = 1040;
                              %[J/(kg*K)]....specific heat of nitrogen
8
   val.MW_a=28.0134*10^—3;
                              %[kg/mol].....molecular weight of nitrogen
                               %[m^2/s].....self-diffusion coefficient
9
   val.D_a=1.5*10^-5;
10 val.R=8.314;
                              %[J/(mol*K)]....univ. gas constant ...
11
                                  % (not a property of air, but simply put in ...
12
                                  % this struct variable)
13 end
```

1 function [val,geom_table] = canister_properties()

2 %CANISTER_PROPERTIES definition of canister properties

```
3 \text{ can_type} = 2;
4
   geom_data_all=load('canister_linear_geometry');
 5
   switch can_type
 6
       case 0
                   % Lavoie canister (1.0 L, linear, constant section)
 7
           geom_table=geom_data_all.can_Lavoie;
 8
           val.WC=173;
                                   %[kg/m^3_C].....(butane) working capacity
 9
           val.rho_app=345;
                                  %[kg/m^3].....apparent carbon density
10
       case 1
                   % US canister (3.5 L, USA truck)
11
           geom_table=geom_data_all.can_DS;
                                   %[kg/m^3_C].....(butane) working capacity
12
           val.WC=113;
13
           val.rho_app=363;
                                   %[kg/m^3]....apparent carbon density
14
       case 2
                   % EU canister (1.0 L, Europe utilitarian)
           geom_table=geom_data_all.can_312;
15
                                   %[kg/m^3_C].....(butane) working capacity
16
           val.WC=120;
17
           val.rho_app=363;
                                 %[kg/m^3].....apparent carbon density
18 end
   val.length=geom_table.x(end);
19
20
   val.P_cross=[geom_table.x';geom_table.P_tot'];
21
   val.A_cross=[geom_table.x';geom_table.A'];
22
   val.V=trapz(val.A_cross(1,:),val.A_cross(2,:));
23
   val.F_g=3;
24
25
   val.m_sat=val.WC/val.rho_app;
                            %[J/(kg*K)]..specific heat of carbon
26 val.Cv_carb=700;
27 val.Cp_plastic=1900;
                            %[J/(kg*K)]..specific heat of plastic
28
   val.k_carb=0.13;
                            %[W/(m*K)]...thermal conductivity of carbon bed
29
   val.m_plastic=0.5;
                            %[kg/kg]....mass of plastic per mass of carbon
                            [-].....axial diffusivity factor in carbon bed
30 val.beta=1;
31
   % to be evaluated experimentally:
                            %[K/K].....wall temperature change on carbon ...
32
   val.dTp_dT=0.34;
33
                               % temperature change (to evaluate experimentally)
                            %[W/(m2*K)]..exterior heat transfer coefficient ...
34
   val.U_loss=13;
                               % (to evaluate experimentally)
36 end
 1
   function val = function_properties()
```

```
%FUNCTION_PROPERTIES definition of adsorption function parameters
2
  \% List of calibration parameters for the function f-v:
3
  % differential free energy of adsorption VS relative total volume of adsorbate
4
  val.adsIso=2;
5
                                %[-]
  switch val.adsIso
6
      case 1 % from Dubinin—Asthakov
7
8
          val.E=8.18e3; %[J/mol].....E=f_1*MW_vap/rho_lig
9
          val.n=1.2:
                          %[-]
      case 2 % edited, from Lavoie
```

```
11
           val.E_0=48.153; %[J/mol].....E_0=f_0*MW_vap/rho_liq
12
           val.E_1=8.18e3; %[J/mol].....E_1=f_1*MW_vap/rho_lig
13
           val.n=1.2:
                           %[-]
14
           val.E_star=385; %[J/mol].....E_star=f_star*MW_vap/rho_lig
15
           val.v_star=0.9; %[-].....parameter for a reference volume
16
           val.A_star=val.v_star*exp((val.E_star/val.E_1)^val.n); %[-] ...
17
                                               % A_star=v_star*exp((E_star/E_1)^n)
18
           val.B_star=val.v_star/(1+val.E_0/val.E_star);
                                                                  %[-]...
19
                                               % B_star=v_star/(1+(E_0/E_star))
20
           val.m_star=val.v_star*canister_properties().WC/ ...
21
               canister_properties().rho_app; %[kg/kg_carb] ...
22
                                      % m_star=v_star*V_0*rho_lig=v_star*WC/rho_app
   %
             val.f_0=0.5e6;
23
                               %[J/m3]
24
   %
             val.f_1=85e6;
                               %[J/m3]
25
   %
             val.f_star=4e6;
                                   %[J/m3]
26 %
             val.V_0=canister_properties().WC/(canister_properties().rho_app* ...
27
                 fuel_properties().rho_liq); %[m3/kgC].....saturatuon volume
   0
28
   end
   end
29
```

```
1 function val = initial_conditions()
2 %INITIAL_CONDITIONS Definition of initial conditions
3 val.m_in = @(x) 0.01 + 0*x; %[kg/kgC]..initial adsorbed mass in canister
4 val.T_in = @(x) 20 +273.15 + 0*x; %[K]....initial temperature in canister
5 end
```

```
1
   function val = boundary_conditions()
2
   %BOUNDARY_CONDITIONS Definition of boundary conditions
3
   val.Y_f_left = 0.5;
   val.m_VXdot_left = 40/(3.6*10^6); %[kg/s]..fuel mass flow (n-butane)
4
   val.m_adot_left = ((1-val.Y_f_left)/val.Y_f_left)*...
5
       (air_properties().MW_a/fuel_properties().MW_vap)*val.m_VXdot_left;
6
7
   val.m_mixdot_left = val.m_VXdot_left + val.m_adot_left;
8
   val.T_amb = 20 + 273.15;
                                       %[K]....ambient temperaturetemperature
   val.p_amb = 101325;
                                       %[Pa]....ambient pressure
9
   val.p_tot = val.p_amb;
                                       %[Pa]....total pressure in tank/flux
10
11
12
   val.T_left = 20 +273.15;
                                   %[K]....left value of temperature (1st type BC)
13
14
   switch function_properties().adsIso
15
   case 1
16
       val.m_left = (canister_properties().WC/canister_properties().rho_app)*...
17
           exp(-((air_properties().R*val.T_left/function_properties().E)*...
18
           log(polyv(fuel_properties().p_sat,val.T_left,fuel_properties().p_mu)...
           /(val.p_tot*val.Y_f_left)))^function_properties().n);
19
```

20	case 2	
21	<pre>if val.Y_f_left <= (polyv(fuel_properties().p_sat,val.T_left,</pre>	
22	<pre>fuel_properties().p_mu)/val.p_tot)*exp(</pre>	
23	<pre>function_properties().E_star/(air_properties().R*val.T_left))</pre>	
24	<pre>val.m_left = (function_properties().A_star*canister_properties().W</pre>	VC/
25	<pre>canister_properties().rho_app)*</pre>	
26	<pre>exp(-((air_properties().R*val.T_left/function_properties().E_2</pre>	L)*
27	<pre>log(polyv(fuel_properties().p_sat,val.T_left,fuel_properties()</pre>	.p_mu)
28	<pre>/(val.p_tot*val.Y_f_left)))^function_properties().n);</pre>	
29	else	
30	<pre>val.m_left = (function_properties().B_star*canister_properties().W</pre>	VC/
31	<pre>canister_properties().rho_app)*</pre>	
32	<pre>(1+function_properties().E_0/(air_properties().R*val.T_left*.</pre>	
33	<pre>log(polyv(fuel_properties().p_sat,val.T_left,fuel_properties()</pre>	.p_mu)
34	<pre>/(val.p_tot*val.Y_f_left))));</pre>	
35	5 end	
36	6 end	
37	<pre>val.Jm_right=0; %[kg/(kgC*m)?]right flux of adsorbed mass (2nd)</pre>	d type BC)
38	<pre>val.JT_right=0; %[degC/m ?]right flux of temperature (2nd temperature)</pre>	ype BC)
39	val.molFrac=1;	
40) end	

```
1
   function val = constants()
 2
   %CONSTANTS Summary of this function goes here
   % Constants
 3
 4
   val.C1 = (boundary_conditions().m_adot_left/canister_properties().rho_app)*...
 5
        (fuel_properties().MW_vap/air_properties().MW_a);
 6
   val.C2 = canister_properties().beta*air_properties().D_a*((...
 7
        boundary_conditions().p_tot*air_properties().MW_a)/(air_properties().R*...
 8
        canister_properties().rho_app))*sqrt(fuel_properties().MW_vap/...
9
        air_properties().MW_a);
10 val.C3 = canister_properties().Cv_carb+canister_properties().m_plastic*...
11
        canister_properties().Cp_plastic*canister_properties().dTp_dT;
12
   val.C4 = fuel_properties().Cp_vap*val.C1;
13
   val.C5 = (boundary_conditions().m_adot_left/canister_properties().rho_app)*...
14
        air_properties().Cp_a;
   val.C6 = canister_properties().k_carb/canister_properties().rho_app;
15
16
   val.C7 = canister_properties().rho_app/canister_properties().U_loss;
17
   val.C8 = 1/(canister_properties().F_g*val.C6);
   switch function_properties().adsIso
18
19
       case 1
20
           val.C9 = canister_properties().WC/canister_properties().rho_app;
21
           val.C0 = function_properties().E/function_properties().n;
22
        case 2
23
           val.C9a = function_properties().A_star*canister_properties().WC/...
```

```
24 canister_properties().rho_app;
25 val.C9b = function_properties().B_star*canister_properties().WC/...
26 canister_properties().rho_app;
27 val.C0a = function_properties().E_1/function_properties().n;
28 val.C0b = function_properties().E_0*val.C9b;
29 end
30 end
```

D.3 Calculation functions

D.3.1 Main functions

```
1
         function fun=function_can(N,Dx,Dx_end,Dt,m,m_p,m_L,Jm_R,T,T_p,T_L,JT_R,v)
  2
                   fun=zeros(2*N,1);
                                                                                            % preallocation for function
  3
                   % function for left BC equation
  4
                   fun(1) = m(1) - m_L;
  5
                   fun(N+1)=T(1)-T_L;
  6
                   for i=2:N-1
  7
                             % function for first equation
  8
                             fun(i) = a1(m(i),T(i),v,i)*(m(i)-m_p(i))/Dt ...
                                                 ... + b1(m(i),T(i),v,i)*(T(i)-T_p(i))/Dt ...
  9
                                                  ... - (alpha1(m(i+1),T(i+1),v,i+1)*m(i+1)-alpha1(m(i-1),T(i-1),v,
                                                           i-1)*m(i-1))/(2*Dx) ...
                                                - (beta1(m(i+1),T(i+1),v,i+1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)*T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-beta1(m(i-1),T(i-1),v,i-1)+T(i+1)-t(i-1)-t(i-1)-t(i-1)+T(i+1)-t(i-1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)-t(i-1)+T(i+1)+T(i+1)-t(i-1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+T(i+1)+
11
                                                           (i−1))/(2*Dx) ...
12
                                                - gamma1(m(i),T(i),v,i)*(m(i+1)-2*m(i)+m(i-1))/(Dx^2) ...
13
                                                - ((gamma1(m(i+1),T(i+1),v,i+1)-gamma1(m(i-1),T(i-1),v,i-1))/(2*
                                                           Dx))*((m(i+1)-m(i-1))/(2*Dx)) ...
14
                                                - delta1(m(i),T(i),v,i)*(T(i+1)-2*T(i)+T(i-1))/(Dx^2) ...
15
                                                - ((delta1(m(i+1),T(i+1),v,i+1)-delta1(m(i-1),T(i-1),v,i-1))/(2*
                                                          Dx))*((T(i+1)-T(i-1))/(2*Dx)) \dots
16
                                                  ... - S1(m(i), T(i), v, i) ...
17
18
                             % function for second equation
19
                             fun(N+i) = a2(m(i),T(i),v,i)*(m(i)-m_p(i))/Dt ...
20
                                                 + b2(m(i),T(i),v,i)*(T(i)-T_p(i))/Dt ...
21
                                                  ... - (alpha2(m(i+1),T(i+1),v,i+1)*m(i+1)-alpha2(m(i-1),T(i-1),v,
                                                           i-1)*m(i-1))/(2*Dx) ...
22
                                                - (beta2(m(i+1),T(i+1),v,i+1)*T(i+1)-beta2(m(i-1),T(i-1),v,i-1)*T
                                                           (i−1))/(2*Dx) ...
23
                                                  ... - gamma2(m(i),T(i),v,i)*(m(i+1)-2*m(i)+m(i-1))/(Dx^2) ...
24
                                                  \dots = ((gamma2(m(i+1),T(i+1),v,i+1)-gamma2(m(i-1),T(i-1),v,i-1)))
                                                          /(2*Dx))*((m(i+1)-m(i-1))/(2*Dx)) ...
```

	<pre>— delta2(m(i),T(i),v,i)*(T(i+1)-2*T(i)+T(i-1))/(Dx^2)</pre>
	<pre>- ((delta2(m(i+1),T(i+1),v,i+1)-delta2(m(i-1),T(i-1),v,i-1))/(2*</pre>
	Dx))*((T(i+1)-T(i-1))/(2*Dx))
	<pre>- S2(m(i),T(i),v,i)</pre>
	;
end	
% function	on for right BC equation
fun(N)=	$a1(m(N),T(N),v,N)*(m(N)-m_p(N))/Dt$
	+ $b1(m(N), T(N), v, N) * (T(N) - T_p(N)) / Dt$
	((alpha1(m(N),T(N),v,N)-alpha1(m(N-1),T(N-1),v,N-1))/Dx_end)*m(
	N) — $alpha1(m(N-1),T(N-1),v,N-1)*Jm_R \dots$
-	<pre>- ((beta1(m(N),T(N),v,N)-beta1(m(N-1),T(N-1),v,N-1))/Dx_end)*T(N) -</pre>
	beta1(m(N—1),T(N—1),v,N—1)*JT_R
-	<pre>- ((gamma1(m(N),T(N),v,N)+gamma1(m(N-1),T(N-1),v,N-1))/Dx_end)*Jm_R -</pre>
	$(2*gamma1(m(N-1),T(N-1),v,N-1)/(Dx_end^2))*(m(N-1)-m(N))$
_	<pre>- ((delta1(m(N),T(N),v,N)+delta1(m(N-1),T(N-1),v,N-1))/Dx_end)*JT_R -</pre>
	(2*delta1(m(N-1),T(N-1),v,N-1)/(Dx_end^2))*(T(N-1)-T(N))
	$\dots - S1(m(N),T(N),v,N) \dots$
	;
fun(2*N)=	= $a2(m(N),T(N),v,N)*(m(N)-m_p(N))/Dt$
	+ b2(m(N),T(N),v,N)*(T(N)-T_p(N))/Dt
	<pre> ((alpha2(m(N),T(N),v,N)-alpha2(m(N-1),T(N-1),v,N-1))/Dx_end)*</pre>
	<pre>m(N) — alpha2(m(N-1),T(N-1),v,N-1)*Jm_R</pre>
	<pre>- ((beta2(m(N),T(N),v,N)-beta2(m(N-1),T(N-1),v,N-1))/Dx_end)*T(N) -</pre>
	beta2(m(N-1),T(N-1),v,N-1)*JT_R
	\dots ((gamma2(m(N),T(N),v,N)+gamma2(m(N-1),T(N-1),v,N-1))/Dx_end)*
	$Jm_R - (2*gamma2(m(N-1),T(N-1),v,N-1)/(Dx_end^2))*(m(N-1)-m(N))$
	<pre>- ((delta2(m(N),T(N),v,N)+delta2(m(N-1),T(N-1),v,N-1))/Dx_end)*JT_R</pre>
	<pre>— (2*delta2(m(N-1),T(N-1),v,N-1)/(Dx_end^2))*(T(N-1)-T(N))</pre>
	$- S2(m(N),T(N),v,N) \dots$
	;
end	
end	
end	

~	Suc-zeros(z=w,z=w); s preactocation for jacobian matrix
3	<pre>% Jacobian element for left BC equation</pre>
4	Jac(1,1)=1;
5	<pre>Jac(N+1,N+1)=1;</pre>
6	for i=2:N-1
7	% Jacobian element for first equation
8	<pre>Jac(i,i-1)= (alpha1(m(i-1),T(i-1),v,i-1)/(2*Dx)) + m(i-1)/(2*Dx)*</pre>
	dalpha1_dm(m(i-1),T(i-1),v,i-1)
9	+ T(i-1)/(2*Dx)*dbeta1_dm(m(i-1),T(i-1),v,i-1)
10	$- \operatorname{gammal}(m(i),T(i),v,i)/(Dx^2) + (\operatorname{gammal}(m(i+1),T(i+1),v,i+1))$

	-gammal(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((m(i+1)-m(i-1))
	/(4*Dx^2))*dgamma1_dm(m(i—1),T(i—1),v,i—1)
11	+ ((T(i+1)—T(i—1))/(4*Dx^2))*ddelta1_dm(m(i—1),T(i—1),v,i—1);
12	<pre>Jac(i,i)= a1(m(i),T(i),v,i)/Dt + ((m(i)-m_p(i))/Dt)*da1_dm(m(i),T(i</pre>
),v,i)
13	<pre> + db1_dm(m(i),T(i),v,i)*(T(i)-T_p(i))/Dt</pre>
14	+ 2*gammal(m(i),T(i),v,i)/(Dx^2) - ((m(i+1)-2*m(i)+m(i-1))/(Dx
	^2))*dgamma1_dm(m(i),T(i),v,i)
15	<pre>- ((T(i+1)-2*T(i)+T(i-1))/(Dx^2))*ddelta1_dm(m(i),T(i),v,i)</pre>
16	dS1_dm(m(i),T(i),v,i)
17	;
18	<pre>Jac(i,i+1)= (alpha1(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (m(i+1)/(2*Dx))*</pre>
	$dalphal_dm(m(i+1),T(i+1),v,i+1)$
19	<pre>- (T(i+1)/(2*Dx))*dbeta1_dm(m(i+1),T(i+1),v,i+1)</pre>
20	<pre>— gammal(m(i),T(i),v,i)/(Dx^2) - (gammal(m(i+1),T(i+1),v,i+1)</pre>
	$-gamma1(m(i-1),T(i-1),v,i-1))/(4*Dx^2) - ((m(i+1)-m(i-1)))$
	/(4*Dx^2))*dgamma1_dm(m(i+1),T(i+1),v,i+1)
21	<pre>- ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta1_dm(m(i+1),T(i+1),v,i+1);</pre>
22	<pre>Jac(i,N+i-1)= m(i-1)/(2*Dx)*dalpha1_dT(m(i-1),T(i-1),v,i-1)</pre>
23	+ (beta1(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)*
	dbeta1_dT(m(i-1),T(i-1),v,i-1)
24	+ ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma1_dT(m(i-1),T(i-1),v,i
	—1)
25	<pre>— delta1(m(i),T(i),v,i)/(Dx^2) + (delta1(m(i+1),T(i+1),v,i</pre>
	+1)—delta1(m(i—1),T(i—1),v,i—1))/(4*Dx^2) + ((T(i+1)—T(
	i-1))/(4*Dx^2))*ddelta1_dT(m(i-1),T(i-1),v,i-1);
26	<pre>Jac(i,N+i)= ((m(i)-m_p(i))/Dt)*dal_dT(m(i),T(i),v,i)</pre>
27	<pre> + b1(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db1_dT(m(i),T</pre>
	(i),v,i)
28	<pre>- ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma1_dT(m(i),T(i),v,i)</pre>
	· · · ·
29	+ 2*delta1(m(i),T(i),v,i)/(Dx^2) - ((T(i+1)-2*T(i)+T(i-1))/(
	<pre>Dx^2))*ddelta1_dT(m(i),T(i),v,i)</pre>
30	dSl_dT(m(i),T(i),v,i)
31	;
32	<pre>Jac(i,N+i+1)= (m(i+1)/(2*Dx))*dalpha1_dT(m(i+1),T(i+1),v,i+1)</pre>
33	<pre>- (beta1(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (T(i+1)/(2*Dx))*</pre>
	<pre>dbeta1_dT(m(i+1),T(i+1),v,i+1)</pre>
34	<pre>- ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma1_dT(m(i+1),T(i+1),v,i</pre>
	+1)
35	<pre>— delta1(m(i),T(i),v,i)/(Dx^2) — (delta1(m(i+1),T(i+1),v,i</pre>
	+1)—delta1(m(i—1),T(i—1),v,i—1))/(4*Dx^2) — ((T(i+1)—T(
	i-1))/(4*Dx^2))*ddelta1_dT(m(i+1),T(i+1),v,i+1);
36	
37	<pre>% Jacobian element for second equation</pre>

<pre>dalpha2_dm(m(i-1), T(i-1), v, i-1) 39 + T(i 1)/(2+Dx)*dbeta2_dm(m(i-1), T(i-1), v, i-1) 40 gamma2(m(i), T(i), v, i)/(Dx^2) + (gamma2(m(i+1), T(i+1), v, i+1)-gamma2(m(i-1), T(i-1), v, i-1))/(4+Dx^2) + ((m(i+1) -m(i-1))/(4+Dx^2))*ddalta2_dm(m(i-1), T(i-1), v, i-1) 41 + ((T(i+1) T(i 1))/(4+Dx^2))*ddalta2_dm(m(i), T(i), v, i-1) 42 ; 43 Jac(N+i,i)= a2(m(i), T(i), v, i)/(Dt + ((m(i)-m.p(i))/Dt)*da2_dm(m(i), T(i), v, v, i) 44 + db2_dm(m(i), T(i), v, i)*(T(i)-T_p(i))/Dt 45 + 2*gamma2(m(i), T(i), v, i)/(Dx^2) - ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dm(m(i), T(i), v, i) 46 ((T(i+1)-2*T(i)+T(i-1))/(Dx^2))*ddelta2_dm(m(i), T(i), v, 1) 47 dS2_dm(m(i), T(i), v, i) 48 ; 49 Jac(N+i, i+1) = (alpha2(m(i+1), T(i+1), v, i+1)/(2*Dx)) - (m(i+1)/(2*Dx))*dalpha2_dm(m(i+1), T(i+1), v, i+1) 50 - (T(i+1)/(2*Dx))*dbeta2_dm(m(i+1), T(i+1), v, i+1) 51 gamma2(m(i), T(i), v, i)/(Dx^2) - (gamma2(m(i+1), T(i+1), v, i) + (m(i+1))-T(i-1))/(4*Dx^2))*ddalta2_dm(m(i+1), T(i+1), v, 51 (T(T(i+1))-T(i-1))/(4*Dx^2))*ddalta2_dm(m(i+1), T(i+1), v, 52 + (beta2(m(i-1), T(i-1), v, i-1)) 53 + ((beta2(m(i-1), T(i-1), v, i-1)) 54 + ((m(i+1))-T(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1), T(i+1), v, 55 + ((beta2(m(i-1), T(i-1), v, i-1)) 56 + ((m(i+1))-T(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1), T(i+1), v, 57 (dta2(m((i-1), T(i-1), v, i-1)) 58 ; 59 Jac(N+i, N+i) = ((m(i)-m, p(i))/Dt)*da2_dT(m(i), T(i), v, i) 50 + b2(m(i), T(i), v, i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i), T(i), v, i)) 51 ((m(i+1))-2*m(i)+m(i-1))/((bx^2))*dgamma2_dT(m(i), T(i), v, i) 52 ((m(i+1))-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i), T(i), v, i) 53 ; 54 ((m(i)-1), v, i)/Dt + ((T(i)-T_p(i)))/Dt)*db2_dT(m(i), T(i), v, i) 55 ((m(i+1))-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i), T(i), v, i) 56 ((m(i+1))-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i), T(i), v, i) 57 ((m(i+1))-2*m(i)+m(i-1)</pre>	38	<pre>Jac(N+i,i-1)= (alpha2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + m(i-1)/(2*Dx)*</pre>
<pre>39 + T(i-1)/(2*Dx)*dbeta2 dm(m(i-1),T(i-1),v,i-1) 40 gama2(m(i),T(i),v,i)/(Dx²) + (gama2(m(i+1),T(i+1), v,i+1)-gama2(m(i-1),T(i-1),v,i-1))/(4+Dx²) + ((m(i+1) m(i 1))/(4+Dx²))*dgama2_dm(m(i 1),T(i 1),v,i 1) 41 + ((T(i+1)-T(i-1))/(4+Dx²))*ddelta2_dm(m(i-1),T(i-1),v ,i-1) 42 ; 43 Jac(N+i,i)= a2(m(i),T(i),v,i)/Dt + ((m(i) m_p(i))/Dt)*da2_dm(m(i),T(i), v,i) 44 + db2_dm(m(i),T(i),v,i)*(T(i)-T_p(i))/Dt 45 + 2*gama2(m(i),T(i),v,i)/(Dx²) - ((m(i+1)-2*m(i)+m(i-1))/(Dx²))*dgama2_dm(m(i),T(i),v,i) 46 ((T(i+1)-2*T(i)+T(i-1))/(Dx²))*ddelta2_dm(m(i),T(i),v, i) 47 d52_dm(m(i),T(i),v,i) 48 ; 49 Jac(N+i,i+1)= (alpha2(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (m(i+1)/(2*Dx))*dalpha2_dm(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (m(i+1)/(2*Dx))*dalpha2_dm(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (m(i+1)/(2*Dx))*dalpha2_dm(m(i-1),T(i-1),v,i-1)/((4*Dx²)) = (gama2(m(i+1),T(i+1),v,i+1) 50 ((T(i+1)-T(i-1))/(4*Dx²)) *ddelta2_dm(m(i+1),T(i+1),v,i+1) 51 gama2(m(i),T(i),v,i)/(Dx²) - (gama2(m(i+1),T(i+1),v,i+1) 52 ((T(i+1)-T(i-1))/(4*Dx²)) *ddelta2_dm(m(i+1),T(i+1),v,i+1) 53 ((T(i+1)-T(i-1))/(4*Dx²)) *ddelta2_dm(m(i+1),T(i+1),v,i+1) 54 Jac(N+i,N+i-1)= m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) 55 + (beta2(m(i-1),T(i-1),v,i-1)) 56 + ((m(i+1)-m(i-1))/(4*Dx²)) *dgama2_dT(m(i-1),T(i-1),v,i-1) 57 ((T(i+1)-m(i-1))/(4*Dx²)) *dgama2_dT(m(i-1),T(i-1),v,i-1) 58 + ((m(i+1)-m(i-1))/(4*Dx²)) *dgama2_dT(m(i-1),T(i-1),v,i-1) 59 Jac(N+i,N+i)= (((m(1)-m,p(i))/Dt)*dd2_dT(m(i),T(i),v,i) 61 (((m(i+1)-2*m(i)+m(i-1))/(Dx²))*dgama2_dT(m(i),T(i),v,i) 61 ((((m(i+1)-2*m(i)+m(i-1))/(Dx²))*dgama2_dT(m(i),T(i),v,i) 61 ((((m(i+1)-2*m(i)+m(i-1))/(Dx²))*dgama2_dT(m(i),T(i),v,i) 61 ((((m(i)-2*m(i)+m(i-1))/(Dx²))*dgama2_dT(m(i),T(i),v,i) 61 ((((m(i)-2*m(i)+m(i-1))/(Dx²))*dgama2_dT(m(i),T(i),v,i) 61 ((((m(i)-2*m(i)+m(i-1))/(Dx²))*dgama2_dT(</pre>		dalpha2_dm(m(i-1),T(i-1),v,i-1) \dots
<pre>40 = gama2(m(i),T(i),v,i)/(Dx²) + (gama2(m(i+1),T(i+1),</pre>	39	+ T(i−1)/(2*Dx)*dbeta2_dm(m(i−1),T(i−1),v,i−1)
$ \begin{array}{c} v, i+1)-gamma2(m(i-1), T(i-1), v, i-1))/(4+Dx^2) + ((m(i+1)) \\ -m(i-1))/(4+Dx^2)) + dgamma2_dm(i-1), T(i-1), v, i-1) \dots \\ i, + (T(i+1)-T(i-1))/(4+Dx^2)) + ddelta2_dm(m(i-1), T(i-1), v \\ i, i-1) \dots \\ i \\ 2 \\ ; \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3 \\ 3$	40	— gamma2(m(i),T(i),v,i)/(Dx^2) + (gamma2(m(i+1),T(i+1),
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		v,i+1)—gamma2(m(i—1),T(i—1),v,i—1))/(4*Dx^2) + ((m(i+1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-m(i-1))/(4*Dx^2))*dgamma2_dm(m(i-1),T(i-1),v,i-1)
$ \begin{array}{c} ,i-1) \dots \\ ; \\ 43 \\ 44 \\ 44 \\ 45 \\ 44 \\ 46 \\ 46 \\ 46 \\ 46$	41	<pre> + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i-1),T(i-1),v</pre>
<pre>42 43 44 45 44 45 44 44 4 4 4 4 4 4 4 4 4</pre>		,i—1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	42	;
<pre>v,i) 44</pre>	43	<pre>Jac(N+i,i)= a2(m(i),T(i),v,i)/Dt + ((m(i)-m_p(i))/Dt)*da2_dm(m(i),T(i),</pre>
<pre>44 + db2_dm(mi),T(i),v,i)*(T(i)-T_p(i))/Dt 45 + 2*gama2(m(i),T(i),v,i)/(Dx^2) - ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dm(m(i),T(i),v,i) 46 ((T(i+1)-2*T(i)+T(i-1))/(Dx^2))*ddelta2_dm(m(i),T(i),v, i) 47 d52_dm(mi),T(i),v,i) 48 ; 49 Jac(N+i,i+1)= (alpha2(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (m(i+1)/(2*Dx)))*dalpha2_dm(m(i+1),T(i+1),v,i+1) 50 (T(i+1)/(2*Dx))*dbeta2_dm(m(i+1),T(i+1),v,i+1) 51 gama2(mi),T(i),v,i)/(Dx^2) - (gama2(m(i+1),T(i+1),v,i+1) 52 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v,i+1) 53 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v,i+1) 54 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v,i+1) 55 + (beta2(m(i-1),T(i-1),v,i-1)) 56 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgama2_dT(m(i-1),T(i-1),v,i-1) 57 delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v,i+1) 58 59 ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 50 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i,v,i) 60 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i) 61 ((m(i)+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i) 61 ((m(i)+1)-2*m(i)+m(i-1))/(Dx^2))*dgama2_dT(m(i),T(i),v,i)</pre>		v,i)
<pre>45 + 2*gama2(m(i),T(i),v,i)/(Dx^2) - ((m(i+1)-2*m(i)+m(i-1)</pre>	44	+ db2_dm(m(i),T(i),v,i)*(T(i)—T_p(i))/Dt
$ \begin{array}{c})/(Dx^{2}))*dgamma2_dm(m(i),T(i),v,i) \dots \\ \dots = ((T(i+1)-2*T(i)+T(i-1))/(Dx^{2}))*ddelta2_dm(m(i),T(i),v,i) \\ i) \dots \\ 1) \dots \\ 1) \dots \\ 1) \dots \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\$	45	<pre> + 2*gamma2(m(i),T(i),v,i)/(Dx^2) - ((m(i+1)-2*m(i)+m(i-1)</pre>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$)/(Dx^2))*dgamma2_dm(m(i),T(i),v,i)
<pre>i) 47 dS2_dm(m(i),T(i),v,i) 48 ; 49 Jac(N+i,i+1)= (alpha2(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (m(i+1)/(2*Dx)))*dalpha2_dm(m(i+1),T(i+1),v,i+1) 50 - (T(i+1)/(2*Dx))*dbeta2_dm(m(i+1),T(i+1),v,i+1) 51 gamma2(m(i),T(i),v,i)/(Dx^2) - (gamma2(m(i+1),T(i+1), v,i+1)-gamma2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) - ((m(i+1)) -m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1),T(i+1),v,i+1) 52 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v, 53 54 Jac(N+i,N+i-1)= m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) 55 + (beta2(m(i-1),T(i-1),v,i-1)) 56 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1), v,v,i-1) 57 delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i),T(i-1),v,i 57 58 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 + output for the fourth of the fourth of</pre>	46	<pre> ((T(i+1)-2*T(i)+T(i-1))/(Dx^2))*ddelta2_dm(m(i),T(i),v,</pre>
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		i)
<pre>48 ; 49 Jac(N+i,i+1)= (alpha2(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (m(i+1)/(2*Dx))*dalpha2_dm(m(i+1),T(i+1),v,i+1) 50 - (T(i+1)/(2*Dx))*dbeta2_dm(m(i+1),T(i+1),v,i+1) 51 gamma2(m(i),T(i),v,i)/(Dx^2) - (gamma2(m(i+1),T(i+1), v,i+1)-gamma2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) - ((m(i+1)) -m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1),T(i+1),v,i+1) 52 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v,i+1) 53 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v,i+1) 54 m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) 55 + (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)* 56 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1),v,i-1) 57 delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v,i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i-1) 58 ; 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + (b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i)))/Dt)*db2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i+1)-</pre>	47	dS2_dm(m(i),T(i),v,i)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	48	;
<pre>)*dalpha2_dm(m(i+1),T(i+1),v,i+1) - (T(i+1)/(2*Dx))*dbeta2_dm(m(i+1),T(i+1),v,i+1) gamma2(m(i),T(i),v,i)/(Dx^2) - (gamma2(m(i+1),T(i+1), v,i+1)-gamma2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) - ((m(i+1)) -m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1),T(i+1),v,i+1) ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v, ,i+1) 3 ; 54 Jac(N+i,N+i-1)= m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) + (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)* dbeta2_dT(m(i-1),T(i-1),v,i-1) 56 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1),v,i-1) 57 delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 ; 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i)</pre>	49	<pre>Jac(N+i,i+1)= (alpha2(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (m(i+1)/(2*Dx)</pre>
<pre>50 - (T(i+1)/(2*Dx))*dbeta2_dm(m(i+1),T(i+1),v,i+1) 51 gamma2(m(i),T(i),v,i)/(Dx^2) - (gamma2(m(i+1),T(i+1), v,i+1)-gamma2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) - ((m(i+1)) -m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1),T(i+1),v,i+1) 52 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v, i+1) 53 54 Jac(N+i,N+i-1)= m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) 55 + (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)* dbeta2_dT(m(i-1),T(i-1),v,i-1) 56 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1)) ,v,i-1) 57 - delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 ; 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i)</pre>)*dalpha2_dm(m(i+1),T(i+1),v,i+1)
<pre>51 gamma2(m(i),T(i),v,i)/(Dx^2) - (gamma2(m(i+1),T(i+1), v,i+1)-gamma2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) - ((m(i+1)) -m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1),T(i+1),v,i+1) 52 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v, i+1) 53 54 Jac(N+i,N+i-1)=m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) 55 + (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)* dbeta2_dT(m(i-1),T(i-1),v,i-1) 56 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1)) ,v,i-1) 57 delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1)))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i))</pre>	50	<pre>- (T(i+1)/(2*Dx))*dbeta2_dm(m(i+1),T(i+1),v,i+1)</pre>
$ \begin{array}{c} v, i+1)-gamma2(m(i-1), T(i-1), v, i-1))/(4*Dx^2) - ((m(i+1) - m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1), T(i+1), v, i+1) \dots \\ - m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1), T(i+1), v, i, i+1) \dots \\ ; \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	51	— gamma2(m(i),T(i),v,i)/(Dx^2) — (gamma2(m(i+1),T(i+1),
<pre>-m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1),T(i+1),v,i+1) ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v ,i+1) 3 3 54 Jac(N+i,N+i-1)= m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) + (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)* dbeta2_dT(m(i-1),T(i-1),v,i-1) 56 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1) ,v,i-1) 57 - delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 ; 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i), ,v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), v,i)</pre>		v,i+1)—qamma2(m(i—1),T(i—1),v,i—1))/(4*Dx^2) — ((m(i+1)
<pre>52 ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v ,i+1) 53 ; 54 Jac(N+i,N+i-1)=m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) 55 + (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)* 65 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1) ,v,i-1) 57 - delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 ; 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i), v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), v,i)</pre>		$-m(i-1))/(4*Dx^2))*dgamma2_dm(m(i+1),T(i+1),v,i+1) \dots$
<pre>,i+1) 33 ; 54 Jac(N+i,N+i-1)= m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) 55 + (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)*</pre>	52	((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dm(m(i+1),T(i+1),v
<pre>53 54 54 55 55 56 56 57 57 58 59 59 59 59 59 59 50 50 51 52 53 53 54 53 54 53 54 54 55 55 55 56 57 57 57 57 57 57 57 57 57 57 57 57 57</pre>		,i+1)
<pre>54 Jac(N+i,N+i-1)= m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1) 55 + (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)* 56 + (m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1)) 57 + (delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, 57 + (delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, 57 + ((T(58 + (m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 58 + ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 59 + Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i), 51 + ((m(i)-m_p(i))/Dt) + ((m(i)-1))/(Dx^2))*dgamma2_dT(m(i),T(i), 53 + ((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), 54 + ((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), 55 + ((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), 56 + ((m(i)-m_p(i))+((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), 57 + ((m(i)-m_p(i))+((m(i)-m_p(i))+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), 58 + ((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i),T(i)), 59 + ((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i),T(i)), 50 + ((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i),T(i)), 51 + ((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i),T(i)), 52 + ((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i),T(i)), 53 + ((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m_p(i))+((m(i)-m</pre>	53	;
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	54	<pre>Jac(N+i,N+i-1)= m(i-1)/(2*Dx)*dalpha2_dT(m(i-1),T(i-1),v,i-1)</pre>
<pre>dbeta2_dT(m(i-1),T(i-1),v,i-1) 56 + ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1) ,v,i-1) 57 - delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i),),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), v,i)</pre>	55	+ (beta2(m(i-1),T(i-1),v,i-1)/(2*Dx)) + T(i-1)/(2*Dx)*
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		<pre>dbeta2_dT(m(i-1),T(i-1),v,i-1)</pre>
<pre>57 , v, i-1) 57 - delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v, i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 ; 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), v,i)</pre>	56	+ ((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i-1),T(i-1)
<pre>57 - delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v,</pre>		,∨,i—1)
<pre>i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i)),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), v,i)</pre>	57	<pre>— delta2(m(i),T(i),v,i)/(Dx^2) + (delta2(m(i+1),T(i+1),v,</pre>
<pre>i+1)-T(i-1))/(4*Dx^2))*ddelta2_dT(m(i-1),T(i-1),v,i -1) 58 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 60 61 61 61 61 61 61 61 61 61 61 61 61 61</pre>		i+1)-delta2(m(i-1),T(i-1),v,i-1))/(4*Dx^2) + ((T(
<pre>-1) 58 59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i),</pre>		i+1)—T(i—1))/(4*Dx^2))*ddelta2_dT(m(i—1),T(i—1),v,i
<pre>58 59 60 61 61 53 54 55 59 59 59 59 59 59 59 59 59 59 59 50 50 50 50 50 50 50 50 50 50 50 50 50</pre>		—1)
<pre>59 Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i) 60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i)),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),v,i)</pre>	58	;
<pre>60 + b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i),v,i) 61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), v,i)</pre>	59	<pre>Jac(N+i,N+i)= ((m(i)-m_p(i))/Dt)*da2_dT(m(i),T(i),v,i)</pre>
61 (interpretation of the second sec	60	+ b2(m(i),T(i),v,i)/Dt + ((T(i)-T_p(i))/Dt)*db2_dT(m(i),T(i
61 ((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i), v,i)),v,i)
v,i)	61	((m(i+1)-2*m(i)+m(i-1))/(Dx^2))*dgamma2_dT(m(i),T(i),
		v,i)
62 + 2*delta2(m(i),T(i),v,i)/(Dx^2) ((T(i+1)-2*T(i)+T(i	62	+ 2*delta2(m(i),T(i),v,i)/(Dx^2) ((T(i+1)-2*T(i)+T(i
<pre>-1))/(Dx^2))*ddelta2_dT(m(i),T(i),v,i)</pre>		<pre>-1))/(Dx^2))*ddelta2_dT(m(i),T(i),v,i)</pre>
$- dS2_dT(m(i),T(i),v,i);$	63	<pre>- dS2_dT(m(i),T(i),v,i) ;</pre>

64	<pre>Jac(N+i,N+i+1)= (m(i+1)/(2*Dx))*dalpha2_dT(m(i+1),T(i+1),v,i+1)</pre>
65	<pre>— (beta2(m(i+1),T(i+1),v,i+1)/(2*Dx)) - (T(i+1)/(2*Dx))*</pre>
	<pre>dbeta2_dT(m(i+1),T(i+1),v,i+1)</pre>
66	((m(i+1)-m(i-1))/(4*Dx^2))*dgamma2_dT(m(i+1),T(i+1)
	,v,i+1)
67	<pre>— delta2(m(i),T(i),v,i)/(Dx^2) — (delta2(m(i+1),T(i+1),v,</pre>
	i+1)—delta2(m(i—1),T(i—1),v,i—1))/(4*Dx^2) — ((T(
	i+1)—T(i—1))/(4*Dx^2))*ddelta2_dT(m(i+1),T(i+1),v,i
0.0	+1)
68	;
69 70	end
70 71	Solution alignment for right PC equation
71	\sim Saturdian element for right be equation lac(N N_1) = ((m(N)/Dx end) = lm R)*delphe1 dm(m(N_1) T(N_1) v N_1)
72	$= \frac{(T(N)/D_{X} \text{ end})}{(T(N)/D_{X} \text{ end})} = \frac{T(N)}{(T(N)/D_{X} \text{ end})} = \frac{T(N)}{(T$
74	$- (1m B/Dx end + (2/(Dx end^2))*(m(N-1)-m(N)))*dgamma1 dm(m(N-1))$
1 -	$T(N-1)$, v , $N-1$) - 2*gamma1(m(N-1), $T(N-1)$, v , $N-1$)/(Dx_end^2)
75	$- (JT_R/Dx_end + (2/(Dx_end^2))*(T(N-1)-T(N)))*ddelta1_dm(m(N-1),$
	T(N-1), v, N-1);
76	<pre>Jac(N,N)= a1(m(N),T(N),v,N)/Dt + ((m(N)-m_p(N))/Dt)*da1_dm(m(N),T(N),v,</pre>
	N)
77	+ ((T(N)-T_p(N))/Dt)*db1_dm(m(N),T(N),v,N)
78	\dots (alpha1(m(N),T(N),v,N)-alpha1(m(N-1),T(N),v,N))/Dx_end - (m(N
)/Dx_end)*dalpha1_dm(m(N),T(N),v,N)
79	$-$ (T(N)/Dx_end)*dbeta1_dm(m(N),T(N),v,N)
80	$-$ (Jm_R/Dx_end)*dgamma1_dm(m(N),T(N),v,N) + 2*gamma1(m(N-1),T(N-1),
	v,N-1)/(Dx_end^2)
81	$- (JT_R/Dx_end) * ddelta1_dm(m(N),T(N),v,N) \dots$
82	$\ldots = dSl_dm(m(N), I(N), v, N) \ldots$
83	; I = c(N - 2 + N - 1) = c(m(N) (Dy and) = Im D) (dalabal dT(m(N - 1) - T(N - 1)) (N - 1))
04	$\operatorname{Jac}(\mathbf{N}, 2*\mathbf{N}-1) = \ldots ((\operatorname{III}(\mathbf{N}))/\operatorname{Dx}_{\operatorname{end}}) - \operatorname{JII}_{\operatorname{R}})*\operatorname{dacpnal}_{\operatorname{di}}(\operatorname{III}(\mathbf{N}-1), 1(\mathbf{N}-1), \mathbf{V}, \mathbf{N}-1)$
85	+ $((T(N)/Dx end) - TR)*dbeta1 dT(m(N-1) T(N-1) v N-1)$
86	$- (Jm R/Dx end + (2/(Dx end^2))*(m(N-1)-m(N)))*dgamma1 dT(m(N-1))$
00	(0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.12, 0.1
87	$- (JT_R/Dx_end + (2/(Dx_end^2))*(T(N-1)-T(N)))*ddelta1_dT(m(N))$
	-1 , T(N-1), v, N-1) - 2*delta1(m(N-1), T(N-1), v, N-1)/(Dx_end
	^2);
88	$Jac(N,2*N) = ((m(N)-m_p(N))/Dt)*da1_dT(m(N),T(N),v,N)$
89	<pre> + b1(m(N),T(N),v,N)/Dt + ((T(N)-T_p(N))/Dt)*db1_dT(m(N),T(N),</pre>
	v,N)
90	\dots - (m(N)/Dx_end)*dalpha1_dT(m(N),T(N),v,N) \dots
91	<pre>— (betal(m(N),T(N),v,N)—betal(m(N—1),T(N),v,N))/Dx_end — (T(N)/</pre>
	<pre>Dx_end)*dbeta1_dT(m(N),T(N),v,N)</pre>
92	$- (Jm_R/Dx_end)*dgamma1_dT(m(N),T(N),v,N) \dots$

93	<pre>— (JT_R/Dx_end)*ddelta1_dT(m(N),T(N),v,N) + 2*delta1(m(N-1),T(N</pre>
	<pre>-1),v,N−1)/(Dx_end^2)</pre>
94	$\ldots - dSl_dT(m(N), T(N), v, N) \ldots$
95	;
96	
97	<pre>Jac(2*N,N-1)= ((m(N)/Dx_end) - Jm_R)*dalpha2_dm(m(N-1),T(N-1),v,N-1)</pre>
98	+ ((T(N)/Dx_end) — JT_R)*dbeta2_dm(m(N—1),T(N—1),v,N—1)
99	\dots (Jm_R/Dx_end + (2/(Dx_end^2))*(m(N-1)-m(N)))*dgamma2_dm(m
	(N−1),T(N−1),v,N−1) - 2*gamma2(m(N−1),T(N−1),v,N−1)/(Dx_end
	^2)
100	\dots - (JT_R/Dx_end + (2/(Dx_end^2))*(T(N-1)-T(N)))*ddelta2_dm(m
	(N-1), T(N-1), v, N-1)
101	;
102	<pre>Jac(2*N,N)= a2(m(N),T(N),v,N)/Dt + ((m(N)-m_p(N))/Dt)*da2_dm(m(N),T(N),v,N)</pre>
103	+ ((T(N)-T_p(N))/Dt)*db2_dm(m(N),T(N),v,N)
104	\dots - (alpha2(m(N),T(N),v,N)-alpha2(m(N-1),T(N),v,N))/Dx_end - (m
	$(N)/Dx_end)*dalpha2_dm(m(N),T(N),v,N)$
105	$- (T(N)/Dx_end)*dbeta2_dm(m(N),T(N),v,N) \dots$
106	\dots (Jm_R/Dx_end)*dgamma2_dm(m(N),T(N),v,N) + 2*gamma2(m(N-1),T
	(N−1),v,N−1)/(Dx_end^2)
107	\ldots - (JT_R/Dx_end)*ddelta2_dm(m(N),T(N),v,N) \ldots
108	$\ldots - dS2_dm(m(N),T(N),v,N) \ldots$
109	
110	<pre>Jac(2*N,2*N-1)= ((m(N)/Dx_end) - Jm_R)*dalpha2_dT(m(N-1),T(N-1),v,N-1)</pre>
111	+ $((T(N)/Dx_end) - JT_R)*dbeta2_dT(m(N-1),T(N-1),v,N-1)$
112	((1, 1, 1, 2, 2, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3,
	(m(N-1),T(N-1),v,N-1)
113	\dots - (JT_R/Dx_end + (2/(Dx_end^2))*(T(N-1)-T(N)))*ddelta2_dT
	(m(N-1),T(N-1),v,N-1)
114	<pre>- 2*delta2(m(N-1),T(N-1),v,N-1)/(Dx_end^2);</pre>
115	$Jac(2*N, 2*N) = ((m(N)-m_p(N))/Dt)*da2_dT(m(N), T(N), v, N)$
116	+ b2(m(N),T(N),v,N)/Dt + ((T(N)-T_p(N))/Dt)*db2_dT(m(N),T(N),v,
	N)
117	<pre> (m(N)/Dx_end)*dalpha2_dT(m(N),T(N),v,N)</pre>
118	$-$ (beta2(m(N),T(N),v,N)-beta2(m(N-1),T(N),v,N))/Dx_end - (T(N)/
	<pre>Dx_end)*dbeta2_dT(m(N),T(N),v,N)</pre>
119	\dots - (Jm_R/Dx_end)*dgamma2_dT(m(N),T(N),v,N) \dots
120	\dots - (JT_R/Dx_end)*ddelta2_dT(m(N),T(N),v,N) \dots
121	+ 2*delta2(m(N-1),T(N-1),v,N-1)/(Dx_end^2)
122	<pre>— dS2_dT(m(N),T(N),v,N);</pre>
123	end

D.3.2 Sub-functions

```
function val=a1(~,~,v,ix)
1
2
  val=v.A_x(ix);
3 end
1 function val=a2(m,T,v,ix)
2
  val=v.A_x(ix)*(v.Cp_vap*T_polyv(v.Dh_vap,T,v.Dh_mu)-(f(m,T,v)/v.MW_vap));
3
  end
  function val=b1(~,~,~,~)
1
  val=0;
2
3
  end
  function val=b2(m,T,v,ix)
1
  val=v.A_x(ix)*(v.C3+m*(v.Cp_vap_polyv(v.Dh_vap_d1/v.Dh_mu(2),T,v.Dh_mu)));
2
3 end
1 function val=alpha1(~,~,~,~)
2
  val=0;
  end
3
  function val=alpha2(~,~,~,~)
1
2
  val=0;
3
  end
1
  function val=beta1(m,T,v,~)
2
  val=(v.C1/T)*(1-1/(1-Y_f(m,T,v)));
3
  end
  function val=beta2(m,T,v,~)
1
2
  val=v.C4*(1-1/(1-Y_f(m,T,v)))-v.C5;
3
  end
1
  function val=gamma1(m,T,v,ix)
2
  val=(v.C2*v.A_x(ix)/T)*dY_f_dm(m,T,v);
3
  end
1
 function val=gamma2(~,~,~,~)
2
  val=0;
3 end
1
  function val=delta1(m,T,v,ix)
2
  val=(v.C2*v.A_x(ix)/T)*dY_f_dT(m,T,v);
3
  end
```

```
1
  function val=delta2(~,~,v,ix)
2 val=v.A_x(ix)*v.C6;
3 end
1 function val=da1_dm(~,~,~,~)
2
  val=0;
3
  end
1
  function val=da2_dm(m,T,v,ix)
2
  val=-(v.A_x(ix)/v.MW_vap)*df_dm(m,T,v);
3
  end
  function val=db1_dm(~,~,~,~)
1
2
  val=0;
3 end
1
  function val=db2_dm(~,T,v,ix)
2 val=v.A_x(ix)*(v.Cp_vap_polyv(v.Dh_vap_d1/v.Dh_mu(2),T,v.Dh_mu));
3 end
1 function val=dalpha1_dm(~,~,~,~)
2
  val=0;
3
  end
1 function val=dalpha2_dm(~,~,~,~)
2
  val=0;
3
  end
1
  function val=dbeta1_dm(m,T,v,~)
2
  val=-(v.C1/T)*(1/((1-Y_f(m,T,v))^2))*dY_f_dm(m,T,v);
3
  end
  function val=dbeta2_dm(m,T,v,~)
1
2
  val=-((v.C4)/((1-Y_f(m,T,v))^2))*dY_f_dm(m,T,v);
3
  end
  function val=dgamma1_dm(m,T,v,ix)
1
2
  val=(v.C2*v.A_x(ix)/T)*d2Y_f_dm2(m,T,v);
3
  end
1 function val=dgamma2_dm(~,~,~,~)
2
  val=0;
3
  end
```

```
1
  function val=ddelta1_dm(m,T,v,ix)
2
  val=(v.C2*v.A_x(ix)/T)*d2Y_f_dmdT(m,T,v);
  end
3
1 function val=ddelta2_dm(~,~,~,~)
2
  val=0;
3
  end
  function val=da1_dT(~,~,~,~)
1
2
  val=0;
3
  end
 function val=da2_dT(~,T,v,ix)
1
2
  val=v.A_x(ix)*(v.Cp_vap_polyv(v.Dh_vap_d1/v.Dh_mu(2),T,v.Dh_mu));
3
  end
1 function val=db1_dT(~,~,~,~)
2
  val=0;
3
  end
1
  function val=db2_dT(m,T,v,ix)
2
  val=-v.A_x(ix)*m*polyv(v.Dh_vap_d2/v.Dh_mu(2)^2,T,v.Dh_mu);
3
  end
1
  function val=dalpha1_dT(~,~,~,~)
2 val=0;
3 end
1 function val=dalpha2_dT(~,~,~,~)
2
  val=0;
  end
3
1
  function val=dbeta1_dT(m,T,v,~)
2
  Y_f_act=Y_f(m,T,v);
3
  val=-(v.C1/T)*((1/T)*(1/(1-Y_f_act))+(1/((1-Y_f_act)^2))*dY_f_dm(m,T,v));
4
  end
1
  function val=dbeta2_dT(m,T,v,~)
2
  val=-((v.C4)/((1-Y_f(m,T,v))^2))*dY_f_dT(m,T,v);
3
  end
1
  function val=dgamma1_dT(m,T,v,ix)
2
  val=(v.C2*v.A_x(ix)/T)*(d2Y_f_dmdT(m,T,v)-(1/T)*dY_f_dm(m,T,v));
3
  end
```

```
1 function val=dgamma2_dT(~,~,~,~)
2 val=0;
3 end
```

```
1 function val=ddelta1_dT(m,T,v,ix)
2 val=(d2Y_f_dT2(m,T,v)-dY_f_dT(m,T,v)/T)*v.C2*v.A_x(ix)/T;
3 end
```

```
1 function val=ddelta2_dT(~,~,~,~)
2 val=0;
3 end
```

```
1
    function val=f(m,~,v)
 2
   switch v.adsIso
 3
        case 1
 4
            val=v.E*(log(v.C9/m))^(1/v.n);
        case 2
 5
 6
            if m<=v.m_star</pre>
 7
                val=v.E_1*(log(v.C9a/m))^(1/v.n);
 8
            else
9
                val=v.C0b/(m-v.C9b);
10
                             v.f_alt_count=v.f_alt_count+1;
11
            end
12
   end
13
   end
```

```
1
    function val=df_dm(m,~,v)
2
   switch v.adsIso
 3
        case 1
 4
            val=-(v.C0/m)*(log(v.C9/m))^(1/v.n-1);
 5
        case 2
 6
            if m<=v.m_star</pre>
 7
                val=-(v.C0a/m)*(log(v.C9a/m))^(1/v.n-1);
 8
            else
9
                val=-v.C0b/(m-v.C9b)^2;
10
            end
11
   end
```

```
12 end
```

```
1 function val=d2f_dm2(m,~,v)
2 switch v.adsIso
3 case 1
4 val=(v.C0/m^2)*(((log(v.C9/m)))^(1/v.n-2))*(log(v.C9/m)+1/v.n-1);
5 case 2
```

```
if m<=v.m_star</pre>
6
7
                val=(v.C0a/m<sup>2</sup>)*(((log(v.C9a/m)))<sup>(1/v.n-2)</sup>)*(log(v.C9a/m)+1/v.n-1);
8
            else
9
                val=-2*v.C0b/(m-v.C9b)^3;
10
            end
11
   end
12
   end
   function val=Y_f(m,T,v)
1
2
   val=(polyv(v.p_sat,T,v.p_mu)/v.p_tot)*exp(-(1/(v.R*T))*f(m,T,v));
3
   end
   function val=dY_f_dm(m,T,v)
1
2
   val=(-1/(v.R*T))*Y_f(m,T,v)*df_dm(m,T,v);
3
   end
1
   function val=dY_f_dT(m,T,v)
2
   val=Y_f(m,T,v)*(polyv(v.p_sat_d1/v.p_mu(2),T,v.p_mu)/polyv(v.p_sat,T,v.p_mu)...
3
        +(1/(v.R*T^2))*f(m,T,v));
   end
4
1
   function val=d2Y_f_dm2(m,T,v)
2
   val=(-1/(v.R*T))*(dY_f_dm(m,T,v)*df_dm(m,T,v)+Y_f(m,T,v)*d2f_dm2(m,T,v));
3
   end
   function val=d2Y_f_dmdT(m,T,v)
1
2
   val=(1/(v.R*T))*df_dm(m,T,v)*((Y_f(m,T,v)/T)-dY_f_dT(m,T,v));
3
   end
   function val=d2Y_f_dT2(m,T,v)
1
2
   val=Y_f(m,T,v)*(polyv(v.p_sat_d2/v.p_mu(2)^2,T,v.p_mu)/polyv(v.p_sat,T,v.p_mu)...
3
        + (1/(v.R*T<sup>2</sup>))*f(m,T,v)*(2*polyv(v.p_sat_d1/v.p_mu(2),T,v.p_mu)/...
        polyv(v.p_sat,T,v.p_mu) + (1/(v.R*T^2))*f(m,T,v) - 2/T));
4
   end
5
1
   function y = polyv(p,x,mu)
2
   x = (x - mu(1))/mu(2);
3 y = p(1);
4
   for i = 2:length(p)
5
        y = x * y + p(i);
6
   end
```

7

end

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