A Model of Bio-Oil Evaporation for Combustion Simulation

by

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in partial fulfilment of the requirements for the degree of
Master of Applied Science (Aerospace Engineering)

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A Model of Bio-Oil Evaporation for Combustion Simulations

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Abstract

A Canadian aerospace company has modified a 2.85-MW industrial gas turbine engine to burn biomass pyrolysis oil (bio-oil). Tests show that the engine runs properly on bio-oil but has to be modified to account for corrosive and erosive properties of bio-oil and the products of its combustion. To assess the effectiveness of various coatings, to protect the gas turbine hot components from erosion and corrosion when burning bio-oil, requires knowledge of the combustion emissions. A critical aspect of emissions prediction in liquid spray combustion is the correct modelling of evaporation. A model of bio-oil droplet evaporation is proposed here. It is based on the quasi-steady evaporation theory and is applicable to multicomponent fuels such as bio-oil. The bio-oil itself and its evaporation/combustion behaviour are modelled with a semi-empirical method for multicomponent fuels, based on distillation data. The chemical composition of the liquid fraction of bio-oil is determined from experimental values found in the literature. This computationally low-cost model is suitable to implement in Computational Fluid Dynamics codes to simulate bio-oil combustion in combustion devices such as furnaces and gas turbine combustors.

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Contents

1	Introduction	1
1.1	Modelling Bio-Oil Combustion	1
1.2	Thesis Organization	2
2	Biomass Pyrolysis Liquid Fuels:	
	Review and Model	4
2.1	An Efficient Use of Biomass	4
2.2	Chemistry and Combustion Behaviour	5
2.3	Chemical Model of the Liquid Part of Bio-Oil	8
2.4	Thermo-Physical Properties	10
2.4.1	Specific Heat of Gaseous Compounds at Constant Pressure	10
2.4.2	Specific Heat of Air at Constant Pressure	11
2.4.3	Specific Heat of Liquid Compounds	11
2.4.4	Enthalpy of Vaporization	11
2.4.5	Saturation Vapour Pressure	12
2.4.6	Thermal Conductivity of Gaseous Compounds	13
3	Liquid Fuel Combustion:	
	Application to Bio-oil	14
3.1	Liquid Spray Combustion:	
	The Importance of Evaporation	14
3.2	Existing Models	16
3.3	The Analytical D-Square Model	18

3.3.1	Hypotheses	18
3.3.2	Gas Phase Analysis	20
3.4	Solution Procedure and Application to Bio-Oil	26
3.4.1	Procedure	26
3.4.2	Multicomponent Approach	27
4	Results and Discussion	27
4.1	Results	28
4.1.1	Single-Component Droplet	28
4.1.1.1	<i>Simple Case</i>	28
4.1.1.2	<i>Influence of Ambient Temperature</i>	29
4.1.1.3	<i>Influence of Forced Convection</i>	29
4.1.1.4	<i>Assessment of the D-Square Model</i>	30
4.1.2	Bio-Oil Droplet	32
4.1.2.1	<i>Simple Case</i>	32
4.1.2.2	<i>Influence of Ambient Temperature</i>	32
4.1.2.3	<i>Influence of Forced Convection</i>	34
4.1.3	Bio-Oil Droplet Diameter Laws	35
4.2	Comparison to Experimental Results and Discussion	37
4.2.1	Comparison to Experimental Results	37
4.2.2	Influence of Thermochemical Properties	39
4.2.2.1	<i>Specific Heat of Vapour Phase</i>	40
4.2.2.2	<i>Saturation Pressure</i>	42
4.2.2.3	<i>Thermal Conductivity of Vapour Phase</i>	44
4.2.2.4	<i>Enthalpy of Vaporization</i>	46
4.3	Summary	47
4.3.1	The Model	47
4.3.2	Bio-Oil Evaporation	48
5	CFD Application Capacity	49
5.1	Introduction	49
5.2	Code Analysis	49

5.3	Simulation Procedures	52
5.3.1	First Procedure	52
5.3.2	Second Procedure	53
5.4	Conclusion	54
6	Conclusions and Perspectives	55
	References	57
	Appendix	
A	Bio-Oil and Properties	65
A.1	Physico-Chemical Properties of Bio-Oil	66
A.2	Bio-Oil Distillation Curve	67
A.3	Specific Heat of Gaseous Compounds	68
	<i>A.3.1 Joback's Method</i>	68
	<i>A.3.2 Specific Heat of Air</i>	69
A.4	Specific Heat of Liquid Compounds	70
B	Droplet Evaporation	71
B.1	Measurement Techniques	72
B.2	Mathcad Program for the D-Square Procedure	73
C	Bio-Oil Evaporation	78
C.1	Evaporation of the Bio-Oil Chemical Compounds	79
D	Preliminary Investigation of CFD Application	80
D.1	Evaporation of Bio-Oil Droplets at Low Temperature	81
D.2	User-Defined Functions	86
	<i>D.2.1 Saturation Pressure as a Function of Evaporated Fraction</i>	86
	<i>D.2.2 Source Terms</i>	87
	<i>D.2.3 First Procedure</i>	89
	<i>D.2.4 Second Procedure</i>	89

List of Figures

2.1	Qualitative Profile of a Bio-Oil Distillation Curve	6
2.2	Bio-Oil Distillation Curve	7
2.3	Alkali Metal and Ca Content in Bio-Oil Aqueous Phase	8
2.4	Molecule of Levoglucosan	9
3.1	Spray Formation	15
3.2	Geometry of the Problem	20
3.3	Temperature and Mass Fraction at the Droplet Surface	21
4.1	Evaporation of an Ethanol Droplet	28
4.2	Effect of Temperature on the Evaporation of an Ethanol Droplet	29
4.3	Effect of Forced Convection on the Evaporation of an Ethanol Droplet	30
4.4	Evaporation of a Bio-Oil Droplet	32
4.5	Effect of Temperature on the Evaporation of a Bio-Oil Droplet	33
4.6	Effect of Forced Convection on the Evaporation of a Bio-Oil Droplet	34
4.7	Diameter-Power-Laws of an Evaporating 100- μm -Diameter Drop	36
4.8	Compared Evaporation of Bio-Oil, Formaldehyde and Levoglucosan	38
4.9	Burning Time of a 320- μm -Diameter Droplet at Different Temperatures	39
4.10	Heat Capacity of Acetic Acid	41
4.11	Influence of Specific Heat on Acetic Acid Evaporation	41
4.12	Influence of Specific Heat on Bio-Oil Evaporation	42
4.13	Saturation Pressure of Levoglucosan	43
4.14	Influence of Saturation Pressure on Levoglucosan Evaporation	44
4.15	Thermal Conductivity of Air, Water and Ethanol Vapour	45
4.16	Influence of Thermal Conductivity on Ethanol Evaporation	46

5.1	Verification of the Code (Ethanol Droplet Evaporation)	50
A.1	Distillation Curve of Bio-Oil and Conventional Fuels	67
C.1	D-Squared Law of the Nine Bio-Oil Compounds	79
D.1	Two-Dimensional Model	81
D.2	Contours of Bio-Oil Vapour Mass Fraction (600 K)	82
D.3	Contours of Bio-Oil Vapour Mass Fraction (800 K)	82

List of Tables

2.1	Chemical Composition of the Bio-Oil	9
4.1	Influence of Enthalpy of Vaporization on Evaporation Results	47
5.1	Verification of the Code for the Nine Compounds ($T_{\infty} = 1000$ K)	51
A.1	Physico-Chemical Properties of Bio-Oil	66
A.2	Δ Contributions of Chemical Groups	68
A.3	Coefficients for the Specific Heat of Air	69
A.4	Group Contributions in Chueh-Swanson Method	70

Nomenclature

Dimensional Parameters

C_p	heat capacity at constant pressure ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
D_d	drop diameter (m)
D	mass diffusivity ($\text{m}^2\cdot\text{s}^{-1}$)
F_D	drag force (N)
k	thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)
L_H	enthalpy of vaporization ($\text{J}\cdot\text{mol}^{-1}$)
m	mass (kg)
$\dot{m}$	mass flow rate ($\text{kg}\cdot\text{s}^{-1}$)
$\dot{m}''$	mass flow rate per unit area ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
MW	molecular weight ($\text{kg}\cdot\text{kmol}^{-1}$ or $\text{g}\cdot\text{mol}^{-1}$)
P	pressure (Pa)
P_c	critical pressure (Bar, in Equation 2.4)
P_{sat}	saturation vapour pressure (Pa)
q	heat needed to vaporize the drop surface ($\text{J}\cdot\text{mol}^{-1}$)
r	radial coordinate (m)
R	droplet radius (m) or gas constant relative to a molecule ($\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$)
R_u	universal constant of perfect gases ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
t	time (s)
T	temperature (K)
T_b	boiling temperature (K)
T_c	critical temperature (K)
T_r	reduced temperature (K)
V	velocity ($\text{m}\cdot\text{s}^{-1}$)

Non-Dimensional Parameters

b_D	mass transfer number
b_T	heat transfer number
B	b_D or b_T (applicable only when $b_D = b_T$)
C_D	drag coefficient
Le	Lewis number ($Le = Sc/Pr = \alpha/D$)
n_A	number of atoms in the molecule
Pr	Prandtl number
Sc	Schmidt number
y_f	vapour fraction
Y	mass fraction

Greek Symbols

α	thermal diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$) $\left(\alpha = \frac{k}{\rho \cdot C_p} \right)$
Δ	Joback group contributions ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) as used in Equation (2.1)
Δp	Joback group contributions for critical pressure
ρ	density ($\text{kg} \cdot \text{m}^{-3}$)
λ_{ev}	evaporation constant ($\text{m}^2 \cdot \text{s}^{-1}$)
χ	mole fraction

Subscripts

a	air
b	at boiling conditions

d	droplet
F	fuel
g	gas
l	liquid
rel	relative
R	interior of the droplet (reservoir)
W	droplet surface (wall)
0	initial condition
∞	surroundings

Acronyms

CFD	Computational Fluid Dynamics
SMD	Sauter Mean Diameter
UDF	User Defined Function

Chapter 1

Introduction

1.1 Modelling Bio-oil Combustion

Biomass-derived liquid fuels have been employed more and more in recent years to fire land-based gas turbines with an efficiency comparable to conventional fossil fuels (e.g., Diesel fuel). However, bio-oil combustion also exhibits strong disadvantages and requires a redesign or at least modifications of the existing gas turbine combustors. A major problem associated with bio-oil combustion is the emission of corrosive products such as alkali metals (principally sodium and potassium), soot (a carbonaceous product of combustion) and unburned char (carbon particles), which are likely to damage the gas turbine hot components.

Orenda Aerospace Corporation, a company based in Mississauga, Ontario, has operated an OGT 2500 gas turbine on bio-oil over the last eight years. To date, more than 13,000 litres of bio-oil have been burnt, resulting in elevated levels of corrosive ash (Fuleki, 2000). Therefore it is necessary to develop coatings specially suited for the bio-oil combustion environment. Identifying the optimum coating requires knowing the nature and quantity of the corrosive products as well as the deposition spots in the combustor. A Computational Fluid Dynamics (CFD) model of the gas turbine combustion chamber is an efficient tool to achieve this task and commercially available CFD codes have proven their capacity to carry out such a model (if not quantitatively, at least qualitatively). However, none of these codes can account for the complexity of bio-oil; thus an analytical bio-oil combustion model must be created to implement in an existing code.

Liquid fuel combustion consists of the atomization of the fuel into a spray of droplets, followed by the evaporation of these droplets and burning of the resulting fuel vapour. Once the fuel drops have been made as fine as possible (with an average diameter under 100 microns) through an effective atomization, combustion emissions

are controlled by the extent of evaporation of the droplets before they enter the flame zone. Moreover, the classical theory of diffusion flame assumes a fast chemistry and considers the combustion process as pure evaporation at flame temperature. These reasons explain why it is possible to limit this work to a study of evaporation and still get a good insight into the bio-oil combustion process.

Many droplet evaporation models exist and will be reviewed in Chapter 3. The classical approach, also called quasi-steady spherico-symmetric model with infinite kinetics has shown good results since it was first proposed in 1953 (Godsave, 1953; Spalding, 1953). It is also a computationally rapid procedure which makes it interesting for implementation in a CFD code. For each particular case of droplet evaporation, modifications or improvements to the classical theory happen to be desirable. In the case of bio-oil, the major task is to take the multicomponent nature of the fuel into account. This is achieved here through the use of a model inspired from the rapid-mixing approach and based on experimental distillation data.

Finally, it must be noted that the solid content of bio-oil is not approached in this work, although it seems to be responsible for a large part of the emissions. Among the large existing literature about bio-oil, very few analytical models have been found and these were all concerned with chemical analyses. The present work should therefore be considered as a first step for a more global bio-oil combustion model.

1.2 Thesis Organization

The existing data about bio-oil, its physical properties and combustion behaviour are reviewed in Chapter 2. The typical fuel modelled here is described with an emphasis on the thermo-chemical properties.

In Chapter 3, the basic theory of spray combustion is reviewed as well as the existing models of droplet evaporation. The classical theory, which is employed here, is explained in details, followed by its application to a multicomponent fuel such as bio-oil.

The results obtained from this new model are presented in Chapter 4, discussed and compared to against experimental data.

Finally, Chapter 5 shows the differences between these results and those of a commercial CFD code. The modifications of the code, necessary to run the bio-oil evaporation model, are explained.

Chapter 2

Biomass Pyrolysis Liquid Fuel:

Review and Model

2.1 An Efficient Use of Biomass

The predictions of an end to cheap petroleum products as well as a growing attention to the greenhouse effect have led many countries to develop the use of renewable energy. One of the most promising sources of this energy is biomass. It consists of all the plants that grow at the surface of the earth, consuming carbon dioxide (a greenhouse gas) and solar energy during their growth. This energy can be retrieved through combustion of these plants without a net increase in atmospheric carbon dioxide. For this reason, biomass is described as a “CO₂-neutral” fuel source. As a result, biomass already represents a significant part of energy supplies and an even higher share is expected in the future.

As a solid fuel, however, biomass has many of the drawbacks of coal, such as particulate emission and a variable composition, while its calorific value is generally lower by twenty percent (Wright *et al.*, 2000). A more efficient use of biomass as a fuel is to transform it into a gas through gasification or into a liquid through pyrolysis. Gasification requires using the gas on site; the ability to store liquid fuel makes pyrolysis oil particularly attractive. Pyrolysis is a thermal decomposition of solid carbonaceous fuels in the absence of air. The liquid fuel produced, called bio-oil, still contains chars, the amount of which can be reduced through the addition of small amounts of air in the pyrolysis process (Moses and Bernstein, 1996).

Bio-oil has already been burnt at the industrial scale in gas turbines (Moses and Bernstein, 1996; Ardy *et al.*, 1995; Kirk *et al.*, 2001) and more rarely in Diesel engines (Shihadeh and Hochgreb, 2000), with an efficiency comparable to classical fuels. However, the data indicate that substantial amounts of corrosive chemical

species, alkali compounds especially, are emitted during bio-oil combustion. Direct observations of these emissions through mass spectrometry techniques (French and Milne, 1994) have shown that potassium, sodium, lithium and chlorine are the most abundant corrosive species. These emissions, along with a specific combustion behaviour of bio-oil, are the main issues for combustor manufacturers.

2.2 Chemistry and Combustion Behaviour

Bio-oils, or pyrolysis oils, are complex mixtures of the degradation products of ligno-cellulose. More than four-hundred organic molecules have been reported in pyrolysis liquids (Diebold, 1999), which can be viewed as poorly defined mixtures of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans and multi-functional compounds, in widely varying proportions, depending on the raw material and the pyrolysis technique employed. The water content is most often around 25%. The solids in bio-oils are tars and chars; tars are more abundant but chars contain the inorganic compounds (calcium, lithium, iron, magnesium, manganese, zinc) that are more likely to corrode the components of the combustor exposed to the hot products. Again, the solid content varies with the type of biomass and the filtering technique.

Compared to conventional liquid fuels, such as Diesel, their main characteristics are: a high density, viscosity, surface tension and acidity, a high water and solid content (see Appendix A.1). The high viscosity and solid particle content increase the risk of occlusion of the narrow fuel paths, therefore air-assist atomizers are preferably chosen. In sprays, the average droplet size is commonly expressed as the Sauter Mean Diameter (SMD). The SMD represents the diameter of a single droplet having the same ratio of volume to surface as the entire spray. It is defined as

$$SMD = \frac{\sum nD^3}{\sum nD^2}$$

where n droplets have a diameter D . The SMD (Sauter Mean Diameter) correlations for the air-assist-types of atomizers give the SMD as an increasing function of density, viscosity and surface tension, so that the atomization air is preheated to 40-

50°C (Krumdieck and Daily, 1998); the fuel also is preheated but its injection temperature must not exceed 90°C so as to avoid any polymerization phenomenon.

Experimental analyses of bio-oil droplets have been carried out in the last years and can be found in the literature (Wornat *et al.*, 1994; D'Alessio *et al.*, 1998). It appears from these publications that the combustion process of a bio-oil droplet is roughly divided in three successive steps as the droplet temperature increases:

- 1) The droplet temperature rises up to about 100°C, its vapour starts burning in a quiescent blue flame; this corresponds to the evaporation of the lighter compounds, the most abundant of them being water.
- 2) As the droplet temperature increases gradually until around 500°C, an intense chemical activity develops: high molecular mass compounds evaporate and burn simultaneously.
- 3) Finally, the remaining fraction of the droplet expands due to internal boiling, microexplosions occur, the solid particles are expelled and burn, producing glassy-like solid residues.

The behaviour is different from that of a single-component liquid, where the droplet temperature remains nearly constant during its evaporation (except for the initial warm up period). From this information, a qualitative profile of bio-oil distillation curve can be drawn (see Figure 2.1). The vapour fraction is defined as the evaporated fraction of the initial droplet liquid.

Figure 2.1: Qualitative Profile of a Bio-Oil Distillation Curve

Kasper *et al.* (1983) and Boucher *et al.* (2000) have proved that this deduced profile is correct, as shown on Figure 2.2.

Figure 2.2: Bio-Oil Distillation Curve
(Adapted from Kasper *et al.*, 1983)

A comparison between the distillation curve of bio-oil and other classical fuels can be found in Appendix A.2 and highlights the specificity of bio-oil evaporation behaviour. In the present work, the analysis focuses on regions 1 and 2 of Figure 2.1: only the evaporation of the liquid part of bio-oil is modelled. As reported by Boucher *et al.* (2000), this liquid phase itself has a content of corrosive elements higher than the gas turbine fuel specifications (0.5-1 ppm for sodium and potassium, 0.5 ppm for calcium). On Figure 2.3, is plotted the concentration of these elements in bio-oil, the pure liquid fraction of bio-oil corresponds to the end of the abscissa (designated as 100% “aqueous” phase concentration).

Figure 2.3: Alkali Metal and Ca Content in Bio-Oil Liquid Phase
(Adapted from Boucher *et al.*, 2000)

These elements are dissolved in the liquid phase of bio-oil and released as the liquid evaporates.

It must be noted finally that the prediction and modelling of microexplosions has been studied by various authors e.g., Yamasaki *et al.* (1993), Li *et al.* (1998), Chang and Kailasanath (1998), Leite and Lage (2000), and could be added to the present model for a more complete combustion analysis.

2.3 Chemical Model of the Liquid Part of Bio-oil

Many chemical analyses of bio-oils, e.g., Bakhshi and Adjaye (1994), Oasmaa *et al.* (1997), Diebold (1999), Radlein (2002), have been used, and their results averaged, to produce a realistic composition of a typical bio-oil. Nine chemicals are retained (see Table 2.1) so that their boiling point cover the whole range of temperature found in

the distillation curves. The final result is very similar to the bio-oil composition of Dynamotive Energy Systems Corporation (Anon., 2001).

Table 2.1: Chemical Composition of the Bio-Oil

Name	Formula (molecular weight in g/mol)	Boiling Temperature (K)	Mass Fraction in Bio-Oil (%)
Formaldehyde	O=CH ₂ (30)	253.5	5.2
Glyoxal	CHO-CHO (58)	324	3.4
Ethanol	CH ₃ -CH ₂ -O-H (46)	351	5.3
Water	H ₂ O (18)	373	22.9
Formic Acid	O=CH-OH (46)	374	9.2
Hydroxyacetaldehyde	O=CH-CH ₂ -O-H (60)	383	22.5
Acetic Acid	O=COH-CH ₃ (60)	391	10.8
Acetol	CH ₃ -CO-CH ₂ -OH (74)	419	9.7
Levoglucosan	1,6-anhydro-β-D-glucopyranose (162)	659	11

The major types of molecules reported in the analyses appear in this composition, water is the most abundant compound and hydroxyacetaldehyde, the most abundant organic compound (Radlein, 2002). The low pH of bio-oils is explained here by the large fraction of acid compounds. Also, levoglucosan is the largest molecule of this composition (see Figure 2.4).

Figure 2.4: Molecule of Levoglucosan (Radlein, 2002)

It is the most abundant of the many products of cellulose (the major constituent of biomass) pyrolysis present in any bio-oil and several references can be found about

its pyrolysis (Oja and Suuberg, 1999; Nimlos *et al.*, 2002; Schwarzingner *et al.*, 2002). Finally, this artificial composition is obviously simple regarding the complexity of bio-oil but it can be modified and refined without any change in the method used here.

2.4 Thermo-Physical Properties

The thermo-physical properties of the nine bio-oil components listed in Table 2.1 could not all be found in the literature, so that they are estimated with semi-empirical methods. Most of these methods must be applied at atmospheric pressure and therefore will have to be checked before application to a gas turbine combustor environment. Following is a summary of the methods used and their references.

2.4.1 Specific Heat of Gaseous Compounds at Constant Pressure

The Joback group contribution method (Reid *et al.*, 1987) is used for glyoxal, hydroxyacetaldehyde, acetol and levoglucosan. The specific heat is given, in (J/mol.K), by:

$$C_p = \left(\sum_j n_j \Delta_a - 37.93 \right) + \left(\sum_j n_j \Delta_b - 37.93 \right) \cdot T + \left(\sum_j n_j \Delta_c - 37.93 \right) \cdot T^2 + \left(\sum_j n_j \Delta_d - 37.93 \right) \cdot T^3 \quad (2.1)$$

where n_j is the number of groups of the j th type and the Δ contributions (see Table A.3) are for the j th atomic or molecular group. The temperature T is in Kelvin. For the other compounds, polynomial expressions for the specific heat have been found in the literature (Reid *et al.*, 1987). The influence of the calculation of specific heat on the final result will be discussed in Chapter 4.

2.4.2 Specific Heat of Air at Constant Pressure

The curve-fit coefficients found in the tables by Chappell and Cockshutt (1974) give a polynomial expression at two different temperature ranges for the specific heat of air, in (J/mol·K) with T in K:

$$Cp_a = 4186.8 \cdot (C_0 + C_1T + C_2T^2 + C_3T^3 + C_4T^4) \quad (2.2)$$

The values of the coefficients C_0 , C_1 , C_2 , C_3 , C_4 are shown in Appendix A.3.

2.4.3 Specific Heat of Liquid Compounds

The Chueh-Swanson group contribution method (Reid *et al.*, 1987) is used for all compounds except water, for which a value can be readily obtained in the literature (Anon., 1997). The Chueh-Swanson method gives a constant specific heat by adding the values of each molecular group of the molecule. Therefore, the effect of temperature on the specific heat is neglected; as reported by Reid *et al.* (1987), this widely used approximation is valid for temperatures below 80% of the critical temperature and the present model neglects near-critical phenomena. A study of these phenomena can be found in the work of Faeth (1983). The values of the group contributions can be found in Appendix A.4.

2.4.4 Enthalpy of Vaporization

The variation of the enthalpy of vaporization with temperature is calculated with the Watson's relation (Reid *et al.*, 1987):

$$L_{H2} = L_{H1} \cdot \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38} \quad (2.3)$$

where subscripts 1 and 2 refer to two different reduced temperatures and the critical temperature is calculated with the relation of Klincewicz (Reid *et al.*, 1987):

$$T_c = 50.2 - 0.16 \cdot MW + 1.41 \cdot T_b$$

Taken as a reference, the value at the boiling temperature is estimated with the method of Riedel (Reid *et al.*, 1987):

$$L_H = 1.093R_u \cdot T_c \left(T_{br} \frac{\ln P_c - 1.013}{0.93 - T_{br}} \right) \text{ (J/mol)} \quad (2.4)$$

where T_{br} is the reduced boiling temperature and P_c is the critical pressure in bars, estimated with the group contribution method of Joback (Reid *et al.*, 1987):

$$P_c = (0.013 + 0.0032n_A - \sum \Delta p)^{-2}$$

where n_A is the number of atoms in the molecule and the Δp 's are the group contributions.

2.4.5 Saturation Vapour Pressure

For a perfect gas, the widely-used Clausius-Clapeyron equation (Law, 1982) gives

$$\frac{dP_{sat}}{dT} = \frac{P_{sat} L_H}{RT^2} \quad (2.5)$$

where R is the perfect gas constant relative to the molecule.

$$R = \frac{R_u}{MW}$$

After integration, Equation (2.5) becomes

$$\ln P_{sat} = -\frac{L_H}{RT} + C \quad (2.6)$$

where C is an integration constant.

Equation (2.6) can also be written as

$$P_{sat} = \exp(C) \cdot \exp\left(-\frac{L_H}{RT}\right) \quad (2.7)$$

At boiling temperature, $T = T_b$, the saturation pressure $P_{sat} = P_\infty$, therefore

$$\exp(C) = P_\infty \cdot \exp\left(\frac{L_{H,b}}{RT_b}\right) \quad (2.8)$$

and substituting Equation (2.8) into Equation (2.7) gives

$$P_{sat} = P_\infty \cdot \exp\left(\frac{L_{H,b}}{RT_b}\right) \cdot \exp\left(-\frac{L_H}{RT}\right). \quad (2.9)$$

By doing the approximation $L_H \approx L_{H,b}$, Equation (2.9) becomes

$$P_{sat} \approx P_{\infty} \cdot \exp \left[\frac{L_{H,b}}{R} \cdot \left(\frac{1}{T_b} - \frac{1}{T} \right) \right] \quad (2.10)$$

Therefore, oppositely to other correlations, the Clausius-Clapeyron equation does not necessitate finding of empirical constants and can be easily applied to the components of bio-oil. For levoglucosan, which is the slowest evaporating compound and thus has an important influence on the evaporation time, an empirical correlation (Oja and Suuberg, 1999) is also used:

$$\ln P_{sat} = 31.19 - \frac{12066}{T} \quad (2.11)$$

where T is in Kelvin. The influence of the equation chosen for P_{sat} will be discussed in Chapter 4.

2.4.6 Thermal Conductivity of Gaseous Compounds

Except for ethanol and water, no relation between thermal conductivity and temperature was found for the different molecules. Rather than using a gas kinetics law with assumed coefficients, the thermal conductivity of air is used as a first approximation. It is calculated with a Sutherland equation, the coefficients of which have been taken from Gauthier (2001):

$$k_a = 418.7 \cdot \frac{5.9776 \cdot 10^{-6} \cdot T^{\frac{3}{2}}}{T + 194.4} \quad (2.12)$$

where k_a is in W/m·K and T in K. The error resulting from this approximation is discussed in Chapter 4.

Chapter 3

Liquid Fuel Combustion:

Application to Bio-Oil

3.1 Liquid Spray Combustion: The Importance of Evaporation

Liquid spray combustion is generally regarded as a succession of three basic processes: fuel atomization, droplet evaporation and oxidation of chemical species. Although the last one is responsible for the formation of a flame and is commonly called combustion by itself, atomization and evaporation are more critical in that they control the combustion efficiency and the resulting products of the process or combustion emissions.

Atomization is the mechanism whereby a volume of liquid fuel is divided into small droplets in order to increase the surface area and enhance the rate of heat and mass transfer. Thus, “the atomization of a 1 cm diameter droplet of liquid into droplets of 100 μm diameter produces one million droplets and increases the surface area by a factor of 10,000” (Williams, 1990). Atomisers produce a sheet of liquid, which becomes unstable and breaks down to form unstable columns (or threads) of liquid that finally disintegrate into droplets (see Figure 3.1), as explained by Lord Rayleigh in 1879 (cited by Williams, 1990).

Figure 3.1: Spray Formation (Williams A., 1990)

Yet no analytical law can predict the resulting droplet diameter with accuracy and semi-empirical laws, based on dimensional analysis and calibration, must be used for each different type of atomizers.

Spray combustion may be regarded as an ensemble of burning droplets. It is even frequently studied as evaporating droplets only since, in the most common models of diffusion flames (flame sheet theory), the chemical kinetics of fuel vapour are assumed to be infinitely fast. Statistical methods are then used to describe the different sizes of droplet inside the spray. Sauter Mean Diameter and Rosin-Rammler distribution (Lefebvre, 1983) are the most common laws; they are based on empirical coefficients and thus need to be calibrated through droplet size measurements. The importance of evaporation in liquid fuel combustion can also be pointed out through a study of emissions, especially soot formation. According to Lefebvre (1983), soot formation in diffusion flames depends on the fuel and droplet size only, whereas “with a premixed flame, soot formation does not occur until the amount of available

air is reduced to around 65 percent of the stoichiometric value". This explains why a complete evaporation, and mixing, of droplets before entering the flame zone is critical to lower emission levels.

3.2 Existing Models

For a single-component fuel, the classical approach of droplet evaporation has been first achieved by Godsave (1953) and Spalding (1953). Their quasi-steady evaporation model, with spherico-symmetric geometry, is based on the simultaneous integration of the energy and species conservation equations. The droplet temperature is assumed to be uniform and constant throughout its lifetime. A law for the temperature dependence of the vapour pressure at the droplet surface (e.g., Clausius-Clapeyron equation) allows closing of the system and finding the fuel vapour mass flux as well as the droplet radius law, known as the d-square law. This method does not account for the liquid phase heat and mass transfer and is basically a gas-phase model.

When the droplet consists of more than one liquid component, the analysis becomes more complicated: the interior of the droplet must be modelled to account for the variation in temperature and composition due to transport process. For spherically symmetric vaporization, three models with different internal heat and mass transport descriptions exist.

In the diffusion-limit model (Landis and Mills, 1974), no internal motion is assumed; heat and mass transfers are achieved through conduction and diffusion. This model represents the lowest limit for transport process and best applies to highly viscous fuels. It is solved through numerical integration and thus requires a large computational effort. Although this model has proved to be accurate for multicomponent evaporation, it depends on the binary diffusivity correlations and therefore becomes inadequate for a large number of components, especially in non-classical fuels.

The rapid-mixing model (Newbold and Amundson, 1973) assumes equilibrium evaporation of the droplet, which is similar to a batch distillation. It is the highest limit for transport processes in the droplet: convective and diffusive transfers are

assumed to be so fast that the droplet temperature is uniform and temporally varying. It applies well to low-viscosity fuels and slow evaporation problems; therefore it was mostly applied to non-combustion problems (Lehtinen *et al.*, 1998).

The thin-skin model (Chen and Aggarwal, 1997) assumes a high liquid Lewis number (i.e., $\alpha \gg D$), no diffusion inside the droplet, a composition and temperature unchanged and only the surface layer of the droplet being heated. It proved to be valid at high temperature only and the final solution highly depends on the thermo-physical properties so that this model becomes inaccurate for a fuel made of radically different components.

For a more precise description of the processes inside the droplet, theories have been developed, which account for internal mixing due to vorticity induced by the shear stress at the drop surface (Sirignano and Law, 1978). The problem becomes non-spherically symmetric and mathematically complex.

A simpler way to calculate multicomponent droplet evaporation was found by Bardon and Rao (1991). The authors recognized the importance of saturation vapour pressure and enthalpy of vaporization, which determine the temperature and fuel concentration at the droplet surface in the d-squared approach. Based on distillation data (ASTM distillation curves), a numerical technique allows computing of the important variables as the evaporation proceeds. Thus, the fuel is treated as a single component with varying properties and this procedure can be easily implemented in the d-square model to account for the multicomponent nature of the fuel. However, as will be shown in Chapter 4, saturation pressure is the critical property for evaporation analysis in a cold environment, whereas specific heat is more important in a hotter atmosphere. The method of Bardon and Rao is therefore particularly suitable for cold conditions (e.g., engine start conditions).

A newer method must also be quoted here: Hallett (2000) uses continuous thermodynamics to calculate the mixture properties. The composition of the fuel is described through a probability density function (pdf), which enables to solve the problem with three variables only, which are the distribution parameters. This method proved to be fast and accurate. However, it requires having specific data (pdf) about

the fuel studied and is only applicable to fuels with a very large number of components since a statistical method is employed.

Finally, an important feature of droplet evaporating in a spray is the influence of interactions among multiple droplets. The presence of fuel in the air has an effect on the two mechanisms that control evaporation: the cool liquid fuel lowers the temperature of the spray region, thus decreasing the heat transfer to the droplets; the concentration gradient between liquid and gas is also lowered and reduces the mass transfer from the fuel to the air. Semi-empirical correlations (Leiroz and Rangel, 1995) are sometimes used but depend on each specific case. An exhaustive theoretical modelling of this phenomenon can be found in the work of Chiu (2000). This interaction effect has more influence on dense sprays (e.g., Diesel injection in cylinders) than on dilute sprays (e.g., gas turbine combustors).

In the present work, due to the lack of information about the components of bio-oil and their thermo-physical properties, the simple d-squared model is applied to an isolated droplet. The multicomponent nature of bio-oil is treated with time-varying droplet variables, as for a rapid-mixing model, and varying properties as the droplet evaporates, following the idea of Bardon and Rao.

3.3 The Analytical D-Squared Model

The classic development presented here is largely based on Catoire *et al.* (1999).

3.3.1 Hypotheses

- The geometry of the problem is strictly spherically symmetric, thus only radial gradients appear in the equations. This assumption has been confirmed by a large number of experimental results: although the droplet is not strictly spherical in those experiments, its evaporation time is consistent with the one predicted by the spherical theory (Williams F.A., 1985).
- The evaporation process is quasi-steady: steady-state conservation equations determine the mass rate leaving the droplet, after which mass conservation determines the rate of change of the droplet diameter.

- The droplet temperature is uniform and remains at its initial value T_R except on an infinitesimally thin surface layer, which evaporates at T_W . Since the liquid phase heat conduction is much faster than mass diffusion, an unrealistic consequence of this assumption is to distribute the enthalpy input required to heat the droplet all over the droplet lifetime. However, this hypothesis is frequently mentioned (Faeth, 1983) and used (Kanury, 1975) and greatly simplifies the problem, since it neglects the transient behaviour of the interior of the droplet, which should be solved through numerical integration.
- The flow is not reacting, pure evaporation is modelled. It should be noted that with the assumption of a single-step, irreversible and infinitely rapid reaction (used in the flame-sheet theory), some authors (e.g., Law, 1982; Turns, 1996) suggest that combustion can be conveniently investigated through an evaporation model with the environment set to flame temperature. The present model does not intend to describe bio-oil combustion but, as will be seen in Chapter 4, the evaporation-combustion analogy can be used to check and discuss some evaporation results with experimental combustion data.
- The transport velocities are low and the pressure is constant; there is no need for a momentum equation in the analysis.
- There is no radiation
- The droplet fully evaporates; there is no dissolved gas (microexplosions) or solid in the fuel ($Y_{FR} = 1$).
- There is no fuel vapour in the surrounding air ($Y_{F\infty} = 0$).
- The surface of the droplet is in vapour-liquid equilibrium: the gas is at its saturation vapour pressure.
- The Lewis number ($Le = Sc/Pr = \alpha/D$) equals 1. This assumption from the kinetic theory of gases is not necessary for evaporation calculations but enables to couple the energy and species equations without calculating the mass diffusivity of species and is frequently employed in evaporation calculations (Kanury, 1975; Faeth, 1977).

3.3.2 Gas Phase Analysis

The following analysis of a single-component droplet evaporation, largely inspired from Catoire *et al.* (1999) and Gauthier (2002), summarizes the approach of the d-square law model. The geometry of the problem is represented in Figure 3.2.

Figure 3.2: Geometry of the Problem

The continuity states:

$$\dot{m}_F = 4\pi \cdot r^2 \rho_g V \quad (3.1)$$

where V is the radial velocity of the gas and $\dot{m}_F$ is spatially constant. In particular,

$$\dot{m}_F = 4\pi \cdot R^2 \dot{m}''_{FW} \quad (3.2)$$

where $\dot{m}''_{FW}$ is the fuel mass flow rate per unit area at the droplet surface and R the droplet radius.

The conservation equations for energy (using Fourier's law) and species (using Fick's diffusion law), with constant density, heat capacity, conductivity and diffusivity are as follows

$$\rho_g C_p \frac{DT}{Dt} = k_g \nabla^2 T \quad (3.3)$$

and

$$\rho_g \frac{DY_F}{Dt} = \rho_g D_F \nabla^2 Y_F \quad (3.3)'$$

Following the analysis of Kanury (1975), the heat transfer equation neglects the interdiffusion (difference between fuel and air enthalpies transported by the mass diffusion flux) and the Dufour effect (heat transfer due to concentration gradient) as well as the mass transfer description does not account for the Soret effect (thermodiffusion). Representative profiles of temperature and fuel mass fraction are shown on Figure 3.3. T_R is the initial temperature of the droplet.

Figure 3.3: Temperature and Mass Fraction Profiles at the Droplet Surface (Adapted from Catoire *et al.*, 1999)

For a steady-state case, with spherically symmetric geometry, the conservation equations become

$$k_g \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \right] - \rho_g C p_g V \frac{\partial T}{\partial r} = 0 \quad (3.4)$$

and

$$\rho_g D_F \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial Y_F}{\partial r} \right) \right] - \rho_g V \frac{\partial Y_F}{\partial r} = 0 \quad (3.4)'$$

With the definition of the fuel mass flow rate in Equation (3.1), Equations (3.4) and (3.4)' become

$$k_g \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) - \frac{\dot{m}_F}{4\pi} C p_g \frac{\partial T}{\partial r} = 0 \quad (3.5)$$

and

$$\rho_g D_F \frac{\partial}{\partial r} \left(r^2 \frac{\partial Y_F}{\partial r} \right) - \frac{\dot{m}_F}{4\pi} \frac{\partial Y_F}{\partial r} = 0 \quad (3.5)'$$

Using the mass flow rate per unit surface of Equation (3.2), the conservation equations finally are

$$k_g \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) - \dot{m}''_{FW} R^2 C_{p_g} \frac{\partial T}{\partial r} = 0 \quad (3.6)$$

and

$$\rho_g D_F \frac{\partial}{\partial r} \left(r^2 \frac{\partial Y_F}{\partial r} \right) - \dot{m}''_{FW} R^2 \frac{\partial Y_F}{\partial r} = 0 \quad (3.6)'$$

The analogy between heat and mass transfer equations is used. A non-dimensional temperature b_T and normalized mass fraction b_D are defined as

$$b_T = \frac{C_{p_g} (T_\infty - T)}{L_H + C_{p_l} (T_W - T_R)} \quad (3.7)$$

and

$$b_D = \frac{Y_{F_\infty} - Y_F}{Y_{FW} - Y_{FR}} \quad (3.7)'$$

so that equations (3.6) and (3.6') become:

$$\rho_g \alpha_g \frac{\partial}{\partial r} \left(r^2 \frac{\partial b_T}{\partial r} \right) - \dot{m}''_{FW} R^2 \frac{\partial b_T}{\partial r} = 0 \quad (3.8)$$

and

$$\rho_g D_F \frac{\partial}{\partial r} \left(r^2 \frac{\partial b_D}{\partial r} \right) - \dot{m}''_{FW} R^2 \frac{\partial b_D}{\partial r} = 0 \quad (3.8)'$$

With the assumption of a Lewis number equal to one, Equations (3.8) and (3.8') become identical.

The solution procedure uses Equations (3.6) and (3.6'), which are solved directly through a double integration; the boundary conditions for the temperature are:

$$\text{at } r = R, T = T_W \quad \text{and} \quad \dot{m}''_{FW} \cdot q = k_g \left. \frac{\partial T}{\partial r} \right|_W$$

where $q = L_H + C_{p_l}(T_W - T_R)$ is defined as the enthalpy required to vaporize an infinitesimally thin layer of liquid initially at T_R .

$$\text{at } r = r_\infty, T = T_\infty$$

and for the mass fraction:

$$\text{at } r = R, Y_F = Y_{FW} \quad \text{and} \quad \dot{m}''_{FW} \cdot Y_{FR} = \dot{m}''_{FW} \cdot Y_{FW} + \left(-\rho_g D_F \frac{\partial Y_F}{\partial r} \Big|_W \right)$$

$$\text{at } r = r_\infty, Y_F = Y_{F\infty}$$

As an example, the solution for the energy equation is shown below:

Equation (3.6) is integrated once to give

$$k_g r^2 \frac{\partial T}{\partial r} - \dot{m}''_{FW} R^2 C_{p_g} T = C_1 \quad (3.9)$$

where C_1 is an integration constant determined by the application of the boundary conditions at $r = R$

$$C_1 = \dot{m}''_{FW} R^2 (q - C_{p_g} T_w) \quad (3.10)$$

Equation (3.9) then can be written

$$\frac{dT}{q + C_{p_g} (T - T_w)} = \frac{\dot{m}''_{FW} R^2}{k_g r^2} \quad (3.11)$$

which is integrated into

$$\ln(q + C_{p_g} (T - T_w)) = -\frac{\dot{m}''_{FW} R^2}{\rho_g \alpha_g} \cdot \frac{1}{r} + C_2 \quad (3.12)$$

where C_2 is the integration constant determined by the boundary condition at $r = r_\infty$

$$C_2 = \ln(q + C_{p_g} (T_\infty - T_w)) \quad (3.13)$$

By applying Equation (3.12) at $r = R$, the final solution is the expression of the fuel vapour mass flow rate at the droplet surface:

$$\dot{m}''_{FW} = \frac{\rho_g \alpha_g}{R} \ln \left(\frac{C_{p_g} (T_\infty - T_w)}{L_H + C_{p_l} (T_w - T_R)} + 1 \right)$$

or from Equation (3.7)

$$\dot{m}''_{FW} = \frac{\rho_g \alpha_g}{R} \ln (b_{TW} + 1) \quad (3.14)$$

With the same integration procedure on Equation (3.6)', and with the boundary conditions of the mass fraction, another expression for this mass flow rate is

$$\dot{m}''_{FW} = \frac{\rho_g D_F}{R} \ln \left(\frac{Y_{F\infty} - Y_{FW}}{Y_{FW} - Y_{FR}} + 1 \right)$$

or from Equation (3.7),

$$\dot{m}''_{FW} = \frac{\rho_g D_F}{R} \ln (b_{DW} + 1) \quad (3.14)'$$

b_T and b_D are respectively called the heat and mass transfer numbers.

At this point, the last two unknowns are the temperature and the fuel mass fraction at the droplet surface. A vapour-liquid equilibrium is assumed at the evaporating droplet surface, thus

$$\chi_{FW} = \frac{P_{F\text{ sat}}}{P_\infty} \quad (3.15)$$

and since

$$\chi_{FW} = \frac{Y_{FW} MW_g}{MW_F} \quad (3.16)$$

with

$$MW_g = (1 - \chi_{FW}) MW_a + \chi_{FW} MW_F \quad (3.17)$$

the mass fraction at the droplet surface is

$$Y_{FW} = \frac{1}{\left(\frac{P_\infty}{P_{\text{sat}}(T_W)} - 1 \right) \frac{MW_a}{MW_F} + 1} \quad (3.18)$$

Finally, the comparison of Equations (3.14) and (3.14)', with a Lewis number equal to unity, gives the equation to solve for T_W :

$$b_{TW} = b_{DW} = B \quad (3.19)$$

The solution procedure is an iterative one since P_{sat} and L_H are calculated at T_W and k_g and Cp_g at T_{ev} and Y_{Fev} , which are determined following the “one-third rule” of Hubbard *et al.* (1975):

$$T_{ev} = T_W + \frac{T_\infty - T_W}{3} \quad (3.20)$$

and

$$Y_{Fev} = Y_{FW} + \frac{Y_{F\infty} - Y_{FW}}{3} \quad (3.20)'$$

To obtain the d-squared law, the droplet mass change is written as

$$\frac{dm_d}{dt} = -\dot{m} \quad (3.21)$$

which is combined with Equations (3.2), (3.14) and (3.19) to give

$$\rho_l \pi \frac{D_d^2}{2} \frac{d(D_d)}{dt} = -2\pi D_d \frac{k_g}{Cp_g} \ln(B+1) \quad (3.22)$$

which can be also written

$$\frac{dD_d^2}{dt} = -\frac{8k_g}{\rho_l Cp_g} \ln(B+1) \quad (3.23)$$

The right-hand-side term in Equation (3.23) represents the evaporation rate (or evaporation constant) λ_{ev} :

$$\lambda_{ev} = \frac{8k_g}{\rho_l Cp_g} \ln(B+1) \quad (3.24)$$

so that

$$D_d^2(t) = D_{d0}^2 - \lambda_{ev} t \quad (3.25)$$

which is the final expression of the d-square law.

Throughout this analysis, the droplet was assumed to evaporate/burn in a quiescent atmosphere. The effect of the ambient air velocity can be accounted through a correlation for forced convection (Williams, 1985).

$$\frac{\lambda}{\lambda^0} = 1 + 0.276 \text{Re}_{D_d}^{\frac{1}{2}} \text{Pr}^{\frac{1}{3}} \quad (3.26)$$

where λ^0 is the evaporation constant of Equation (3.24). Since the Reynolds number depends on the drop diameter, it has to be updated when the droplet shrinks. The drag force on the droplet also depends on the diameter through its expression:

$$F_D = \frac{1}{2} C_D \rho_a V_{rel}^2 \cdot \frac{\pi D_d^2}{4} \quad (3.27)$$

where the drag coefficient is determined from an experimental result for liquid particles (Williams, 1985)

$$C_D = \frac{27}{\text{Re}^{0.84}} \quad (3.28)$$

It must be noted that, in accordance with the simplicity of the model, this correlation has been chosen for its wide usage and simplicity. However, it does not account for the variations of drag with heat and mass transfer and some newer correlations (Warnica *et al.*, 1995) could be used for better predictions. Assuming that drag is the only force applied to the droplet, a simple application of Newton's second law gives the variation of velocity due to the drag force:

$$\Delta V = \frac{F_D \Delta t}{m_d} \quad (3.29)$$

Again, the Reynolds number has to be implemented with this velocity variation, as will be explained in next part.

3.4 Solution Procedure and Application to Bio-Oil

3.4.1 Procedure

For each chemical compound, the previous analysis gives an evaporation constant, which allows drawing an evaporation curve (droplet diameter as a function of time). The procedure is the following:

- The inputs are the initial drop diameter and temperature, the ambient temperature and pressure.
- The thermochemical properties that depend on the droplet temperature and ambient pressure (see Chapter 2) are computed.
- A numerical algorithm is used to find a new value of droplet temperature, the one for which Equation (3.19) is satisfied (heat and mass transfer numbers are made equal).
- The last two steps are repeated until convergence. The final temperature is the temperature at which evaporation proceeds. It is always lower than the boiling temperature of the compound.
- The evaporation constant is computed with Equation (3.24).
- For the case of a quiescent atmosphere, the procedure stops here. In the presence of forced convection, the evaporation constant now depends on the

droplet diameter through the Reynolds number in the correlation (3.26).and the calculation procedure becomes iterative in time: a new evaporation constant has to be computed at each time step to finally obtain the evaporation time.

A flow chart summarizing this procedure and the *Mathcad* program created to solve this problem can be found in Appendix B.1 and B.2.

3.4.2 Multicomponent Approach

A last assumption must be made to model the multicomponent evaporation; comparing with the single-component case, the crucial factors to be modelled are the liquid-phase mass diffusion and volatility differentials. As suggested by Lederlin and Gauthier (2002), it is assumed that the liquid components of the fuel fully evaporate one after another, according to their boiling point (see Table 2.1). Therefore the evaporation is described as a batch-distillation process, which was common practice before the investigation of diffusion in the liquid phase by Landis and Mills (1974). This hypothesis is inspired from the idea of Bardon and Rao (1984), who treat a multicomponent fuel as a single-component one with varying properties. However, their model is based on formulas and numerical procedures (Bridgeman, 1934), which only apply to hydrocarbons. In the present case, due to the various types of molecules in bio-oil and their different thermochemical behaviour, the nature of each compound has to be treated separately. The coupling effects are neglected, at each instant the process is similar to single-component evaporation. Therefore, the interior of the droplet is idealized as a set of concentric shells arranged in order of volatility. This hypothesis is equivalent to approximating the bio-oil distillation curves presented in Chapter 2, by a stepwise curve. This model does not account for the mixing inside the droplet, thus greatly simplifying the calculations. The evaporation curve of bio-oil, diameter versus time, is finally obtained as a piecewise-linear one, the successive slopes being determined by the evaporation constant of the successively evaporating compounds. These results will now be presented and checked in the following chapter.

Chapter 4

Results and Discussion

4.1 Results

4.1.1 Single-Component Droplet

In this part, the different evaporation results obtained with the classic d-squared model for single-component droplets are shown for one of the bio-oil components. Based on these results and conclusions of various authors, an assessment of this model is developed. Ethanol is taken as an example, since its thermodynamic properties are known with fair accuracy.

4.1.1.1. Simple Case

Figure 4.1 shows the d-squared profile of a 100- μm -diameter ethanol droplet evaporating in a quiescent atmosphere at 1000 K.

Figure 4.1: Evaporation of an Ethanol Droplet

The drop temperature during evaporation is 349.5 K, which is, as expected, slightly lower than the boiling point of ethanol (351 K) and the evaporation time is about 12 ms, which is a reasonable value, as will be explained later (§ 4.1.1.4). Such a curve can be found in Appendix C.1 for each of the nine bio-oil components.

4.1.1.2 Influence of Ambient Temperature

The same droplet is studied at different ambient temperatures in Figure 4.2.

Figure 4.2: Effect of Temperature on the Evaporation of an Ethanol Droplet

As the ambient temperature increases, the vaporization time is reduced as expected and the droplet temperature approaches a limit which is the boiling temperature of ethanol (351 K).

4.1.1.3 Influence of Forced Convection

The ambient air velocity relative to the droplet is varied now and the ambient temperature is kept at 1000 K (see Figure 4.3). As explained in Chapter 3, the

procedure becomes time marching and the number of steps multiplied by the time increment gives the evaporation time.

Figure 4.3: Effect of Forced Convection on the Evaporation of an Ethanol Droplet

The heat and mass transfer processes are clearly enhanced by the relative velocity between air and droplet since the evaporation time is decreased. It is also clear that the difference with the quiescent case is obtained even at low velocities (below 10 m/s).

4.1.1.4 Assessment of the D-Squared Model

As explained in Chapter 3, the present model is about pure evaporation but for a qualitative check of the results, “understanding gained from studying droplet combustion frequently can be applied to the modelling of droplet vaporization (...) The flame now conveniently serves as a high-temperature, constant-pressure chamber within which vaporization takes place” (Law, 1982). The accuracy of the previous results can be checked with the experimental results of Godsave (1953) about a burning ethanol droplet. The article does not mention the flame temperature of the

test, therefore the adiabatic flame temperature of ethanol, calculated at 2200 K, is set as the temperature surrounding the droplet. The burning rate, calculated as an evaporation rate at flame temperature, is found to be $14.1 \cdot 10^{-3} \text{ cm}^2/\text{s}$, while the article of Godsave reports a maximum value of $8.7 \cdot 10^{-3} \text{ cm}^2/\text{s}$. The orders of magnitude are the same but the relative error is still important (47 %) and must be further explored.

This value is the superior limit of the possible error; since the adiabatic flame temperature, higher than the actual one, has been used, one expects to over-predict the burning rate. In the model itself, the main reason for the discrepancy lies in the assumption of liquid heating spread over the droplet life-time. Since the transient heating of the liquid is not taken into account, one expects to over-predict the evaporation rate. Moreover, a study of the results obtained by various authors and summarized by Kanury (1975) shows that the error in predicting burning rates with the d-squared model varies from one to fifty percent. Reasons for this inaccuracy have been suggested by Williams (1973) and Law (1982); it appears from their work that the most important source of quantitative error is the flame-sheet hypothesis of infinite chemical kinetics. In reality, the finite-rate reaction occurring at the flame causes an accumulation of unburned fuel vapour around the droplet, in violation of the conservation of mass expressed in Equation (3.1). The lower concentration gradient resulting from the fuel vapour accumulation also has a slowing effect on the evaporation rate. Finally, for burning rate purposes, an estimation of the flame temperature based on infinite kinetics leads to a higher flame temperature than the actual one. Deeper investigation about the influence of chemical kinetics can be found in the work of Tarifa (1962) and Bellan and Summerfield (1978).

In spite of these known inaccuracies, the d-square law is widely used in practical applications because it has the advantages of giving a good qualitative description of the phenomena, and being simple enough to be incorporated in the complex spray computations. The same reason justifies the assumption employed here about transient heating.

4.1.2 Bio-Oil Droplet

As explained in Chapter 3, the following graphs are obtained by calculating successively the evaporation time of each of the nine compounds.

4.1.2.1 Simple Case

The evaporation of a 100- μm -diameter bio-oil droplet, in the same conditions as previously, is shown on Figure 4.4. The evaporation curve consists of a series of successive linear segments corresponding to each of the chemical compounds.

Figure 4.4: Evaporation of a Bio-Oil Droplet

The markers on the graph show the successive evaporation of the nine chemical compounds, each one being associated with a different slope (evaporation constant). The evaporation curve is not linear anymore. The evaporation rate decreases with time, as the heavier compounds evaporate.

4.1.2.2 Influence of Ambient Temperature

Figure 4.5 shows the same droplet, evaporating at different ambient temperatures.

Figure 4.5: Effect of Temperature on the Evaporation of a Bio-Oil Droplet

Again, the evaporation becomes faster as the ambient temperature increases and the profile of the curves tends to be linear which means that the nine evaporation constants are all in the same range. In the formula of the evaporation constant (Equation 3.24), the important parameter is the heat transfer number (also called Spalding number); this number is defined mainly by the temperature difference between the droplet and the ambient (Equation 3.7). As a consequence, when the ambient temperature is far higher than the boiling point of each compound, the differences between the evaporation constant of each of the nine compounds are damped and the d-square profile approaches the one of a single-component droplet. One can also note that, at 600 K, the last-evaporating compound, levoglucosan, has not reached its boiling point (659 K). Hence, its slow evaporation rate clearly appears on the bio-oil evaporation curve.

At this point, it is interesting to further analyze the characteristics of bio-oil as a fuel for spray combustion. Bio-oil spray flame temperatures reported in different studies (Anon., 1992; Buhre and Andries, 2000) are typically between 1100 and 1300

K. As explained previously, the bio-oil evaporation curve at 1200 K can be approximated by a linear d-squared plot, which gives a representative value, for the bio-oil burning constant, of $6.45 \cdot 10^{-3} \text{ cm}^2/\text{s}$. No value about the burning constant of bio-oil has been found in the literature but if the result obtained is compared to the burning constant of Diesel fuel ($7.9 \cdot 10^{-3} \text{ cm}^2/\text{s}$), it appears that bio-oil combustion is slower than Diesel's. The relative difference is about 20 % and it must be remembered that the evaporation rate is certainly over estimated due to the hypotheses of the model: those of the d-square approach itself (discussed previously) and those of the multicomponent evaporation process, i.e., due to the high viscosity of bio-oil in particular, the different components do not evaporate sequentially as in an ideal distillation process.

4.1.2.3 Influence of Forced Convection

The influence of the relative air/droplet velocity is shown on Figure 4.6. The ambient temperature is still 1000 K. The initial relative velocities are indicated.

Figure 4.6: Effect of Forced Convection on the Evaporation of a Bio-Oil Droplet

As expected, an increase in the ambient air velocity enhances the heat and mass transfer but, unlike an increase of ambient temperature, it keeps the same ratio between the slope of each part of the curve because the change in the evaporation rate comes from a correlation (Equation 3.26) which directly corrects the final value of λ_{ev} in a quiescent atmosphere.

4.1.3 Bio-Oil Droplet Diameter Laws

Up to this point, the results obtained can describe the evaporation of a bio-oil droplet in various situations but still have a limited application to practical situations. The final purpose of this model is to implement a CFD code so as to simulate bio-oil combustion and this will be discussed in Chapter 5. In this section, a simple idea is presented, which, in the long run, might be applicable to bio-oil spray combustion models.

A regression analysis of the evaporation data is carried out and provides a power law for the diameter (see Figure 4.7).

Figure 4.7: Diameter Power-Laws of an Evaporating 100 μm -Diameter Drop

The average numerical error between the regression power-law and the analytical values is 3% at 1200 K and 1.4% at 800 K. Each power law describes the evaporation process for one set of operating conditions; a further improvement of this technique would be to achieve a three-dimensional mapping of the diameter law against temperature and initial droplet size so as to obtain “look-up” tables, ready for use in a bio-oil combustion code, which “calls” the diameter law corresponding to the instantaneous temperature and velocity of the droplet.

4.2 Comparison to Experimental Results and Discussion

4.2.1 Comparison to Experimental Results

Due to the small number of studies that have been achieved on bio-oil evaporation, it is difficult to perform a reliable validation of an analytical model. As a first check of the model, it is interesting to compare the evaporation law of bio-oil with the single-component evaporation laws obtained for the pure components that are present in the bio-oil. The graph on Figure 4.8 shows the evaporation at 1000 K of three 100- μm -diameter droplets of bio-oil, formaldehyde and levoglucosan, respectively the fastest and the slowest evaporating constituents of bio-oil.

Figure 4.8: Compared Evaporation of Bio-Oil, Formaldehyde and Levoglucosan

As expected, the bio-oil evaporation time is between those of formaldehyde and levoglucosan, which is consistent with the composition of bio-oil defined here.

In the experimental work of Wornat *et al.* (1994), the combustion of a 320- μm -diameter bio-oil droplet is investigated. As mentioned by the authors, “the biomass oils are filtered prior to the combustion experiments” to remove the char particles. The burning time obtained after the ignition delay is 132 ms. The Reynolds number of the droplets is approximately 2. The flame temperature is not measured but in a similar experiment on single bio-oil droplet combustion, D’Alessio *et al.* (1998) report a flame temperature of 1473 K. Therefore, the predictions of the model can be compared to these results, provided the liquid-phase heating term $C_{pL}(T_W - T_R)$ is set to zero since the experimental burning time is given for an ignited droplet. It is clear that, with the uncertainty about the flame temperature, this comparison is limited to a check of orders of magnitude. The model is run in the conditions explained and at different ambient temperatures (representing the flame temperature, as discussed previously). The results are shown on Figure 4.9.

Figure 4.9: Burning Time of a 320- μm -Diameter Droplet at Different Flame Temperatures

The value of 132 ms is reached for a flame temperature of about 1000 K, which is significantly lower than the one reported by D'Alessio et al. (1998) but in the same range of order of magnitude. Consistently with the analysis of the results for a single-component droplet (§ 4.1.1.4), the evaporation rate of bio-oil is largely over-predicted due to the assumption on the heating of the droplet surface. Another phenomenon expected during bio-oil heating is a chemical transformation (through pyrolysis and/or polymerization) of the components and must have an influence on the evaporation results.

4.2.2 Influence of the Thermochemical Properties

As explained in Chapter 2, an accurate calculation of the important properties, heat capacity, saturation pressure, thermal conductivity and enthalpy of vaporization, of the bio-oil components, was not always possible and approximations had to be used.

By analyzing the theory developed in Chapter 3, the respective influence of heat capacity and saturation pressure on the evaporation rate can be explained. Equations (3.8) and (3.8)' show the analogy between heat and mass transfer in the gas phase when they are described through a normalized temperature (b_T) for the heat and normalized concentration (b_D) for the mass. This mathematical formulation simply describes the physical evaporation process: heat from the ambient environment supplies the energy necessary to vaporize the liquid fuel. But depending on the ambient temperature, either the temperature or the concentration gradient is the driving force of the process. At low air temperature, evaporation is due to Stefan-flow effects, whereas, at high temperature, evaporation is due to the rapid heating of the liquid at the drop surface. Mathematically, one can observe the same thing when solving Equation (3.19) for T_w . At low ambient temperature, b_D is almost a constant function of T_w and so is b_T at high ambient temperature. Therefore, the evaporation constant in Equation (3.24) is determined by b_D in the low range of ambient temperature and by b_T in the high one, the limit between these two being around the fuel boiling point. Finally, by analyzing the formulas for b_T and b_D , Equations (3.7) and (3.18), it becomes clear that specific heat and saturation pressure, as well as enthalpy of vaporization and thermal conductivity are the most influential properties in the heat and mass transfer calculations.

4.2.2.1 Specific Heat of Vapour Phase

To assess the accuracy of the specific heat calculations, the influence of the Joback's method is checked here. As an example, the heat capacity of acetic acid is calculated with the two different methods seen in Chapter 2 (see Figure 4.10), the specific coefficients for acetic acid being taken as the reference. The resulting error on the 100- μm -acetic-acid-droplet evaporation curve at 1000 K is quite insignificant (evaporation times are 13.9 ms and 14.16 ms) as can be seen on Figure 4.11.

Figure 4.10: Heat Capacity of Acetic Acid

Figure 4.11: Influence of Specific Heat on Acetic Acid Evaporation

When the method of Joback is applied to all compounds for which coefficients of Reid (1987) were used in Chapter 2, the change in the evaporation behaviour of a bio-oil droplet at 1000 K (see Figure 4.12) is not noticeable.

Figure 4.12: Influence of Specific Heat on Bio-Oil Evaporation

This excellent result with the Joback's estimation method is also due to the fact that the heat capacity used in the calculations is a mass-averaged value for the fuel-air mixture (Reid, 1987):

$$Cp_g = Y_{Fev} Cp_F + (1 - Y_{Fev}) Cp_a$$

and the heat capacity of air is known with accuracy.

4.2.2.2 Saturation Pressure

Owing to its simplicity, as discussed in Chapter 2, the equation of Clausius-Clapeyron is used to calculate the saturation pressure of all compounds. The influence of this choice on evaporation results can be tested with levoglucosan, for which an empirical equation (Oja and Suuberg, 1999) is also computed. Figures 4.13 and 4.14

show the value of saturation pressure and its influence on the levoglucosan evaporation curve at different temperatures.

Figure 4.13: Saturation Pressure of Levoglucosan

Figure 4.14: Influence of Saturation Pressure on Levoglucosan Evaporation

In the evaporation analysis, the saturation pressure is calculated at the drop surface temperature T_w , which is always close to the boiling temperature of the fuel (659 K for levoglucosan). At this temperature, Figure 4.13 shows a large difference in the two calculated values of P_{sat} . In accordance with the previous analysis, the effect of this difference on the evaporation results decreases as the ambient temperature grows (see Figure 4.14) and becomes negligible as from 1000 K. Hence, the choice of the saturation pressure calculation method will not influence the model when applied at a classical combustion regime. For cold conditions (start of engine), more reliable saturation pressure data are needed. (N.B. In industrial bio-oil applications, the engine is always started with a conventional fuel before being fed with bio-oil.)

4.2.2.3 Thermal Conductivity of Vapour Phase

Thermal conductivity is another major property in the calculation of the evaporation constant, as Equation (3.24) shows. The conductivity of air is chosen for all

compounds as a first approximation because the correlations for mixture conductivity are complex and temperature-conductivity correlations are difficult to find, especially for non common molecules as those of bio-oil. Empirical polynomial expressions were found for water and ethanol (Reid *et al.*, 1987) and are plotted on Figure 4.15 with the conductivity of air, obtained from a Sutherland equation.

Figure 4.15: Thermal Conductivity of Air, Water and Ethanol Vapour

In the evaporation analysis, the thermal conductivity is calculated at the temperature given by the one-third rule (which is close to the boiling point). At the boiling point of water (373 K) and ethanol (351 K), the relative difference between the conductivity of air and these two compounds is quite large (28.6 % for water and 44% for ethanol). Figure 4.16 shows the evaporation of ethanol computed with the conductivity of air and a mole-fraction averaged of the conductivities of ethanol and air (this method, which is not recognized as valid, is only shown here as an approximate example for comparisons and not used in the model itself).

Figure 4.16: Influence of Thermal Conductivity on Ethanol Evaporation

The error increases with the ambient temperature because, at high temperature, the higher fuel mole fraction at the droplet surface triggers a more important relative weight of the fuel conductivity in the calculation of the mixture conductivity. Therefore, the approximation used to calculate the thermal conductivity may be a cause of significant error.

4.2.2.4 Enthalpy of Vaporization

The last property checked here is the enthalpy of vaporization at boiling temperature L_{Hb} . Intuitively and as shown by the formula of b_T , this property must have a significant influence on the evaporation results. As explained in Chapter 2, the enthalpy of vaporization at the boiling point was calculated with the empirical formula of Riedel and its variations with the Watson relation. The formula of Riedel can be checked here. For formic and acetic acid, water and ethanol, other values were found in the literature (Anon., 1997) and used to calculate the evaporation constant of these components in two different manners (see Table 4.1).

Table 4.1: Influence of Enthalpy of Vaporization on Evaporation Results (100- μ m-diameter droplet at 1000 K)

Chemical Compound	Evaporation Constant in m^2/s (L_H from the formula of Riedel)	Evaporation Constant in m^2/s (L_H from the literature)	Relative Error
Ethanol	$8.338 \cdot 10^{-7}$	$8.413 \cdot 10^{-7}$	0.9 %
Water	$7.703 \cdot 10^{-7}$	$7.777 \cdot 10^{-7}$	0.9 %
Formic Acid	$9.335 \cdot 10^{-7}$	$7.826 \cdot 10^{-7}$	17 %
Acetic Acid	$7.06 \cdot 10^{-7}$	$7.93 \cdot 10^{-7}$	5.8 %

The error is globally acceptable, but seems to be larger for acids. It is difficult to estimate the discrepancy introduced by the formula of Riedel, since it does not have the same influence (over or under-prediction) on all compounds. Once again, specific values for each component would improve the accuracy of the model.

4.3 Summary

4.3.1 The Model

The present model can predict the evaporation behaviour of the liquid phase of a bio-oil droplet with the limitations stated previously. The evaporation time is obtained and the respective influence of all compounds can be analyzed. These results can be expressed through diameter laws obtained from a regression analysis. Qualitatively, the results are in accordance with the experimental observations from the literature. The numerical values are of the same order of magnitude as the results from these experimental studies but the model clearly over-estimates the evaporation rate. This is mainly due to the assumption of a liquid phase heating spread over the droplet lifetime. Another source of error was thought to be the accuracy of the correlations used to estimate the thermochemical properties. The results have shown that the error

induced by these estimations is globally acceptable in the conditions of gas turbine combustion, except for the thermal conductivity of gaseous species, the accuracy of which decreases at high ambient temperatures. Finally the chemical phenomena, which occur in the liquid residue during evaporation, are not accounted for and need further chemical analysis.

4.3.2 Bio-Oil Evaporation

The results presented in this chapter give an insight into the characteristics of bio-oil fuel. The global bio-oil burning rate is slower than the one of conventional fuels such as Diesel and faster than the rate of the heavier compounds such as levoglucosan. An evaporating bio-oil droplet does not follow a diameter-square law, like a single-component droplet, but a diameter-power law. At high ambient temperature, all compounds tend to evaporate at a similar rate and the bio-oil evaporation law approaches a d -squared shape. The range of boiling points of the bio-oil compounds is large (more than 400 K), therefore the evaporation rate at low temperature can be significantly decreased when some compounds do not reach their boiling point. Finally, remembering that a strict evaporation order of the nine compounds was assumed, it is clear that the actual mixing of the liquid inside the droplet may cause the hot light compounds to be forced out of the droplet through a microexplosion phenomenon.

Chapter 5

CFD Application Capacity

5.1 Introduction

In this part are proposed different procedures to apply the bio-oil evaporation model, using the commercially-available CFD program Fluent 6. It is a general-purpose CFD software, based on the finite-volume discretization method. As a consequence of their ability to treat various types of fluid problems, these kinds of codes have theoretical and practical limitations when used for very specific or unusual case studies, and need testing and modifications. For that reason, the first part of this chapter consists of an analysis of the specific software's treatment of droplet evaporation. It will be seen that the classical user inputs do not allow modelling bio-oil evaporation accurately and that a more complex numerical adaptation of the model is required.

5.2 Code Analysis

For a low ambient temperature, around or below the fuel boiling point, the code's droplet vaporization law is governed by concentration gradient diffusion, as in a Stefan-flow problem. The concentration of vapour at the droplet surface is calculated through liquid-vapour equilibrium, therefore the saturation pressure determines the driving force of the process. As discussed in Chapter 4, the result is similar with the present model at low temperature, where the mass transfer number b_D determines the evaporation constant.

For a hot environment ($T_\infty > T_B$), when the droplet has reached its boiling temperature, the software applies a boiling rate equation is applied to the droplet diameter:

$$\frac{dD_d}{dt} = -\frac{4k_g}{\rho_l C p_g D_d} \ln \left(1 + \frac{C p_g (T_\infty - T_w)}{L_H} \right) \quad (5.1)$$

which is equivalent to

$$\frac{dD_d^2}{dt} = -\frac{8k_g}{\rho_l C p_g} \ln \left(1 + \frac{C p_g (T_\infty - T_w)}{L_{Hb}} \right) \quad (5.2)$$

For a droplet that has reached its boiling point (after the transient heating period) Equation (5.2) is similar to Equation (3.23) with $B = b_T$, which is the case at high temperature. However, the major difference stands in the boiling droplet temperature. While in the d-squared approach, the drop temperature is fixed through a heat and mass transfer balance and is always below the boiling point, the code assumes an independent drop temperature, fixed at the boiling point. It is therefore necessary to check the difference in the final results, induced by this approximation. As an example, the evaporation of an ethanol droplet is computed with the two methods in Figure 5.1.

Figure 5.1: Verification of the Code (Ethanol Droplet Evaporation)

Since, in the d-squared analysis, the droplet surface temperature is always lower than the boiling point, the evaporation rate is overestimated by the software, which

sets the droplet temperature to the boiling point T_b . This discrepancy tends to disappear at higher temperature, when the fuel temperature almost reaches its boiling point. Table 5.1 shows the evaporation constant of the nine bio-oil compounds at 1000 K, calculated with the two methods.

Table 5.1: Verification of the Code for the Nine Compounds ($T_\infty = 1000$)

Chemical Species	Evaporation Constant from the d-square approach (m^2/s)	Evaporation Constant from FLUENT's approach (m^2/s)	Relative Error
Formaldehyde	$11.41 \cdot 10^{-7}$	$11.36 \cdot 10^{-7}$	0.4 %
Glyoxal	$6.71 \cdot 10^{-7}$	$6.66 \cdot 10^{-7}$	0.8 %
Ethanol	$8.34 \cdot 10^{-7}$	$8.24 \cdot 10^{-7}$	1.2 %
Water	$7.7 \cdot 10^{-7}$	$7.62 \cdot 10^{-7}$	1 %
Formic acid	$6.77 \cdot 10^{-7}$	$6.7 \cdot 10^{-7}$	1 %
Hydroxy-acetaldehyde	$5.24 \cdot 10^{-7}$	$5.16 \cdot 10^{-7}$	1.5 %
Acetic acid	$7.06 \cdot 10^{-7}$	$6.96 \cdot 10^{-7}$	1.7 %
Acetol	$5.87 \cdot 10^{-7}$	$5.75 \cdot 10^{-7}$	2.1 %
Levogluconan	$3.48 \cdot 10^{-7}$	$3.15 \cdot 10^{-7}$	10 %

The results are globally good; the error logically increases with the boiling temperature of the species. The important error for levogluconan comes from the large difference between its boiling point and drop surface temperature, which is actually underestimated because of the poor accuracy of levogluconan properties. The accuracy level of the software's procedure is therefore acceptable, considering the approximations that had to be done in the present model.

From these observations, a first possibility to simulate bio-oil evaporation is to apply Fluent's boiling law to a single-component fuel with varying properties (saturation pressure, specific heat and heat of vaporization), following the method of Bardon and Rao (1991). As evaporation proceeds, the properties used in the

calculations are those of the chemical compound currently evaporating, therefore they must be defined as stepwise functions of the percentage of liquid evaporated. This can not be done for C_p and L_H with Fluent; these two properties are defined as functions of temperature only and can not be reached through a user-defined-function. Moreover, once activated, the boiling law fixes the droplet temperature at the specified boiling point and keeps it constant until complete evaporation. Hence, no sort of mixing can be modelled inside the droplet, which is a serious limitation for multicomponent evaporation simulations. Such a method could still be applied at low temperature, where saturation pressure is determining the evaporation rate and droplet heating is taken into account through a heat transfer balance between the continuous and discrete phase. As seen before, this does not have practical applications for bio-oil combustion but could be used for a specific study of bio-oil evaporation. Some results of such a two-dimensional model with single droplet injection are presented in Appendix D.1 to illustrate the feasibility of the method.

5.3 Simulation Procedures

For the practical reasons previously explained, the software's boiling procedure can not be employed and user-defined-functions (UDF) have to be employed to model multicomponent evaporation. These functions are written in C and compiled by the software, which implements them in the code. To access the code parameters (flow variables, physical properties, geometry...), specific variable types are defined in a C library included in the code itself. Two methods of programming the evaporation model are presented.

5.3.1 First Procedure

The idea is to use the simple diameter-power laws derived in Chapter 4 (§ 4.1.3). Fluent's boiling law is deactivated and replaced by the diameter law found previously for 100- μm -diameter bio-oil droplets evaporating at an ambient temperature of 1200 K:

$$D(t) = -1.34t^{1.63} + 96.7 \quad (5.3)$$

As seen before, these laws apply to a specific set of operating conditions (initial droplet diameter, ambient temperature and velocity), therefore, in spray calculations (with varying temperature and velocity), a set of these power laws at different conditions should be employed. Moreover the diameter of all droplets must be the same, which is achieved through the use of one of the classical Fluent's injection types (single drop, group or cone). There is no possibility of using a droplet size distribution or run this simulation at different ambient temperatures, unless the coefficients for the power law are calculated for a representative number of conditions. The heat and mass transfer to the droplet do not have to be modelled since they are already taken into account in the diameter law. However, a source-term UDF must be created, which models the mass and energy transfer from the fuel into the ambient air. In this case, the energy term is negative and equal to the mass lost by the droplet, multiplied by the heat of vaporization (at boiling temperature) of the compound evaporating. Hence, a stepwise definition of T_B and L_H , varying with the droplet evaporated fraction, must be created. Assuming the validity of the diameter law, the only approximation in this method comes from the calculation of L_H at boiling temperature, which was discussed previously. The necessary UDF's for this simulation can be found in Appendix D.2.

5.3.2 Second Procedure

For a more global simulation, the original d-squared law can be used:

$$D_d^2(t) = D_{d0}^2 - \left[\frac{8k_g}{\rho_l C p_g} \ln(B+1) \right] \cdot t \quad (5.4)$$

along with the definition of B as the heat transfer number:

$$B = \frac{C p_g (T - T_\infty)}{L_H} \quad (5.5)$$

As before, a stepwise definition of all properties (T_B , $C p_g$, L_H , k_g , ρ_l) must be entered. For the specific heat of the gaseous mixture ($C p_g$), a mass weighted average value must be used, which requires the fuel mass fraction at the drop surface. This one is calculated with Equation (3.18). The same source term UDF as before must be created and the restrictions associated with the previous case disappear: this

simulation can be run at various ambient temperatures (higher than the boiling point of all compounds) and all types of atomizers provided by Fluent can be used. The same approximation about boiling temperature remains. The UDF corresponding to this method can be found in Appendix D.2.

5.4 Conclusion

The basic foundations of a simulation of bio-oil evaporation using Fluent have been set. A study of the code's physical analysis has provided practical considerations, intended to respect the analytical model when using the software. The last method proposed here has the theoretical ability to model bio-oil evaporation in any practical case. For the technical implementation itself, a thorough description of the procedure can be found in Fluent's user's manual (Anon., 2002).

Chapter 6

Conclusions and Perspectives

An evaporation model for bio-oil droplets is proposed. It is based on the quasi-steady theory of vaporization with a spherically symmetric geometry. Char burnout is not included; only the liquid fraction of bio-oil is accounted for and its composition is estimated from different experimental studies found in the literature and can be easily refined. The transient heating of the droplet is not modelled, it is assumed to be spread over the droplet lifetime.

Based on experimental bio-oil distillation curves, the main hypothesis to model multicomponent evaporation assumes a full evaporation of the successive chemical compounds, following their boiling temperature and without coupling effect. The thermo-physical properties of the chemicals are estimated through the use of semi-empirical correlations.

The result is an evaporation curve for any droplet size, ambient temperature and air/droplet relative velocity. This curve, after regression analysis, gives a diameter law, easy to implement in a CFD code.

The results show a good qualitative agreement with the few experimental results found in the literature and an encouraging quantitative accuracy. The characteristics of bio-oil shown by the model are:

- a lower burning rate than a conventional fuel
- a diameter power law for an evaporating droplet, unlike the diameter-square law of single component liquids

More specifically, the evaporation of bio-oil predicted by the model, at low temperature ($T \leq 600$ K), exhibits a strongly varying rate due to the successive evaporation of the different compounds. Assuming a non-perfect mixing, when a high-volatility compound is in the interior of the droplet, the cause of the experimentally observed microexplosions lies in these different evaporation rates. At

high temperature however, the evaporation of a bio-oil droplet has been found to approach a diameter-squared profile.

Among the possible improvements of this model, the most necessary would be a detailed analysis of the interior of the droplet. A proper modelling of the transient heating period would diminish the over-prediction of the evaporation rate. Important too are the chemical processes occurring in the liquid fuel during heat-up and vaporization: at high temperature, polymerization and pyrolysis of species that have not evaporated are known to affect the composition of the fuel and thus to modify the evaporation characteristics. Also, specific values for the important properties of the components of bio-oil would improve the accuracy of the results. To apply the model in a realistic gas turbine combustion simulation, correlations of these properties with the ambient pressure are essential.

Finally, it is believed that, with the modelling assumptions kept in mind, this evaporation model, combined with a char combustion model and a description of the chemical kinetics, could become a powerful tool for the prediction of bio-oil combustion emissions.

References

Anon., *Preliminary Pilot-Scale Combustion Evaluation of ENSYN RTP Oils*, Canada Centre for Mineral and Energy Technology (CANMET), Energy, Mines and Resources Canada, June 1992

Anon., *CRC Handbook of Chemistry and Physics*, 78th Edition, CRC Press, 1997

Anon., *Fast Pyrolysis of Bagasse to Produce Biooil Fuel for Power Generation*, Dynamotive Energy Systems Corporation, 2001, retrieved from www.dynamotive.com/biooil/technicalpapers/2001SugarConferencePaper.pdf (Nov. 2002)

Anon., FLUENT Version 6.0, *User's Guide*, FLUENT Incorporated, April 2002, retrieved from www.fluentusers.com (Nov.2002)

Ardy P.L., Barbucci P., Benelli G., Rossi C. and Zanforlin S., *Development of Gas Turbine Combustor fed with Bio-Fuel Oil*, Proceedings of the 2nd Biomass Conference of the Americas, Portland, Oregon, pp 429-438, 1995

Bakhshi N.N. and Adjaye J.D., *Properties and Characteristics of ENSYN Bio-Oil*, Catalysis & Chemical Reaction Engineering Laboratory, University of Saskatchewan, Sept. 1994

Bardon M.F. and Rao V.K., *Brief Communication*, Combustion and Flame, Vol. 84, p 427, 1991

Bardon M.F. and Rao V.K., *Calculation of Gasoline Volatility*, Journal of the Institute of Energy, Vol. 57, N432, p 343, Sept.1984

Bellan J. and Summerfield M., *Theoretical Examination of Assumptions Commonly Used for the Gas Phase Surrounding a Burning Droplet*, Combustion and Flame, Vol. 33, pp 107-122, 1978

Boucher M.E., Chaala A. and Roy C., *Bio-oils Obtained by Vacuum Pyrolysis of Softwood Bark as a Liquid Fuel for Gas Turbines. Part1: Properties of Bio-Oils and its Blends with Methanol and a Pyrolytic Aqueous Phase*, Biomass and Bioenergy, Vol. 19, N5, p 337, 2000

Bridgeman O.C., *Equilibrium Volatility of Motor Fuels from the Standpoint of their Use in Internal Combustion Engines*, Research Paper RP694, Journal of Research of the National Bureau of Standards, Vol. 13, July 1934

Buhre B.J.P. and Andries J., *Biomass-Based, Small-Scale, Distributed Generation of Electricity and Heat Using Integrated Gas Turbine-Fuel Cell Systems*, Paper 2000-GT-22, Paper Presented at the International Gas Turbine & Aeroengine Congress & Exhibition, Munich, May 8-11, 2000

Catoire F., Gauthier J.E.D., Bardon M.F. and Benaissa A., *Quasi-Steady-State Evaporation Model for Real Multi-Component Fuel Droplets*, Journal of the Institute of Energy, Vol. 72, N493, p 134, 1999

Chang J. and Kailasanath K., *Dynamics and Microexplosion of High Energy Fuels Injected into a Combustor*, Combustion Science and Technology, Vol. 137, N1, p 217, 1998

Chappell M.S. and Cockshutt E.P., *Gas Turbine Cycle Calculations: Thermodynamic Data Tables for Air and Combustion Products for Three Systems of Units*, Division of Mechanical Engineering, National Research Council Canada, Ottawa, August 1974

Chen G. and Aggarwal S.K., *Experimental Study of Pure and Multicomponent Fuel Droplet Evaporation in a Heated Air Flow*, Atomization and Sprays, Vol. 7, p 317, 1997

Chiu H.H., *Advances and Challenges in Droplet and Spray Combustion*. Progress in Energy and Combustion Science, Vol. 26, pp 381-416, 2000

D'Alessio J., Lazzaro M., Massoli P. and Moccia V., *Thermo-Optical Investigation of Burning Biomass Pyrolysis Oil Droplets*, 27th Symposium (Int.) on Combustion, The Combustion Institute, p 1915, 1998

Diebold, J.P., *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils*, Aug.26, 1999, retrieved from www.eren.doe.gov/biopower/bplib/library/reviewchemicalphysical.pdf (Nov. 2002)

Faeth G.M., *Current Status of Droplet and Liquid Combustion*, Progress in Energy and Combustion Science, Vol. 3, pp 191-224, 1977

Faeth G.M., *Evaporation and Combustion of Sprays*, Progress in Energy and Combustion Science, Vol. 9, pp 1-76, 1983

French R.J. and Milne T.A., *Vapor Phase Release of Alkali Species in the Combustion of Biomass Pyrolysis Oils*, Biomass and Bioenergy, Vol. 7, N1-6, pp. 315-325, 1994

Fuleki D., *Private Communication on OGT 2500 Bio-Oil Tests*, Ottawa, Canada, Aug. 2000

Gauthier J.E.D., *Program for the Calculation of Water Droplet Evaporation in Air*, Nov. 2001

Gauthier J.E.D., *Droplet Evaporation and Combustion*, Lecture Notes of the *Gas Turbine Combustion* Graduate Course Given at Carleton University in Winter Term 2002

Godsave G.A.E., *Studies of the Combustion of Drops in a Fuel Spray-The Burning of Single Drops of Fuel*, Fourth Symposium (Int.) On Combustion, The Combustion Institute, Pittsburgh, PA, pp 847-864, 1953

Hallett W.L.H., *A Simple Model for the Vaporization of Droplets with Large Numbers of Components*, *Combustion and Flame*, Vol.121, N1-2, p 334, 2000

Hubbard G.L., Denny V.E. and Mills A.F., *Droplet Evaporation: Effects of Transient and Variable Properties*, *International Journal of Heat and Mass Transfer*, Vol. 18, pp 1003-1008, 1975

Kanury A.H., *Introduction to Combustion Phenomena*, Gordon and Breach, New York, 1975

Kasper J.M., Jasas G.B. and Trauth R.L., *Use of Pyrolysis-Derived Fuel in a Gas Turbine Engine*, ASME Paper 83-GT-96, 1983

Kirk D.W., Li Z.R., Fuleki D. and Patnaik P.C., *Materials Compatibility with Pyrolysis Biofuel*, Proceedings of ASME Turbo Expo, New Orleans, Louisiana, 2001

Krumdieck S.P. and Daily J.W., *Evaluating the feasibility of Biomass Pyrolysis Oil for Spray Combustion Applications*, *Combustion Science and Technology*, Vol. 134, pp 351-365, 1998

Landis R.B. and Mills A.F., *Effects of Internal Resistance on the Vaporization of Binary Droplets*, Fifth Int. Heat Transfer Conf., Tokyo, Japan, Paper B7-9, 1974

Law C.K., *Recent Advances in Droplet Vaporization and Combustion*, Progress in Energy and Combustion Science, Vol. 8, pp 171-201, 1982

Lederlin T. and Gauthier J.E.D., *An Evaporation Model for Bio-Oil Fuel*, Paper Presented at the “Expert Meeting on Pyrolysis and Gasification of Biomass and Waste”, Strasbourg, France, October 2002

Lefebvre A.H., *Gas Turbine Combustion*, Taylor & Francis, 1983

Lehtinen K.E., Kulmala M., Vesala T. and Jokiniemi J.K., *Analytical Methods to Calculate Condensation Rates of a Multicomponent Droplet*, Journal of Aerosol Science, Vol.29, N9, p 1035, 1998

Leiroz A.J.K. and Rangel R.H., *Interaction Effects During Droplet-Stream Combustion*, 8th International Symposium on Transport Phenomena (ISTP-8) in Combustion, San Francisco, USA, July 1995.

Leite L.F.T. and Lage P.L.C., *Modeling of Emulsion Droplet Vaporization and Combustion Including Microexplosion Analysis*, Combustion Science and Technology, Vol.157, p 213, 2000

Li T., Zhu D.L. and Law C.K., *Droplet Combustion, Microexplosion, and Sooting Characteristics of Several Energetic Liquid Propellants*, Journal of Propulsion and Power, Vol.14, N1, p 45, 1998

Moses C.A. and Bernstein H.L., *Fuel-Specification Considerations for Biomass Pyrolysis Liquids to Be Used in Stationnary Gas Turbines*, Presented at the International Gas Turbine and Aeroengine Congress & Exhibition, Birmingham, UK, June 1996

Newbold F.R. and Amundson N.R., *A Model for Evaporation of a Multicomponent Droplet*, AIChE Journal, Vol.19, N1, p 22, 1973

Nimlos M.R. and Evans R.J., *Levoglucosan Pyrolysis*, Fuel Chemistry Division Preprints, Vol. 47(1), p 393, 2002

Oasmaa A., Leppamäki E., Koponen P., Levander J. and Tapola E., *Physical Characterization of Biomass-Based Pyrolysis Liquids, Application of Standard Fuel Oil Analyses*, VTT Publications, Technical Research Centre of Finland, ESPOO 1997

Oja V. and Suuberg E.M., *Vapor Pressures and Enthalpies of Sublimation of D-Glucose, D-Xylose, Cellobiose, and Levoglucosan*, Journal of Chemical Engineering Data, Vol. 44, pp26-29, 1999

Radlein D., *Chemicals and Materials from Bio-Oil-Part 1*, Transforms International Ltd., retrieved from www.pyne.co.uk/pdf/apps1a.pdf (Nov. 2002)

Reid R.C., Prausnitz J.M. and Poling B.E., *The Properties of Gases and Liquids*, 4th Edition, McGraw Hill, New York, 1987

Schwarzinger C., Tanczos I. and Schmidt H., *Levoglucosan, Cellobiose and their Acetates as Model Compounds for the Thermally Assisted Hydrolysis and Methylation of Cellulose and Cellulose Acetate*, Journal of Analytical and Applied Pyrolysis, Vol. 62, pp179-196, 2002

Shihadeh A. and Hochgreb S., *Diesel Engine Combustion of Biomass Pyrolysis Oils*, Energy and Fuels, Vol. 14, pp 260-274, 2000

Sirignano W.A. and Law C.K., *Transient Heating and Liquid-Phase Mass Diffusion in Fuel Droplet Vaporization*, Evaporation-Combustion of Fuels, American Chemical Society, p 3, 1978

Spalding D.B., *The Combustion of Liquid Fuels*, Fourth Symposium (Int.) On Combustion, The Combustion Institute, Pittsburgh, PA, pp 847-864, 1953

Tarifa C.S., *On the Influence of Chemical Kinetics on the Combustion of Fuel Droplets*, Congrès International des Machines à Combustion, Paper B9, Copenhagen, 1962

Turns S.R., *An Introduction to Combustion, Concepts and Applications*, MacGraw-Hill, Inc., 1996

Warnica W.D., Renksizbulut M. and Strong A.B., *Drag Coefficients of Spherical Liquid Droplets*, Experiments in Fluids, Vol. 18, N. 4, pp 258-277, 1995

Williams A., *Combustion of Liquid Fuel Sprays*, Butterworth, 1990

Williams A., *Combustion of Droplets of Liquid Fuels: A Review*, Combustion and Flame, Vol. 31, pp 1-31, 1973

Williams F.A., *Combustion Theory*, 2nd Edition, Benjamin/Cummings, 1985

Wornat M.J., Porter B.G., and Yang N.Y.C., *Single Droplet Combustion of Biomass Pyrolysis Oils*, Preprints from Energy and Fuels 8, p 1131, 1994

Wright I.G., Leyens C., and Pint B.A., *An Analysis of the Potential for Deposition, Erosion, or Corrosion in Gas Turbines Fueled by the Products of Biomass Gasification or Combustion*, Paper 2000-GT-19, Paper Presented at the International Gas Turbine & Aeroengine Congress & Exhibition, Munich, Germany, May 2000

Yamasaki Hiroshi, Tsue Mitsuhiro, Kadota Toshikazu, *Evaporation and Combustion of Emulsified Fuel (Onset of Microexplosion)*, JSME International Journal-Series B, Vol.36, N4, 1993

Appendix A

Bio-Oil and Properties

A.1 Physico-Chemical Properties of Bio-Oil

Table A.1: Physico-Chemical Properties of Bio-Oil
(Adapted from Shihadeh and Hochgreb, 2000)

Manufacturer batch number	NREL M2-10	ENSYN RTP 15TPD	Diesel fuel
Water content (wt%)	16.9	26.3	
Viscosity at 30 °C (cSt)	80	96	
Surface tension at 20 °C (mN/m)	34.7	40.0	29.3
Specific gravity at 20 °C	1.2	1.2	0.84
LHV (MJ/kg)	17.0	16.3	44
LHV stoichiometric mixture (MJ/kg)	2.28	2.46	2.79
A/F stoichiometric	6.45	5.62	14.5
Whole oil ultimate analysis (wt % dry)			
C	58.25	57.95	87
H	7.4	7.23	13
N	1.52	1.64	
O	32.83	33.19	

A.2 Bio-Oil Distillation Curve

Figure A.1: Distillation Curve of Bio-Oil and Conventional Fuels (Moses and Bernstein, 1996)

A.3 Specific Heat of Gaseous Compounds

A.3.1 Joback's Method

Table A.2: Δ Contributions of Chemical Groups
(Reid *et al.*, 1987)

	Δ_H	Δ_G	Δ_a	Δ_b	Δ_c	Δ_d
	kJ/mol	kJ/mol	 J/mol K	 J/mol K	 J/mol K	 J/mol K
Non-ring increments						
-CH ₃	-76.45	-43.96	1.95E+1	-8.08E-3	1.53E-4	-9.67E-8
>CH ₂	-20.64	8.42	-9.09E-1	9.50E-2	-5.44E-5	1.19E-8
>CH-	29.89	58.36	-2.30E+1	2.04E-1	-2.65E-4	1.20E-7
>C<	82.23	116.02	-6.62E+1	4.27E-1	-6.41E-4	3.01E-7
=CH ₂	-9.63	3.77	2.36E+1	-3.81E-2	1.72E-4	-1.03E-7
=CH-	37.97	48.53	-8.00	1.05E-1	-9.63E-5	3.56E-8
=C<	83.99	92.36	-2.81E+1	2.08E-1	-3.06E-4	1.46E-7
=C=	142.14	136.70	2.74E+1	-5.57E-2	1.01E-4	-5.02E-8
≡CH	79.30	77.71	2.45E+1	-2.71E-2	1.11E-4	-6.78E-8
≡C-	115.51	109.82	7.87	2.01E-2	-8.33E-6	1.39E-9
Ring increments						
-CH ₂ -	-26.80	-3.68	-6.03	8.54E-2	-8.00E-6	-1.80E-8
>CH-	8.67	40.99	-2.05E+1	1.62E-1	-1.60E-4	6.24E-8
>C<	79.72	87.88	-9.09E+1	5.57E-1	-9.00E-4	4.69E-7
=CH-	2.09	11.30	-2.14	5.74E-2	-1.64E-6	-1.59E-8
=C<	46.43	54.05	-8.25	1.01E-1	-1.42E-4	6.78E-8
Halogen increments						
-F	-251.92	-247.19	2.65E+1	-9.13E-2	1.91E-4	-1.03E-7
-Cl	-71.55	-64.31	3.33E+1	-9.63E-2	1.87E-4	-9.96E-8
-Br	-29.48	-38.06	2.86E+1	-6.49E-2	1.36E-4	-7.45E-8
-I	21.06	5.74	3.21E+1	-6.41E-2	1.26E-4	-6.87E-8
Oxygen increments						
-OH (alcohol)	-208.04	-189.20	2.57E+1	-6.91E-2	1.77E-4	-9.88E-8
-OH (phenol)	-221.65	-197.37	-2.81	1.11E-1	-1.16E-4	4.94E-8
-O- (nonring)	-132.22	-105.00	2.55E+1	-6.32E-2	1.11E-4	-5.48E-8
-O- (ring)	-138.16	-98.22	1.22E+1	-1.26E-2	6.03E-5	-3.86E-8
>C=O (nonring)	-133.22	-120.50	6.45	-6.70E-2	-3.57E-5	2.86E-9
>C=O (ring)	-164.50	-126.27	3.04E+1	-8.29E-2	2.36E-4	-1.31E-7
O=CH- (aldehyde)	-162.03	-143.48	3.09E+1	-3.36E-2	-1.60E-4	-9.88E-8
-COOH (acid)	-426.72	-387.87	2.41E+1	4.27E-2	8.04E-5	-6.87E-8
-COO- (ester)	-337.92	-301.95	2.45E+1	4.02E-2	4.02E-5	-4.52E-8
=O (except as above)	-247.61	-250.83	6.82	1.96E-2	1.27E-5	-1.78E-8
Nitrogen Increments						
-NH ₂	-22.02	14.07	2.69E+1	-4.12E-2	1.64E-4	-9.76E-8
>NH (nonring)	53.47	89.39	-1.21	7.62E-2	-4.86E-5	1.05E-8
>NH (ring)	31.65	75.61	1.18E+1	-2.30E-2	1.07E-4	-6.28E-8
>N- (nonring)	123.34	163.16	-3.11E+1	2.27E-1	-3.20E-4	1.46E-7
-N= (nonring)	23.61	-	-	-	-	-
-N= (ring)	55.52	79.93	8.83	-3.84E-3	4.35E-5	-2.60E-8
=NH	93.70	119.66	5.69	-4.12E-3	1.28E-4	-8.88E-8
-CN	88.43	89.22	3.65E+1	-7.33E-2	1.84E-4	-1.03E-7
-NO ₂	-66.57	-16.83	2.59E+1	-3.74E-3	1.29E-4	-8.88E-8
Sulfur increments						
-SH	-17.33	-22.99	3.53E+1	-7.58E-2	1.85E-4	-1.03E-7
-S- (nonring)	41.87	33.12	1.96E+1	-5.61E-3	4.02E-5	-2.76E-8
-S- (ring)	39.10	27.76	1.67E+1	4.81E-3	2.77E-5	-2.11E-8

A.3.2 Specific Heat of Air

Equation (2.2) gives the specific heat of air in (J/mol.K) as:

$$Cp_a = 4186.8 * (C_0 + C_1T + C_2T^2 + C_3T^3 + C_4T^4) \quad (2.2)$$

The coefficients are shown below.

**Table A.3: Coefficients for the Specific Heat of Air
(Chappell and Cockshutt, 1974)**

Symbol	Temperature range	
	200 K- 800 K	800 K- 2200 K
C ₀	+0.243E+00	+0.191E+00
C ₁	-0.329E-04	+0.128E-03
C ₂	+0.473E-07	-0.547E-07
C ₃	+0.101E-09	+0.894E-11
C ₄	-0.899E-13	+0.000E+00

A.4 Specific Heat of Liquid Compounds

Table A.4: Group Contributions in Chueh-Swanson Method (Reid *et al.*, 1987)

Group	Value†	Group	Value†
Alkane		Oxygen	
—CH ₃	36.8	—O—	35
—CH ₂ —	30.4	>C=O	53.0
		H	
—CH—	21.0		
		—C=O	53.0
—C—	7.36	O	
Olefin		—C—OH	79.9
=CH ₂	21.8	O	
=C—H	21.3	—C—O—	60.7
		—CH ₂ OH	73.2
=C—	15.9		
Alkyne		—CHOH	76.1
—C≡H	24.7		
—C≡	24.7	—CCOH	111.3
In a Ring			
		—OH	44.8
—CH—	18	—ONO ₂	119.2
		Halogen	
—C= or —C—	12	—Cl (first or second on a carbon)	36
		—Cl (third or fourth on a carbon)	25
—CH=	22	—Br	38
—CH ₂ —	26	—F	17
Nitrogen		—I	36
H		Sulfur	
		—SH	44.8
H—N—	58.6	—S—	33
H		Hydrogen	
		H— (for formic acid, formates, hydrogen cyanide, etc.)	15
—N—	43.9		
—N—	31		
—N= (in a ring)	19		
—C≡N	58.2		

†Add 18.8 for any carbon group which fulfills the following criterion: a carbon group which is joined by a single bond to a carbon group connected by a double or triple bond with a third carbon group. In some cases a carbon group fulfills the above criterion in more ways than one. In these cases 18.8 should be added each time the group fulfills the criterion. The following are exceptions to the 18.8 addition rule:

1. No 18.8 additions for —CH₃ groups.
2. For a —CH₂— group fulfilling the 18.8 addition criterion, add 10.5 instead of 18.8. However, when the —CH₂— group fulfills the addition criterion in more ways than one, the addition should be 10.5 the first time and 18.8 for each subsequent addition. (See Example 5-7.)
3. No 18.8 addition for any carbon group in a ring.

Appendix B

Droplet Evaporation

B.1 Flow Chart of the D-Squared Procedure

B.2 Mathcad Program for the D-Square Procedure

This program computes the evaporation laws of an ethanol droplet, by the d-square method.

All the values are in SI units

1) Definition of constants and properties:

$R_u := 8314.5$	perfect gas constant	
$D_0 := 100 \cdot 10^{-6}$	initial radius of the droplet	/
$T_l := 298$	initial droplet temperature	/
$T_{\infty} := 1000$	surrounding temperature	/ INPUTS
$P := 101325$	surrounding pressure	/
$V_{rel} := 0$	velocity of air around the droplet	/
$T_{nb} := 351$	boiling temperature of ethanol	
$\rho_l := 789.3$	density of ethanol	
$C_l := 112$	specific heat of liquid ethanol J/mol*K	
$MW_f := 46$	molecular weight of ethanol	
$MW_a := 28.97$	molecular weight of air	
$R := \frac{R_u}{MW_f}$	gas constant relative to ethanol	
$R_a := \frac{R_u}{MW_a}$	gas constant relative to air	
$Y_{foo} := 0$	Mole fraction of fuel in the air	
$Y_{fr} := 1$	Mole fraction of fuel in the droplet	

coefficients for the Cp of air at low temperature

$$u0 := 0.24336328 \quad u1 := -0.32921648 \cdot 10^{-4} \quad u2 := -0.4739514 \cdot 10^{-7}$$

$$u3 := 0.10126885 \cdot 10^{-9} \quad u4 := -0.89883655 \cdot 10^{-13}$$

$$C_{pal}(x) := 4186.8 \cdot (u0 + u1 \cdot x + u2 \cdot x^2 + u3 \cdot x^3) \quad \text{specific heat of air at low temperature (J/mol}\cdot\text{K)}$$

coefficients for the Cp of air at high temperature

$$a0 := 0.19075549 \quad a1 := 0.12752498 \cdot 10^{-3}$$

$$a2 := -0.54651988 \cdot 10^{-7} \quad a3 := 0.89378182 \cdot 10^{-11}$$

$$C_{pah}(x) := 4186.8 \cdot (a0 + a1 \cdot x + a2 \cdot x^2 + a3 \cdot x^3) \quad \text{specific heat of air at high temperature (J/mol}\cdot\text{K)}$$

$$C_{pa}(x) := \begin{cases} C_{pal}(x) & \text{if } x \leq 800 \\ C_{pah}(x) & \text{if } x > 800 \end{cases} \quad \text{specific heat of air}$$

$$C_{pv}(x) := \frac{1000}{MW_f} \cdot (9.014 + 2.141 \cdot 10^{-1} \cdot x - 8.39 \cdot 10^{-5} \cdot x^2 + 1.373 \cdot 10^{-9} \cdot x^3) \quad \text{specific heat of gaseous ethanol (J/mol}\cdot\text{K)}$$

$$h_{fgnb} := 40091 \quad \text{enthalpy of vaporization of ethanol at } T_{nb} \text{ (J/mol) (formula of Riedel)}$$

$$P_{sat}(x) := 101325 \cdot e^{\left[\frac{h_{fgnb}}{8.314} \cdot \left(\frac{1}{T_{nb}} - \frac{1}{x} \right) \right]} \quad \text{Clausius-Clapeyron equation for the saturation pressure of the fuel (Pa)}$$

$$h_{fg}(x) := h_{fgnb} \cdot \left(\frac{1 - \frac{x}{513.9}}{1 - \frac{T_{nb}}{513.9}} \right)^{0.38} \quad \text{enthalpy of vaporization of the fuel (Watson relation)}$$

$$Y_{fw}(x) := \frac{1}{1 + \left(\frac{P}{P_{sat}(x)} - 1 \right) \cdot \frac{MW_a}{MW_f}} \quad \text{fuel mole fraction at the droplet surface}$$

$$T_{ev}(x) := x + \frac{T_{oo} - x}{3} \quad \text{reference temperature (one-third rule)}$$

$$Y_{fev}(x) := Y_{fw}(x) + \frac{Y_{foo} - Y_{fw}(x)}{3} \quad \text{reference composition (one-third rule)}$$

$$k_a(x) := 418.7 \cdot \frac{5.9776 \cdot 10^{-6} \cdot x^{1.5}}{x + 194.4} \quad \text{thermal conductivity of air in W/m}^2\text{K}$$

$$k_v(x) := -7.797 \cdot 10^{-3} + 4.167 \cdot 10^{-5} \cdot x + 1.214 \cdot 10^{-7} \cdot x^2 - 5.184 \cdot 10^{-11} \cdot x^3 \quad \text{thermal conductivity of ethanol in W/m}^2\text{K}$$

$$k_g(x) := (1 - Y_{fev}(x)) \cdot k_a(T_{ev}(x)) + Y_{fev}(x) \cdot k_v(T_{ev}(x)) \quad \text{mass averaged conductivity and specific heat of the mixture}$$

$$C_{pg}(x) := (1 - Y_{fev}(x)) \cdot C_{pa}(T_{ev}(x)) + Y_{fev}(x) \cdot C_{pv}(T_{ev}(x))$$

2) Main Procedure

$$B_d(x) := \frac{Y_{foo} - Y_{fw}(x)}{Y_{fw}(x) - Y_{fr}} \quad \text{mass transfer number}$$

$$B_t(x) := \frac{C_{pg}(x) \cdot (T_{oo} - x)}{h_{fg}(x) + C_l \cdot (x - T_l)} \quad \text{heat transfer number}$$

Subroutine to find the droplet surface temperature:

$x := 350$ first guess

Given

$$B_t(x) = B_d(x)$$

$$y := \text{Find}(x)$$

$y = 349.45$ droplet surface temperature

$$Bt(y) = 25.268 \quad \text{heat and mass transfer numbers}$$

$$Bd(y) = 25.268$$

$$\lambda_{evq}(y) := \frac{8 \cdot kg(y)}{\rho l \cdot Cpg(y)} \cdot \ln(1 + Bt(y)) \quad \text{evaporation constant in quiescent air}$$

3) Influence of Forced Convection

$$\mu_a(y) := \frac{1.4584 \cdot 10^{-6} \cdot y^{1.5}}{y + 110.33} \quad \text{viscosity of air}$$

$$Re_d(y) := \frac{P}{Ra \cdot y} \cdot V_{rel} \cdot \frac{D_0}{\mu_a(y)} \quad \text{Reynolds number}$$

$$Pr(y) := \frac{Cpa(y) \cdot \mu_a(y)}{ka(y)} \quad \text{Prandtl number}$$

$$te_{vq}(y) := \frac{D_0^2}{\lambda_{evq}(y)} \quad \text{evaporation time in quiescent air}$$

$$\Delta t := 0.000001 \quad \text{time step}$$

```

iter := | i ← 0
        Di ← D0
        Vi ← Vrel
        while 1
            Rei ←  $\frac{P}{Ra \cdot y} \cdot Vi \cdot \frac{Di}{\mu a(y)}$ 
            lambda ←  $8 \cdot \frac{kg(y)}{\rho l \cdot Cpg(y)} \cdot \ln(Bt(y) + 1) \cdot (1 + 0.276 \cdot Rei^{0.5} \cdot Pr(y)^{0.33})$ 
            (break) if Vi = 0
            Di ←  $\sqrt{Di^2 - lambda \cdot \Delta t}$ 
            Rei ←  $\frac{P}{Ra \cdot y} \cdot Vi \cdot \frac{Di}{\mu a(y)}$ 
            mi ←  $\rho l \cdot \pi \cdot \frac{Di^3}{6}$ 
            Fi ←  $\frac{12}{Rei} \cdot \frac{P}{Ra \cdot y} \cdot Vi^2 \cdot \pi \cdot \frac{Di^2}{4}$ 
            Vi ←  $Vi - Fi \cdot \frac{\Delta t}{mi}$ 
            i ← i + 1
            (break) if  $Di^2 - lambda \cdot \Delta t < 0$ 
        | i

```

tev := iter · Δt **evaporation time**

3)Instructions of use:

The operating conditions can be modified by changing the highlighted values .

4) References

Gauthier, J.E.D. Eng 88.580 Course Notes, 2002
 Reid R.C., Prausnitz J.M. and Poling B.E., *The Properties of Gases and Liquids*.
 1987 Fourth Ed. Mac Graw-Hill Book Company

Appendix C

Bio-Oil Evaporation

C.1 Evaporation of the Bio-Oil Chemical Compounds

Figure C.1: D-Squared Law of the Nine Bio-Oil Compounds

Appendix D

Preliminary Investigation of CFD Application

D.1 Evaporation of Bio-Oil Droplets at Low Temperature

A simple two-dimensional model is created, as shown on Figure D.1.

Figure D.1: Two-Dimensional Model

No velocity is set, the pressure is one atmosphere; the droplets are injected with a diameter of 100 μm , a velocity as low as accepted by the software (0.01 mm/s), at a rate of fifty per second, and the model discussed in (5.2) is run at 600 K and 800 K (see Figures D.2 and D.3).

Figure D.2: Contours of Bio-Oil Vapour Mass Fraction (600 K)

Figure D.3: Contours of Bio-Oil Vapour Mass Fraction (800 K)

After forty seconds (2000 droplets injected), the simulation clearly gives a higher vapour mass fraction at 800 K than at 600 K. However, the evaporation time is much lower than the one predicted in Figure (4.5) in both cases (less than five seconds).

This is clearly due to the global boiling temperature assumed in the software's procedure and after which the boiling law is activated.

Below is a transcript of the important parameters of the simulation:

Models

Model	Settings
Space	2D
Time	Steady
Viscous	Laminar
Heat Transfer	Enabled
Species Transport	Non-Reacting (2 species)
Coupled Dispersed Phase	Enabled

Boundary Conditions

Zones

name	id	type
fluid.3	2	fluid
outlet	3	pressure-outlet
boxwall	4	wall
default-interior	6	interior

outlet

Condition	Value
Gauge Pressure	0
Backflow Total Temperature	600

boxwall

Condition	Value
Temperature	600
Heat Flux	0

Solver Controls

Equations

Equation	Solved
Flow	yes

h2o	yes
Energy	yes

Relaxation

Variable	Relaxation Factor
Pressure	0.1
Density	0.1
Body Forces	0.1
Momentum	0.1
h2o	0.5
Energy	0.5
Discrete Phase Sources	0.5

Discretization Scheme

Variable	Scheme
Pressure	Standard
Pressure-Velocity Coupling	SIMPLE
Density	First Order Upwind
Momentum	First Order Upwind
h2o	First Order Upwind
Energy	First Order Upwind

Material Properties

Material: water-liquid (droplet-particle)

Property	Units	Method	Value(s)
Density	kg/m3	constant	1160
Cp (Specific Heat)	j/kg-k	constant	4182
Thermal Conductivity	w/m-k	constant	0.026000001
Latent Heat	j/kg	constant	3699891
Vaporization Temperature	k	constant	253
Boiling Point	k	constant	400
Volatile Component Fraction	%	constant	99.999899
Binary Diffusivity	m2/s	constant	3.0499999e-05
Saturation Vapor Pressure	pascal	user-defined	(SAT_PRESSURE)
Heat of Pyrolysis	j/kg	constant	0

Material: mixture-template (mixture)

Property	Units	Method
Mixture Species		names
Density	kg/m3	ideal-gas
Cp (Specific Heat)	j/kg-k	mixing-law
Thermal Conductivity	w/m-k	ideal-gas-mixing-law

Viscosity	kg/m-s	ideal-gas-mixing-law
Mass Diffusivity	m ² /s	constant-dilute-appx
Thermal Expansion Coefficient	1/k	constant

Material: water-vapor (fluid)

Property	Units	Method	Value(s)
Cp (Specific Heat)	j/kg-k	constant	2014
Thermal Conductivity	w/m-k	constant	0.0261
Viscosity	kg/m-s	constant	1.34e-05
Molecular Weight	kg/kgmol	constant	18.015341
L-J Characteristic Length	angstrom	constant	2.605
L-J Energy Parameter	k	constant	572.4
Degrees of Freedom		constant	0

Material: air (fluid)

Property	Units	Method	Value(s)
Cp (Specific Heat)	j/kg-k	polynomial	1019 -0.138 -0.0001984 4.2400001e-07 -3.7629999e-10
Thermal Conductivity	w/m-k	polynomial	-0.001424421 0.0001087497 6.0290382e-08 1.942716e-11
Viscosity	kg/m-s	sutherland	(1.7894e-05 273.11 110.56)
Molecular Weight	kg/kgmol	constant	28.966

Material: aluminum (solid)

Property	Units	Method	Value(s)
Density	kg/m ³	constant	2719
Cp (Specific Heat)	j/kg-k	constant	871
Thermal Conductivity	w/m-k	constant	202.4

D.2 User-Defined Functions

D.2.1 Saturation Pressure as a Function of Evaporated Fraction

```
/* This program is a UDF that gives the saturation pressure at the
surface of a bio-oil droplet as a function of the fraction
evaporated*/

#include "udf.h"          /* includes Fluent's C library*/

DEFINE_DPM_PROPERTY(SAT_PRESSURE, c, t, p) /*declaration of the
                                           UDF*/

{

/*****Variable Declaration*****/

    double mp0= P_INIT_MASS(p);    /*initial mass of the droplet*/
    double mp = P_MASS(p);         /*current mass of the droplet*/
    double vf;                     /*vapour fraction*/
    double psat;                   /*saturation pressure*/
    double h,T;                    /*enthalpy of vaporization and
                                   boiling temperature*/

/*****Variable Initialization*****/

    h=0;
    T=0;
    vf=(mp0-mp)/mp0;

/*****Main Procedure*****/

    if (vf<=0.052)
    {
        h=23300;
        T=253.5;
    }
    else if (vf<=0.086)
    {
        h=27422;
        T=324;
    }
    else if (vf<=0.139)
    {
        h=38640;
        T=351;
    }
    else if (vf<=0.368)
    {
        h=40660;
        T=373;
    }
}
```

```

    }
    else if (vf<=0.46)
    {
        h=22908;
        T=374;
    }
    else if (vf<=0.685)
    {
        h=34140;
        T=383;
    }
    else if (vf<=0.793)
    {
        h=24120;
        T=391;
    }
    else if (vf<=0.89)
    {
        h=36358;
        T=419;
    }
    else if (vf<=1)
    {
        h=59663;
        T=659;
    }
}

psat= 101325*exp((h/8.314)*((1/T)-(1/P_T(p))));
/*Clausius-Clapeyron equation for the saturation pressure*/

    return psat;
}

```

D.2.2 Source Terms

```

/* This program is a UDF that defines the mass and energy
source terms from an evaporating bio-oil droplet*/

#include "udf.h" /* includes Fluent's C library*/

DEFINE_DPM_SOURCE(biovap_source, c, t, S, strength, p)
/*declaration of the UDF*/

{
    /*****Variable Declaration*****/

    double mp0= P_INIT_MASS(p); /*initial mass of the droplet*/
    double mp = P_MASS(p); /*current mass of the droplet*/

    double vf; /*vapour fraction*/

```

```

double h;
real mp_dot;

/*enthalpy of vaporization*/
/*mp_dot is the (positive) mass
source to the continuous
phase***/

/*****Variable Initialization*****/

h=0;
vf=(mp0-mp)/mp0;

/*****Main Procedure*****/

mp_dot = (P_MASS0(p) - P_MASS(p)) * strength;
/*(Difference in mass between entry and exit from cell)
multiplied by strength (Number of particles/s in stream)*/

if (vf<=0.052)
{
h=23300;
}
else if (vf<=0.086)
{
h=27422;
}
else if (vf<=0.139)
{
h=38640;
}
else if (vf<=0.368)
{
h=40660;
}
else if (vf<=0.46)
{
h=22908;
}
else if (vf<=0.685)
{
h=34140;
}
else if (vf<=0.793)
{
h=24120;
}
else if (vf<=0.89)
{
h=36358;
}
else if (vf<=1)
{
h=59663;
}

S->mass += mp_dot;
S->energy -= mp_dot * h;

/*Source of Mass */
/*Source of Energy*/
}

```

D.2.3 First Procedure

```
/* This program is a UDF that defines the diameter power law
of a bio-oil droplet evaporating at 1200 K*/

#include "udf.h" /* includes Fluent's C library*/

DEFINE_DPM_LAW(BIO_BOIL, p, ci) /*declaration of the UDF*/
{
    /*****Variable Declaration*****/

    double mp0= P_INIT_MASS(p); /*initial mass of the droplet*/
    double mp = P_MASS(p); /*current mass of the droplet*/
    double vf; /*vapour fraction*****/

    /*****Variable Initialization*****/

    vf=(mp0-mp)/mp0;

    /*****Main Procedure*****/

    if (P_T(p)>=253.5 && vf>=0.0001)
    /*conditions to start and end the boiling law*/
    {
        P_DIAM(p)=P_INIT_DIAM(p)-0.00134*pow(P_TIME(p),1.63);
        /*diameter law*/

        P_MASS(p)=P_RHO(p)*3.14159*pow(P_DIAM(p),3)/6;
        /*droplet mass update*/

    }
}
```

D.2.4 Second Procedure

```
/* This program is a UDF that computes the evaporation of a bio-oil
droplet*/

#include "udf.h" /* includes Fluent's C library*/

DEFINE_DPM_LAW(BIO_BOIL2, p, ci) /*declaration of the UDF*/
{
    /*****Variable Declaration and Initialization*****/

    cell_t cell;
    /*cell that the particle is currently in*/
```

```

        Thread *cthread;
/* thread of the particle cell*****/

        double mp0= P_INIT_MASS(p);
/*initial mass of the droplet*****/

        double mp = P_MASS(p);
/*current mass of the droplet*****/

        double vf;
/*vapour fraction*****/

        double kg=0;
/*thermal conductivity of the gas*****/

        double rol=0;
/*density of liquids*****/

        double cpG=0;
/*specific heat of the gas*****/

        double lh=0;
/*heat of vaporization*****/

        double B=0;
/*heat transfer number*****/

        double lamb=0;
/*evaporation constant*****/

        vf=(mp0-mp)/mp0;
/*vapour fraction*****/

/******Main Procedure*****/

        if (P_T(p)>=253.5 && vf>=0.0001)
/*conditions to start and end the boiling law*/
        {

            if (vf<=0.052)

                {
                    P_T(p)=253.5;
                    kg=0.023;
                    rol=815;
                    cpG=1039.5;
                    lh=23300;
                }

            else if (vf<=0.086)

                {
                    P_T(p)=324;
                    kg=0.028;
                    rol=1290;
                    cpG=1027.5;
                }

```



```

lh=27420;
}

else if (vf<=0.139)

{
P_T(p)=351;
kg=0.03;
rol=789.3;
cpg=1285;
lh=38640;
}

else if (vf<=0.368)

{
P_T(p)=373;
kg=0.032;
rol=998;
cpg=1350;
lh=40660;
}

else if (vf<=0.46)

{
P_T(p)=374;
kg=0.032;
rol=1220;
cpg=1069;
lh=22910;
}

else if (vf<=0.685)

{
P_T(p)=383;
kg=0.032;
rol=1366;
cpg=1150;
lh=34140;
}

else if (vf<=0.793)

{
P_T(p)=391;
kg=0.033;
rol=1044;
cpg=1152;
lh=24120;
}

else if (vf<=0.89)

{
P_T(p)=419;

```

```

kg=0.035;
rol=1082;
cpg=1234;
lh=36360;
}

else if (vf<=1)

{
P_T(p)=659;
kg=0.05;
rol=1500;
cpg=679;
lh=59660;
}

cell = P_CELL(p);
/* get the cell that the particle is currently in***/

cthread = P_CELL_THREAD(p);
/* get the thread that the particle is currently in*/

B=cpg*(P_T(p)-C_T(cell,cthread))/lh;
/*computes the heat transfer number*****/

lamb=(8*kg/(rol*cpg))*log(B+1);
/*computes the evaporation constant*****/

P_DIAM(p)=pow(P_INIT_DIAM(p)*P_INIT_DIAM(p)-
lamb*P_TIME(p),0.5);
/*d-square law*****/

P_MASS(p)=P_RHO(p)*3.14159*pow(P_DIAM(p),3)/6;
/*droplet mass update*****/

}
}

```