



LIFE Project Number
LIFE09 ENV/GR/000307

Deliverable 4.1
Report on RDF/SRF gasification properties

Reporting Date
15/01/2012

LIFE + PROJECT NAME or Acronym
ENERGY WASTE

Data Project

Project location	Greece
Project start date:	01/01/2011
Project end date:	31/12/2013
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Contents

1	Introduction.....	3
1.1	Need for determination of gasification properties.....	3
2	Methodology – Lab Scale Analyses	4
2.1	RDF Proximate, Ultimate and Heating value analysis.....	4
2.1.1	RDF proximate analysis procedure.....	4
2.1.1.1	Moisture.....	4
2.1.1.2	Volatile matter	5
2.1.1.3	Ash.....	5
2.1.1.4	Fixed Carbon	6
2.1.2	RDF ultimate analysis procedure.....	6
2.1.2.1	Carbon, Hydrogen, Nitrogen, Sulphur, Oxygen.....	6
2.1.2.2	Chlorine (Cl).....	6
2.1.3	RDF Heating Value determination procedure	7
2.2	RDF Thermogravimetric Analysis – analyser and process.....	8
2.2.1	Thermogravimetric Analyser	9
2.2.2	Process Description.....	10
2.3	RDF gasification modeling	11
2.3.1	Process Description.....	12
2.3.2	Methodology	12
3	Results: Lab-Scale Analyses.....	14
3.1	RDF Proximate, Ultimate and Heating value Analysis.....	14
3.2	Thermogravimetric Analysis.....	17
3.2.1	Paper TG Analysis	17
3.2.2	Plastic TG Analysis.....	19
3.2.3	Tetra pack TG Analysis	20
3.2.4	EPANA RDF TG Analysis	21
4	Results:RDF gasification modeling	26
4.1	Model description.....	26
4.2	Results	29
5	Conclusions.....	36
6	Literature.....	38

1 Introduction

1.1 Need for determination of gasification properties

The main scope of the project is the development and demonstration of a lab scale gasification facility for the conversion of Refuse Derived Fuel into syngas, with high energy content. As the inlet material stream quality plays a key role in the gasification process the analysis of the material properties is a key issue for the design and optimisation of the lab scale gasifier. For this reason, the following analyses, which are necessary for the characterisation of RDF properties, were carried out:

- Proximate analysis (water, ash volatiles, fixed carbon),
- Ultimate Analysis (C,H,N,O,S,Cl)
- Heating value
- Thermogravimetric Analysis

Through the results of the ultimate analysis the Carbon and Hydrogen content is determined, which affects the final heating value of the gas, and the produced gas quality. Chlorine is a technological indicator that may influence the operational behaviour through potential corrosion problems. Moreover, the ultimate analysis is required for the determination of the process energy and mass balance.

Through the proximate analysis two significant factors for the operation of the gasifier are determined. The first factor is moisture; that affects the produced gas quality, the thermal energy consumption for the procedure and may influence the behaviour of RDF in the feeding system. The second factor is the ash content of RDF. High ash content, may lead to high amounts of leftover ash in the gasifier and may create the following drawbacks: i) higher energy losses, due to the removal of preheated ash and ii) operational problems due to ash melting, that will result in agglomerations with the inert material and possible blockages of the gasifier.

As a next step thermogravimetric analysis is used for the determination of reactions taking place during the gasification process. Through the post-processing of the thermogravimetric analysis data, the kinetic rates of the reaction model can be calculated.

Based on the fuel analysis data presented above, a process model of the gasifier is developed and tested. Process modeling is a useful tool in the design of a thermal process installation, while it also supports the investigation of the ongoing reaction mechanisms. Based on the fuel analysis data thermodynamic calculations are carried out, in order to predict the gasifier's operational behavior and the whole energy and mass balance.

2 Methodology – Lab Scale Analyses

2.1 RDF Proximate, Ultimate and Heating value analysis

Chemical composition of the Refuse Derived fuel is defined in terms of its proximate and ultimate (elemental) analysis. As mentioned before the determination of the fuel composition is required, for the simulation and the prediction of the syngas quality by the gasification process.

The parameters of proximate analysis are moisture, volatile matter, ash and fixed carbon. Elemental or ultimate analysis encompasses the quantitative determination of carbon (C), hydrogen (H), nitrogen (N), oxygen (O), sulphur (S) and other elements within the fuel. Moreover according to the followed standard CEN/TC 343, it is necessary to determine the chlorine (Cl) concentration in the fuel, as a technological indicator. Consequently, in RDF ultimate analysis, Cl is accounted along with the five basic elements (C, H, N, O, S) in the final concentration calculation. Furthermore, the additional aspect that is essential for the fuel behavior is the determination of calorific value. Calorific value represents the amount of heat that the fuel is able to produce if it is combusted.

2.1.1 RDF proximate analysis procedure

A brief description of the procedure followed for the determination of each analysis, is given bellow:

2.1.1.1 Moisture

The total moisture of the RDF sample is determined according to standard CEN/TS 15414-1. The required apparatus includes: i) aluminium pan ii) Analytical balance (Kern 770) iii) desiccator and iv) drying oven with natural convection (Heraeus Thermo Scientific T-12). The procedure is as follows [1]:

1. The aluminium pan that will be used as a sample carrier is weighted
2. A sample of at least 300g and for better results of more than 500g is placed in the aluminium pan, while it's evenly and uniformly distributed on the whole surface of the pan
3. The pan with the sample is weighted before the insertion to the drying oven
4. The pan with the sample is inserted to the oven at $105^{\circ}\text{C}\pm 2^{\circ}\text{C}$ for 24h maximum, while another empty aluminum pan is inserted in the oven
5. After the passage of 24h, the pan with the sample is extracted and it's weighted within 15s.
6. The empty pan is also weighted after the passage of 24h. The weight difference will be used for correcting the total moisture of the sample

2.1.1.2 Volatile matter

The volatile matter of the RDF sample is determined according to standard CEN/TS 15402. The required apparatus includes: i) crucible with a lid ii) Analytical balance (Kern 770) iii) oven (Lindberg Blue) and iv) drying oven with natural convection (Heraeus Thermo Scientific T-12). The determination of volatile matter for each sample must be done at least two times [2]:

1. The crucible along with the lid is placed empty in the oven at the temperature of 900 °C for 7 minutes. Afterwards it is removed, left to cool down to ambient temperature and then is weighted with a precision of 0,1 mg.
2. A sample of 1g is placed in the crucible, while it's evenly and uniformly distributed on the bottom
3. The crucible is then weighted again, and placed in the oven for at 900 °C for 7 minutes.
4. Afterwards it is removed and left to cool down to ambient temperature
5. Then it's weighted again and the volatile matter is calculated numerically

2.1.1.3 Ash

The ash of the RDF sample is determined according to standard CEN/TS 15403. The apparatus used are: i) crucible (HCT 102/35 DIN) ii) Analytical balance (Kern 770) iii) oven (Lindberg Blue) iv) drying oven with natural convection (Heraeus Thermo Scientific T-12) and v) desiccator. The determination of volatile matter for each sample must be done at least two times [3]:

1. The empty crucible along is placed empty in the oven at the temperature of 550 °C for 1 hour. The crucible is then left in the desiccator until it cools down to ambient temperature
2. Afterwards it is weighted with a precision of 0.1 mg.
3. A sample of 1g is placed in the crucible, while it's evenly and uniformly distributed on the bottom
4. The crucible is then weighted again, placed in the oven and the following heating program is followed
 - i) The oven is heated with a rate of 5°C/min to 250 °C, where it's left for 60 minutes
 - ii) Afterwards, the oven is heated with a steady rate of 5°C/min to 550 °C where it's left for 120 minutes
5. The crucible is then removed from the oven and left to cool down for 5-10 minutes on a metal plate. Then it is placed in a desiccator without silica gel and left to cool down to ambient temperature
6. Then it is weighted again and the ash content is calculated numerically

2.1.1.4 Fixed Carbon

The fixed carbon is calculated as a subtraction of the moisture, volatile matter and the ash content from the total percentage (100%).

2.1.2 RDF ultimate analysis procedure

A brief description of the procedure followed for the determination of the ultimate analysis, is given below:

2.1.2.1 Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S), Oxygen (O)

The concentration of the RDF sample in carbon, hydrogen, nitrogen and sulphur is determined according to standard CEN/TS 15407. The apparatus used are: i) CHNS elemental analyzer (Perkin Elmer – type: Series II CHN/CHNS) crucible (HCT 102/35 DIN) ii) Analytical balance (Perkin Elmer AD-6 Autobalance) with a sensitivity of 0,001mg. The procedure is semi-automated and it includes several chemical reactants and carrier gases that are used for the calibration of the elemental analyzer and the process. In few steps the procedure is the following [4]:

1. The analyzer is purged by using the gases He, O₂, N₂
2. The analyzer is tested for leakages
3. The sample is carefully prepared and then it is loaded in the analyzer
4. After the test run, the results for C, H, N, S are presented in the computer screen and are saved in a folder
5. Oxygen is calculated by subtracting the percentages of C, H, N, S from the whole percentage (100%)

2.1.2.2 Chlorine (Cl)

The concentration of the RDF sample in chlorine is determined according to standard CEN/TS 15408 and by using the method of sample combustion in oxygen cylinder and the absorption of the flue gases from an appropriate solution. The apparatus used are: i) ion meter / pH meter (Fischer Scientific Model 25) ii) Analytical balance (Kern 770) iii) Bomb (1108CL – Cl resistant) iv) bomb ignition unit. In few simple steps the procedure is the following [5]:

1. The ph meter is calibrated
2. The bomb and the sample are prepared for analysis
3. After the burning of the sample, the remaining of the sample on the crucible, and the bomb walls are washed with deionised water.
4. The solution is then measured with the ion meter for Cl⁻ in mg/l

5. The final chloride concentration is calculated as the average of two test runs from the same sample

2.1.3 RDF Heating Value determination procedure

The heating value of the Refuse derived fuel is determined according to the technical specification 15400: Solid recovered fuels – Methods for the determination of calorific value. With this test the higher heating value of the Solid Recovered Fuel under constant volume conditions, in cylindric calorimeter, which has been calibrated by incinerating sample of benzoic acid sample.

The apparatus used is i) Calorimeter LECO AC-350 (S/N:3637, Mode 1:603-300-100) ii) Analytical balance KERN 770 iii) Bomb 1136

The procedure takes place under oxygen (99,5% pure) atmosphere of 3MPa. The rest of the procedure is described briefly in the following steps [6].

1. The crucible where the sample will be placed on, is weighted
2. Afterwards sample is loaded on the crucible, with caution not to overcome a heating content of 8000 kcal. Usually this corresponds to 0,8-1 g of sample. Specifically in samples with a high percentage of plastic or rubber, the weight of the sample used, ranges from 0,4g to 0,8 g.
3. The sample is weighted to the nearest fourth decimal, and that value is inserted to the calorimeter program
4. Afterwards the oxygen canister is opened, so that there is a constant flow into the bomb cylinder. The flow regulation takes place with a special pressure regulator, until the bomb is fully filled with oxygen and the pressure is constant at 3MPa. Then the flow is stopped
5. The cask of the calorimeter is filled with water
6. The bomb is placed into the calorimeter and two electrodes are connected
7. At the end of the measurement, the higher heating value (HHV) indication is shown at the calorimeter screen in units Kcal/kg
8. After the removal of the cylinder, there is an inspection of the sample. If any sample amount remains unburned, the test is rejected
9. For each sample at least two analysis of the calorific value are be made, and the final higher heating value is calculated as the average of two values that don't differ more than 200 J/g
10. After the measurement of the higher heating value, a corrective procedure is followed in order to subtract the heat amount generated from other parameters such as the production of Nitric Acid and Sulfuric acid

After the calculation of the corrected Higher heating value, the following calculations are made in order to determine the lower heating value (LHV) of the sample as received (ar) and in dry basis (db)

$$\mathbf{LHV_{ar}} = \mathbf{HHV_{ar}} - 2.442 \cdot \{8.936 \mathbf{H}/100 (1 - \mathbf{w}/100) + \mathbf{w}/100\} \quad \text{in [MJ/Kg]}$$

$$\text{where } \mathbf{HHV_{ar}} = \mathbf{HHV_{db}} \cdot (1 - \mathbf{w}/100), \quad \text{in [MJ/Kg]}$$

$$\mathbf{LHV_{db}} = [100/(100 - \mathbf{w})] \cdot \mathbf{LHV_{ar}} \quad \text{in [MJ/Kg]}$$

Where:

H: H₂ concentration in the sample as determined in ultimate analysis

W: The water content of the sample as received

2.2 RDF Thermogravimetric Analysis – analyser and process

Thermogravimetric analysis is a technique that belongs to the group of thermal analyses. The term thermal analysis (TA) is frequently used to describe analytical experimental techniques which investigate the behaviour of a sample as a function of temperature. The ability of TA to characterize, quantitatively and qualitatively, a huge variety of materials over a considerable temperature range has been pivotal in its acceptance as an analytical technique. TA is widely used in basic research and other applications by numerous scientists and engineers all over the world. The definitions of the most important thermoanalytical techniques available are given below [7]:

- **Thermogravimetry (TG) or thermogravimetric analysis (TGA):** A technique in which the mass of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature program. The record is the thermogravimetric or TG curve.
- **Differential thermal analysis (DTA):** A technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature program. For the DTA curve, the temperature difference (ΔT) should be plotted on the ordinate with endothermic reactions downwards.
- **Differential scanning calorimetry (DSC):** A technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature, whilst the substance and reference material are subjected to a controlled temperature program. Two modes, power-compensation DSC and heat-flux DSC, can be distinguished, depending on the method of measurement used. Usually, for the power compensation DSC curve, heat flow rate should be plotted on the ordinate with endothermic reactions upwards, and for the heat-flux DSC curve with endothermic reactions downwards.
- **Dynamic thermomechanometry or dynamic mechanical analysis (DMA):** A technique in which the dynamic modulus and/or damping of a substance under oscillatory load is measured as a function of temperature whilst the substance is subjected to a controlled temperature program.

The aforementioned techniques are used in a great variety of analyses, in order to provide general qualitative and quantitative information on matters as:

- Determination of kinetic parameters for reactions
- Reaction mechanisms
- Mechanism of isothermal reaction
- Glass transition point

- Crystallization and melting point
- Miscibility and phase behaviour of polymer blends
- Thermal analysis of metals and alloys

The most common experimental factors that are used as variables in thermal analyses are the following [7]:

- Heating rate
- Mass and Particle Size of Sample
- Atmosphere
- Packing density of sample

2.2.1 Thermogravimetric Analyser

Measurements of changes in sample mass with temperature are made using a thermobalance or sometimes referred to as a thermogravimetric analyzer. A thermobalance is a combination of a suitable electronic microbalance with a furnace, a temperature programmer and computer for control that allows the sample to be simultaneously weighed and heated or cooled in a controlled manner, and the mass, time, temperature data to be captured. The balance should be in a suitably enclosed system so that the nature and pressure of the atmosphere surrounding the sample can be controlled. Care is usually taken to ensure that the balance mechanism is maintained at, or close to ambient temperature, in an inert atmosphere.

Several types of balance mechanism are possible. Null point weighing mechanisms are favoured in TG as they ensure that the sample remains in the same zone of the furnace irrespective of changes in mass. Various sensors have been used to detect deviations of the balance beam from the null-position. The sensitivity of a thermobalance and the maximum load, which it can accept, without damage, are related. Typical values are maximum loads of 1g and sensitivities of the order of 1 μ g [8]. A typical schematic of the thermobalance is given below:

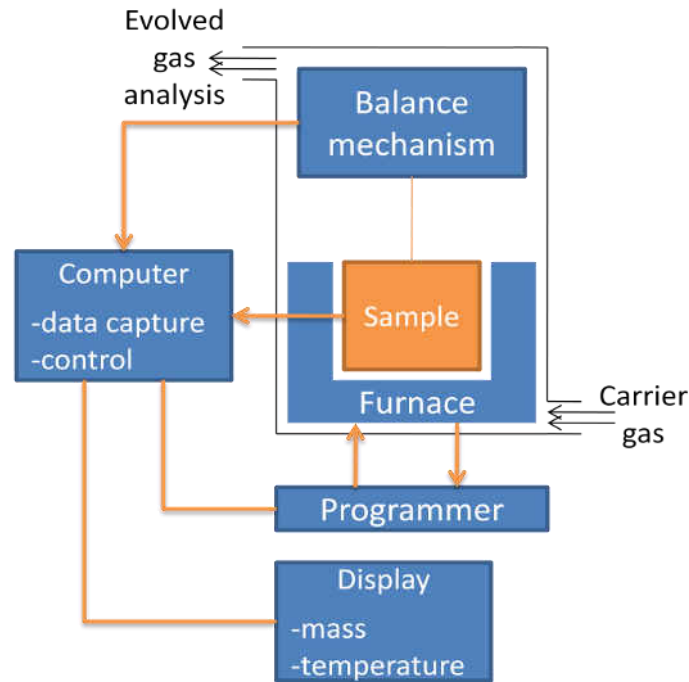


Figure 1: Typical schematic of a thermobalance

Regarding the position of the sample in conventional thermobalances, there are three main variations in the position of the sample, relative to the furnace. i) The sample may be suspended from the balance beam and hang down into a furnace or controlled temperature environment. ii) Alternatively, the sample may be placed upon a rigid vertical support above the balance beam and the furnace suitably modified for this position. iii) the third major configuration is when the sample support is a horizontal extension of the balance beam and the furnace is also arranged horizontally [8].

TG is measured under various atmospheric conditions, such as static, flowing and dynamic conditions. In static conditions, the gas composition around the sample varies when a gas generating reaction occurs. On this account, the reaction rate of the sample varies in accordance with the partial pressure of the gas. Usually, dynamic gas flow is recommended. Gases employed in TG analysis are air, Ar, Cl₂, CO₂, H₂, HCN, H₂O, N₂, O₂ and SO₂ [7].

2.2.2 Process Description

A typical TG procedure takes place according to the following description: Specimen powder is placed on a refractory pan (often porcelain or platinum). The pan in the hot zone of the furnace is suspended from a high precision balance. A thermocouple is in close proximity to the specimen but not in contact, so as not to interfere with the free float of the balance. The balances are electronically compensated so that the specimen pan does not move when the specimen gains or loses weight. Due to the weight alteration there is a transposition in the balance and usually a dc voltage proportional to this displacement is created for external data acquisition. Also, at the same time with TG plot created there is a numerical derivative TG trace (DTG) created, which is

a smoothed plot of the instantaneous slope of the specimen mass with respect to time. DTG does not contain any new information; however it clearly identifies the temperatures at which mass loss is at maximum (a DTG peak)[9].

More specifically the procedure followed for the analyses of the RDF samples is divided in three stages. The first stage is water evaporation, the second stage is sample devolatilization and the third stage is char combustion. In the following steps, a brief description of the whole process is given.

1. The sample is heated to 107°C with a heat rate of 9°C/min under N₂ atmosphere.
2. The sample is left at this temperature for five minutes. This procedure is the water evaporation step.
3. The sample is heated to 900°C with a heat rate of 50°C/min under N₂ atmosphere.
4. The sample is left at this temperature for five minutes. This procedure is the devolatilization step.
5. Afterwards the sample is left to cool down to 250°C
6. The sample is then reheated up to 550 °C with a heat rate of 5°C/min under O₂ atmosphere. This procedure is the char combustion step.
7. The received data are saved in raw data form for further processing.

The second most important thermal analysis type is differential thermal analysis (DTA). DTA consists of the monitoring of the difference in temperature existing between a solid sample and a reference as a function of temperature. Differences in temperature between the sample and reference are observed when a process takes place that requires a finite heat of reaction. Typical solid-state changes of this type would be phase transformations, structural conversions, decomposition reactions, and desolvation of solvatomorphs. These processes require either the input or the release of energy in the form of heat, which in turn translates into events that affect the temperature of the sample relative to a non-reactive reference. Although a number of attempts have been made to use DTA as a quantitative tool, such applications are not trivial. However, the technique has been used to study the kinetics associated with interphase reactions, and as a means to study enthalpies of fusion and formation. However, for most studies, DTA has been mostly used in a qualitative sense as a means to determine the characteristic temperatures of thermally induced reactions. Owing to the experimental conditions used for its measurement, the technique is most useful for the characterization of materials that evolve corrosive gases during the heating process. The technique has been found to be highly useful as a means for compound identification based on the melting point considerations, and has been successfully used in the study of mixtures [9].

2.3 RDF gasification modeling

Process modeling is a useful tool towards the design of energy schemes. Process simulation employs complicated mechanisms or combinations of simple steps. This is

also the case for lab scale RDF/SRF gasifier: the main assumption is the chemical equilibrium corrected by pseudo-kinetic corrections.

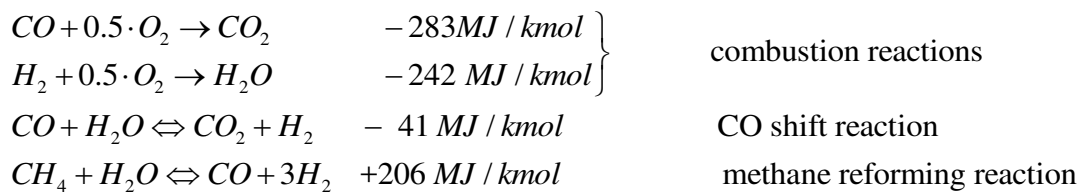
2.3.1 Process Description

The gasification of waste recovered fuels (RDF/SRF) undergoes the same sub-process with any kind of biomass.

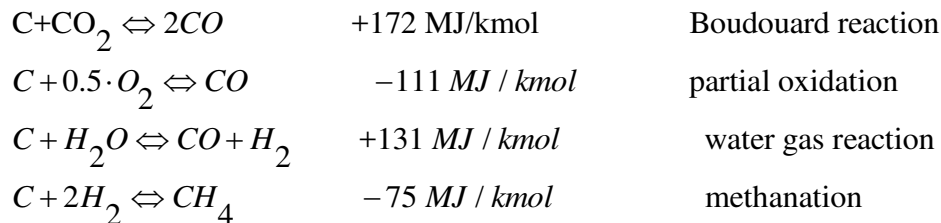
In the beginning of the heating process moisture is removed (drying).



Further heating of RDF causes the volatiles to be released (pyrolysis - devolatilization). The volatile species react in the rich oxygen /steam atmosphere towards the final composition of the product gas.



The remaining char (here assumed as solid graphite $C_{(s)}$) continues to react with the available atmosphere, producing more gases:



2.3.2 Methodology

Gasification simulation and modelling needs to be energetically consistent. The gasification vessel must take into account any heat losses through the vessel walls. A literature study reveals that most of the studies on gasification modeling at some point extent and employ a chemical equilibrium for some part of the gas. More advanced works combine this with chemical kinetics for some of reaction and species determination [10]. In fluidized bed gasifiers the process can be approached to a large extent as being close to equilibrium. [11]. The basic assumptions adopted in this work are:

1. Steady state conditions
2. Zero-D approach of the process
3. 2% of the char does not take part to the equilibrium and is considered as unreacted carbon
4. Heat losses from the gasifier ~3% LHVinput fuel

5.

The required gasification agent - air - is evaluated so as to keep a certain operating temperature of the reactor at which it is assumed phase and chemical equilibrium. The definition of equivalent rate is given in Equation 1:

$$\lambda = \frac{\text{*oxygen flow in the oxidizing agent (kmol/s)*}}{\text{*stoichiometric amount of oxygen - oxygen in the fuel (kmol/s)*}} \quad 1$$

Properties Methods:

The Equation of State chosen for the gas phase components was the Peng-Robinson with Boston-Mathias alpha function (PR-BM). This combination is suitable for such mixtures at high temperatures [12]. For waste and ash enthalpy and density calculation HCOALGEN and DCOALIGT models are used, respectively.

3 Results: Lab-Scale Analyses

3.1 RDF Proximate, Ultimate and Heating value Analysis

As mentioned before the proximate analysis is necessary in order to determine two very important parameters for the gasification process, namely the total moisture and the ash content of the input fuel stream. In the following tables (tables 1a, 1b) an indicative proximate, ultimate and heating value analysis of the produced EPANAs RDF, along with the analyses of five papers and seven types of plastic that compose RDF. Moreover the analysis of Tetra pack, a packaging waste mainly composed of plastic and paper is given, in terms of comparison with the RDF.

Table 1a: Proximate Analysis of RDF, papers and plastics

Proximate Analysis										
		RDF 0 June 2011	RDF 1 July 2011	RDF 2 August 2011	RDF 3 Sept. 2011	RDF 4 Oct. 2011	RDF Average	Magazine paper	Copy Paper	Recycling Paper
Proximate analysis (dry)	Ash (% wt.)	14,92	14,62	8,07	11,33	10,02	12,54	23,49	6,25	12,86
	Volatiles (% wt.)	76,62	84,36	88,65	82,89	85,00	83,50	68,13	82,71	81,95
	Fixed Carbon (% wt.)	8,46	1,03	3,28	5,78	4,98	4,70	8,38	10,52	5,20
Proximate analysis (as received)	Moisture (total) (% wt.)	17,55	24,84	26,76	23,56	39,85	26,51	2,10	4,00	7,50
	Ash (% wt.)	12,30	10,99	5,91	8,66	6,03	8,78	23,00	6,00	11,90
	Volatiles (% wt.)	63,18	63,41	64,92	63,36	51,13	61,20	66,70	79,40	75,80
	Fixed Carbon (% wt.)	6,97	0,77	2,40	4,42	3,00	3,51	8,20	10,10	4,81

Table 1b: Proximate Analysis of RDF, papers and plastics

Proximate Analysis											
		Newspaper	Cardboard	LDPE	HDPE	PA	PC	PP	PS	PVC	TETRA pack
Proximate analysis (dry)	Ash (% wt.)	9,41	7,16	0,00	0,10	0,30	0,10	0,00	0,00	7,62	6,58
	Volatiles (% wt.)	81,29	86,42	97,70	97,40	99,49	83,58	100,00	100,00	86,07	84,41
	Fixed Carbon (% wt.)	9,25	6,34	2,30	2,50	0,20	16,32	0,00	0,00	6,31	9,01
Proximate analysis (as received)	Moisture (total) (% wt.)	5,40	5,00	0,10	0,10	1,10	0,10	0,00	0,00	0,20	1,20
	Ash (% wt.)	8,90	6,80	0,00	0,10	0,30	0,10	0,00	0,00	7,60	6,50
	Volatiles (% wt.)	76,90	82,10	97,60	97,30	98,40	83,50	100,00	100,00	85,90	83,40
	Fixed Carbon (% wt.)	8,75	6,02	2,30	2,50	0,20	16,30	0,00	0,00	6,30	8,90

As seen in the tables above magazine paper has a high percentage of ash concentration in contrast with other types of paper. The existence of magazine paper in the RDF influences the percentage of ash measured. On the contrary, the plastic fraction of the RDF has very low ash content. The measured ash content does not impose a factor that will create a critical problem during the gasification tests.

Regarding the moisture, RDF has a higher moisture content compared with all other types of paper and plastic. This may be reasoned by the existence of other materials high in moisture, in RDF. Assuming that the fuel will be inserted at a constant mass rate, high moisture content in the input fuel leads to low heating value and correspondingly to low thermal input. In this sense, the operation of the facility shall be supported by external electrical resistances. The increased moisture content may also lead to a deterioration of the produced syngas quality. This can be outreached by pre-drying of the input fuel. The air used in the syngas cooler is heated and can then be led to the drier, in order to use the waste heat for drying. Tetra pack shows a very similar analysis in terms of volatiles and fixed carbon, thus making the comparison of RDF to Tetra pack feasible.

Fixed carbon and volatiles represent the part of the fuel that will end up in gaseous form, thus constituting (along with the input air) the mass of the produced syngas. From the concentrations calculated no specific conclusions can be conducted, since the volatiles can be constituted from different kinds of simple and complex hydrocarbons which influence differently the chemical equilibrium of the reactions taking place during the gasification procedure.

Another essential data for a better understanding of the gasification process, for the calculation of mass balance, and for the process modeling is ultimate analysis. Below is given the ultimate analysis of RDF along with the papers and plastics composing it for comparison reasons.

Table 2a: Ultimate Analysis of RDF, papers and plastics

Ultimate Analysis										
		RDF 0 June 2011	RDF 1 July 2011	RDF 2 August 2011	RDF 3 Sept. 2011	RDF 4 Oct. 2011	RDF Average	Magazine paper	Copy Paper	Recycling Paper
Proximate analysis (dry)	C (% wt.)	36,49	52,21	45,77	50,89	46,95	48,52	35,5	40,8	41,9
	H (% wt.)	4,10	7,62	5,96	6,28	6,01	6,45	4,60	5,70	5,50
	N (% wt.)	1,27	1,35	1,16	0,51	1,89	1,20	0,45	0,21	0,27
	S (% wt.)	0,00	0,05	0,00	0,17	0,11	0,27	0,00	0,00	0,00
	O (% wt.)	42,88	23,51	38,61	30,33	34,53	31,29	35,96	47,04	79,47
	Cl (% wt.)	0,34	0,64	0,43	0,49	0,49	0,48	-	-	-
Proximate analysis (as received)	C (% wt.)	30,09	39,24	33,52	38,90	28,24	35,60	34,75	39,17	38,76
	H (% wt.)	3,38	5,73	4,36	4,80	3,62	4,73	4,50	5,47	5,09
	N (% wt.)	1,05	1,01	0,85	0,39	1,14	0,86	0,44	0,20	0,25
	S (% wt.)	0,00	0,04	0,00	0,13	0,07	0,20	0,00	0,00	0,00
	O (% wt.)	35,35	17,67	28,28	23,18	20,77	22,96	35,20	45,16	73,51
	Cl (% wt.)	0,28	0,48	0,31	0,37	0,29	0,35	-	-	-

Table 2b: Ultimate Analysis of RDF, papers and plastics

Ultimate Analysis											
		Newspaper	Cardboard	LDPE	HDPE	PA	PC	PP	PS	PVC	TETRA pack
Proximate analysis (dry)	C (% wt.)	44,10	42,2	84,10	85,40	62,70	74,10	84,4	90,70	35,90	48,00
	H (% wt.)	5,60	5,60	12,15	11,37	9,70	5,50	n.a.	7,70	4,40	6,30
	N (% wt.)	0,17	0,20	0,00	0,09	10,67	0,22	0,28	0,05	0,11	0,08
	S (% wt.)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
	O (% wt.)	40,72	44,84	3,75	3,04	16,63	20,08	15,32	1,55	51,97	39,04
	Cl (% wt.)	-	-	-	-	-	-	-	-	-	-
Proximate analysis (as received)	C (% wt.)	41,72	40,09	84,02	85,31	62,01	74,03	84,40	90,70	35,83	47,42
	H (% wt.)	5,30	5,32	12,14	11,36	9,59	5,49	n.a.	7,70	4,39	6,22
	N (% wt.)	0,16	0,19	0,00	0,09	10,55	0,22	0,28	0,05	0,11	0,08
	S (% wt.)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
	O (% wt.)	38,52	42,60	3,75	3,04	16,44	20,06	15,32	1,55	51,87	38,57
	Cl (% wt.)	-	-	-	-	-	-	-	-	-	-

*n.a.: not available

According to the ultimate analysis of the RDF, carbon and hydrogen measured is closer to the percentage concentration of paper. This indicates that the amount of paper in RDF is higher than that of plastic, thus influencing more the outcome percentage. As far as nitrogen is concerned, the measured concentration is several times more than the ones measured in all papers and plastic, except Polyamide (PA). Conclusively, the measured nitrogen is due to the presence of an adequate concentration of Polyamide in RDF. Regarding chloride, there have been a number of studies by different working teams and different approaches [13-16]. The concentration calculated is believed to originate mainly from PVC, a plastic with high chlorine concentration, while the quantity measured is not believed to cause any significant technical disorders or environmental problems. In comparison with other RDF samples tested and for the moment being the concentrations measured make EPANAs RDF stand in a satisfactory level [14, 17-20].

Table 3a: Heating Value of RDF, papers and plastics

Heating Value									
	RDF 0 June 2011	RDF 1 July 2011	RDF 2 August 2011	RDF 3 Sept. 2011	RDF 4 Oct. 2011	RDF Average	Magazine paper	Copy Paper	Recycling Paper
High Heating Value (kJ/kg)	19150	24462	19282	20391	21494	20956	12340	13820	15200
Lower Heating Value (kJ/kg) (dry)	18256	22800	17982	19022	20183	19550	11337	12577	14000
Lower Heating value (kJ/kg) (as received)	14623	16531	12515	13965	11167	13682	11047	11975	12767

Table 3b: Heating Value of RDF, papers and plastics

Heating Value										
	Newspaper	Cardboard	LDPE	HDPE	PA	PC	PP	PS	PVC	TETRA pack
High Heating Value (kJ/kg)	15870	14480	45700	45150	32600	32200	39100	41950	18100	18520
Lower Heating Value (kJ/kg) (dry)	14648	13258	43050	42670	30484	31000	n.a.	40270	17140	17146
Lower Heating value (kJ/kg) (as received)	13725	12473	43003	42624	30121	30966	n.a.	40270	17101	16910

*n.a.: not available

As observed in the tables above (tables 3a, 3b), the calculated heating value of RDF on dry basis that RDF lays between the corresponding value of paper and plastics. More specifically the HHV is closer to the paper's, a fact which depicts that the paper fraction is considerably higher than the plastic fraction. Moreover the average value of the lower heating value is higher than that of the tetra packs in dry basis, while in as received basis it is notably lower. This fact shows the effect of moisture percentage in the heating value of the input stream.

3.2 Thermogravimetric Analysis

As mentioned before, a crucial factor for the better understanding of the gasification properties of the used RDF is the thermogravimetric analysis (TGA). TGA is used, in order to investigate the reaction model used for the breakdown of the main RDF fractions and to find the kinetics for the proposed reaction mechanism. Three parameters are included in the kinetic parameter set to characterise each chemical reaction: a) the pre-exponential factor, b) the activation energy and c) the rate constant. Since RDF is a mixture of mainly paper and plastic, the determination of the TG curves of these fractions (types of plastics and paper), is required in order to investigate, whether it is possible to analyse its combustion behaviour as an extrapolation of the main fraction, so as to be able to compare with the RDF curves. In this sense five different types of paper (Magazine paper, Cardboard, Recycling paper, Newspaper, Copy paper) and seven different types of plastic (PA, PC, LDPE, HDPE, PP, PS, PVC) were analysed.

3.2.1 Paper TG Analysis

According to literature, it is mainly consisted from cellulose, hemicellulose and lignin, due to its origin from woody biomass. Regarding the papers analysis, only the devolatilization stage was studied, which is used to identify the reactions and the kinetics behind the breakdown of the RDF components. A comparative analysis of the obtained TG (weight loss) and DTG (weight loss rate) curves for all the paper samples is presented in the figure below (figure 2).

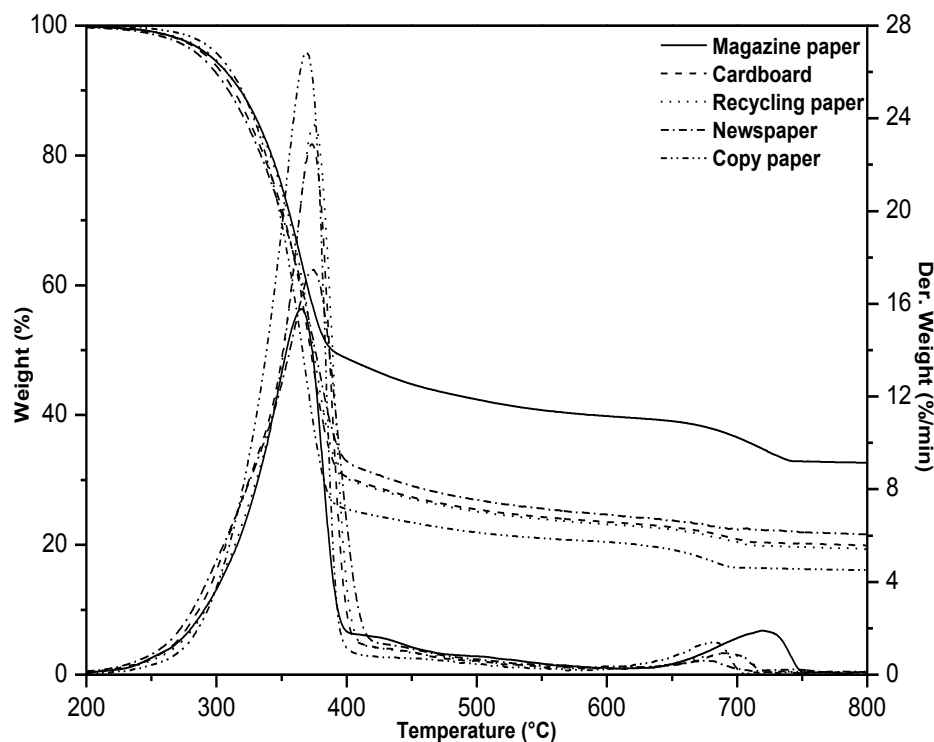


Figure 2: Paper weight loss and rate of weight loss as a function of temperature

The shape of the curves indicates that pyrolysis proceeds in almost the same way for all the paper samples tested. Their major weight losses occur between 300 and 400°C, while the maximum pyrolysis rate is reached in the range of 365–375°C. However, quite important deviations in peak heights and total conversions show that samples differ in reactivity. DTG curves clearly point out that copy paper is the most reactive among the samples and simultaneously yields the smallest amount of char. The almost identical devolatilisation behaviour of recycling and magazine paper at temperatures lower than 350°C is worth noting. From this temperature onwards, recycling paper devolatilisation resembles well the corresponding one of the cardboard. It is also important to remark that these two paper samples exhibit the same total weight loss owing to their similar fixed carbon and ash contents. A more in depth analysis of the curves reveals a shoulder located at the low temperatures of the degradation of the lignocellulosic samples. This curve, which is more pronounced in the DTG curve of newspaper, represents the decomposition of hemicellulose. However, this shoulder is less evident for magazine paper and cardboard than for the rest paper samples, probably due to the partial removal of hemicellulose. The latter occurs during the production process in order to achieve the desired properties for the product. The shoulder located between 365 and 375 °C arises from the decomposition of cellulose, whereas the flat tailing section showed above 400 °C corresponds to the degradation of lignin.

3.2.2 Plastic TG Analysis

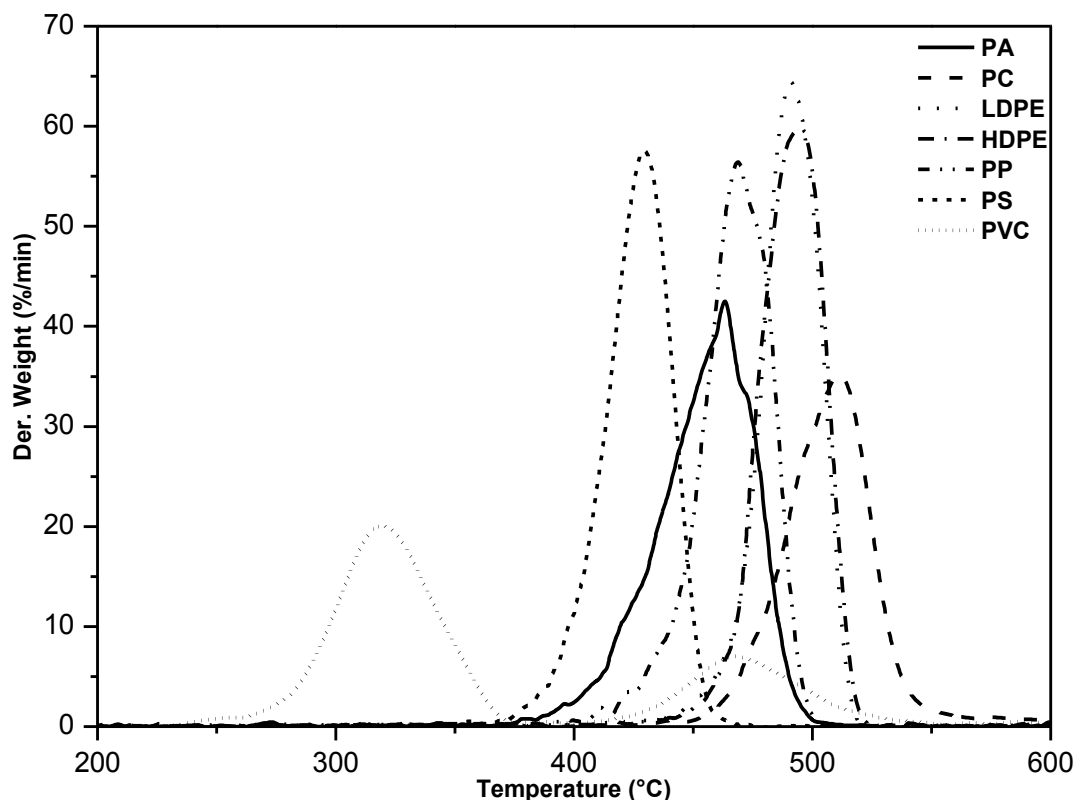


Figure 3: Plastics rate of weight loss as a function of temperature

As previously noted, the plastic fraction of RDF mainly consists of PE and PVC. The DTG curves corresponding to the devolatilisation of plastics are shown in figure 3. As can be seen from the degradation curves, the decomposition of the plastics starts at higher temperatures, with the exception of PVC, when compared to the lignocellulosic materials. Essentially, the plastics are thermally more stable than the paper samples and therefore, degrade at higher temperatures, reaching the maximum decomposition rate in the vicinity of 500°C. In contrary, PVC presents two distinct curves located at 320 and 470°C, respectively [21]. In this line, the pyrolysis behavior of the PC is somewhat different from the other plastics. The devolatilisation of PC starts at a quite high temperature (480°C) and reaches the maximum rate at 510°C, while presenting the highest peak among the plastic fractions. PS starts decomposing at 365°C, and the low temperature corresponding to the maximum rate is indicative of its low stability. According to Bockhorn et al. [22] the devolatilisation of PE and PS follow the same radical chain mechanism. However, a detailed study on the evolved gases during pyrolysis revealed that the devolatilisation of PS differs from the ones of PE and PP [23]. The decomposition of HDPE and LDPE starts at 430°C and exhibits a maximum rate of pyrolysis at 495°C, whilst is followed from the evolution of paraffines and olefines [22]. The devolatilisation of LDPE and HDPE is realized almost in the same way apart from a single minor variation concerning the peak heights. This could be explained by the weak-link model, according to which the side branch bonds presented in HDPE are breaking with higher rates. Therefore, their

breakage occurs with the initiation of the reaction and leads to a lower peak height [23].

The thermal stability of the examined plastic samples can be derived from the conversion rate curves and the following order can be constructed (stability lowered from right to left): PC > HDPE > LDPE > PP > PA > PS > PVC. The experimental results are in accordance with the results of previous studies [24]. It is believed that the degradation of PVC is a multi-stage mechanism consisting of a variety of intermediate products.

This is reflected by the fact that PVC pyrolysis exhibits two devolatilisation steps, represented by two shoulders on the DTG curve. From the first stage a thermally stable char is produced, which is decomposed at higher temperatures. The first shoulder presents a maximum at 320°C and is accompanied by the dehydrochlorination of the plastic fraction [22]. The dehydrochlorination results in the production of an intermediate fraction, namely polyene, and the simultaneous evolution of benzene, naphthalene and phenanthrene. According to Zevenhoven et al. [25] in this stage 99.5% of the chlorine contained in PVC has been evolved in the gas phase. The intermediate polyene can be decomposed at higher temperatures to produce volatile hydrocarbons. In an effort to more accurately explain the phenomena occurred during the first pyrolysis stage of PVC, Wu et al. [24] ascribed the initiation of the reaction to the tertiary CA-Cl bonds or to the chlorine atoms located next to a C=C bond. The second stage of PVC is located in the temperature range of 400–550°C with a significantly less pronounced curve and is accompanied with the evolution of toluene and alkyl aromatics [26].

3.2.3 Tetra pack TG Analysis

The pyrolysis curve of tetra pack presents two distinct weight loss steps located in the temperature regions of 200–400 °C and 450–550 °C, respectively. Tetra pack is a mixture of a wood based material (usually cardboard) and a plastic coating. The pyrolysis behaviour of the first shoulder is similar to that of paper samples. Thus, tetra pack begins to decompose at a low temperature (270 °C) and reaches the maximum pyrolysis rate at 370 °C, close to the corresponding temperature of cardboard (373°C). The maximum rate of the second shoulder is attributed to the plastic fraction of the tetra pack and located at 488 °C, which is similar to the temperatures that plastics are decomposing. More specifically, the plastic fractions that devolatilise at almost the same temperature are HDPE and LDPE. At figure 4 the TG diagram of tetra pack pyrolysis curve is shown.

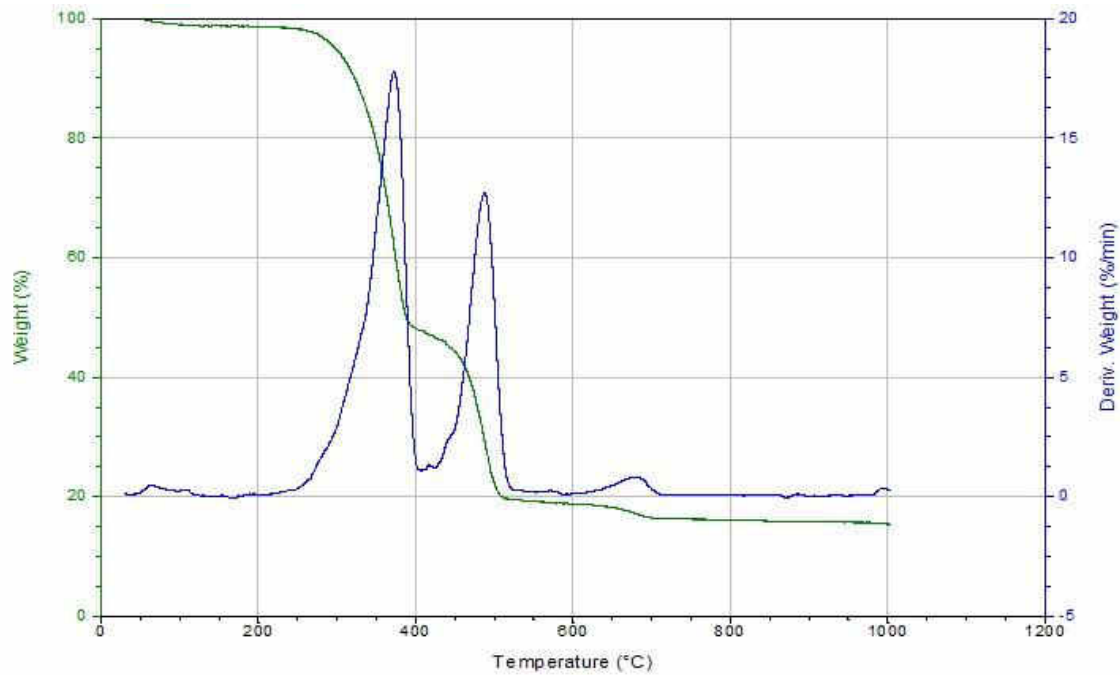


Figure 4: Tetra pack weight and rate of weight loss as a function of temperature

3.2.4 EPANA RDF TG Analysis

The samples undergone the Thermogravimetric Analysis are taken from the lots of June and July 2011. These lots are created during the sampling procedure according to the European standard EN15442.

More specifically three samples have been analysed. The first sample is from the sampling lot of June 2011 (Named RDF0) and the second (named RDF 1 (A)) and third sample (named RDF 1 (B)) are from the sampling lot of July 2011.

For the analysis, the procedure followed is as described in Chapter 1.3.2. At first the heat up and drying takes place. The second step is to heat up to 900°C for the devolatilization process and the third step (after letting the sample to cool down) is reheating up to 550 °C for char combustion.

In the figures bellow (figs 5, 6, 7) the curves of weight loss for the complete thermogravimetric analysis (all of the analysis steps) of the three samples are given. The temperature and weight loss data gathered are presented as a function of the data increment received.

In the diagrams there are two regions highlighted, which are of interest. The yellow one represents the second step of the TG analysis, which corresponds to devolatilization. The green region represents the char combustion. The intermediate region is the cooling down of the sample, as described in the process.

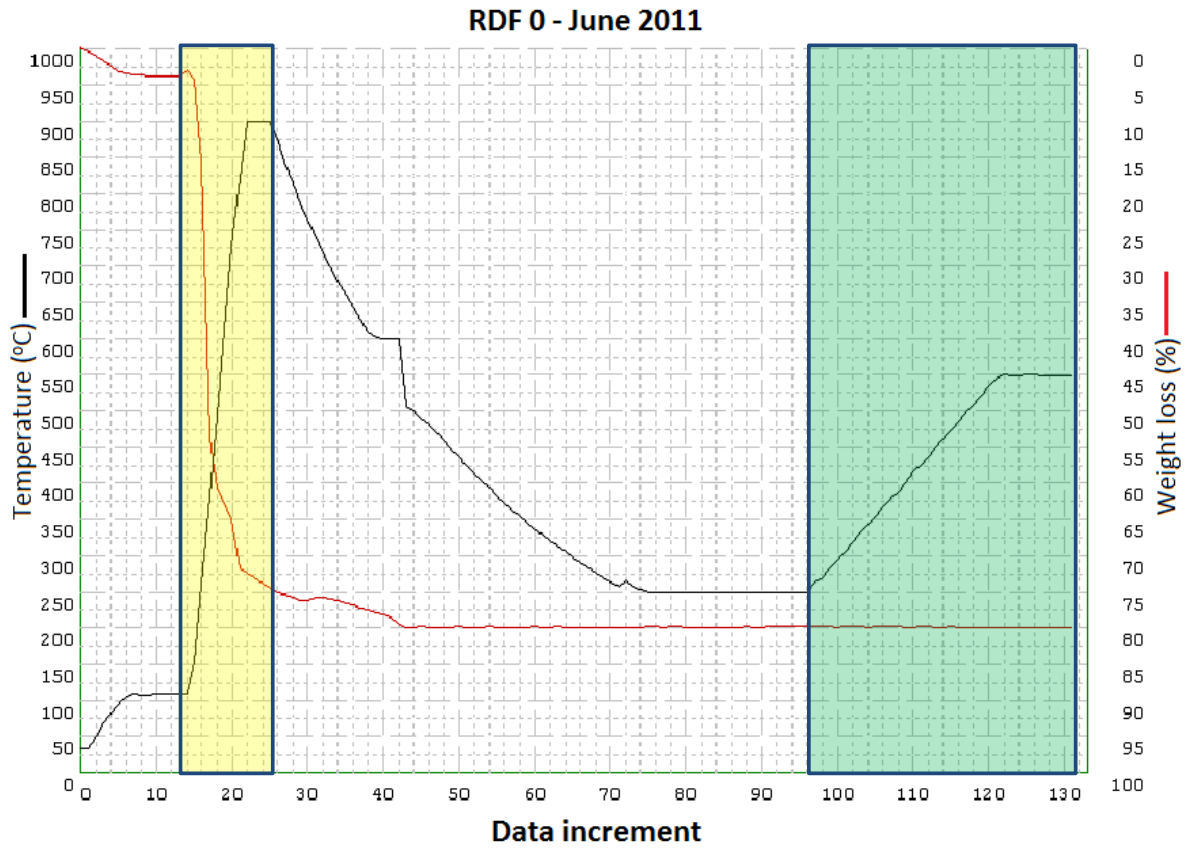


Figure 5: RDF 0 – Complete thermogravimetric analysis

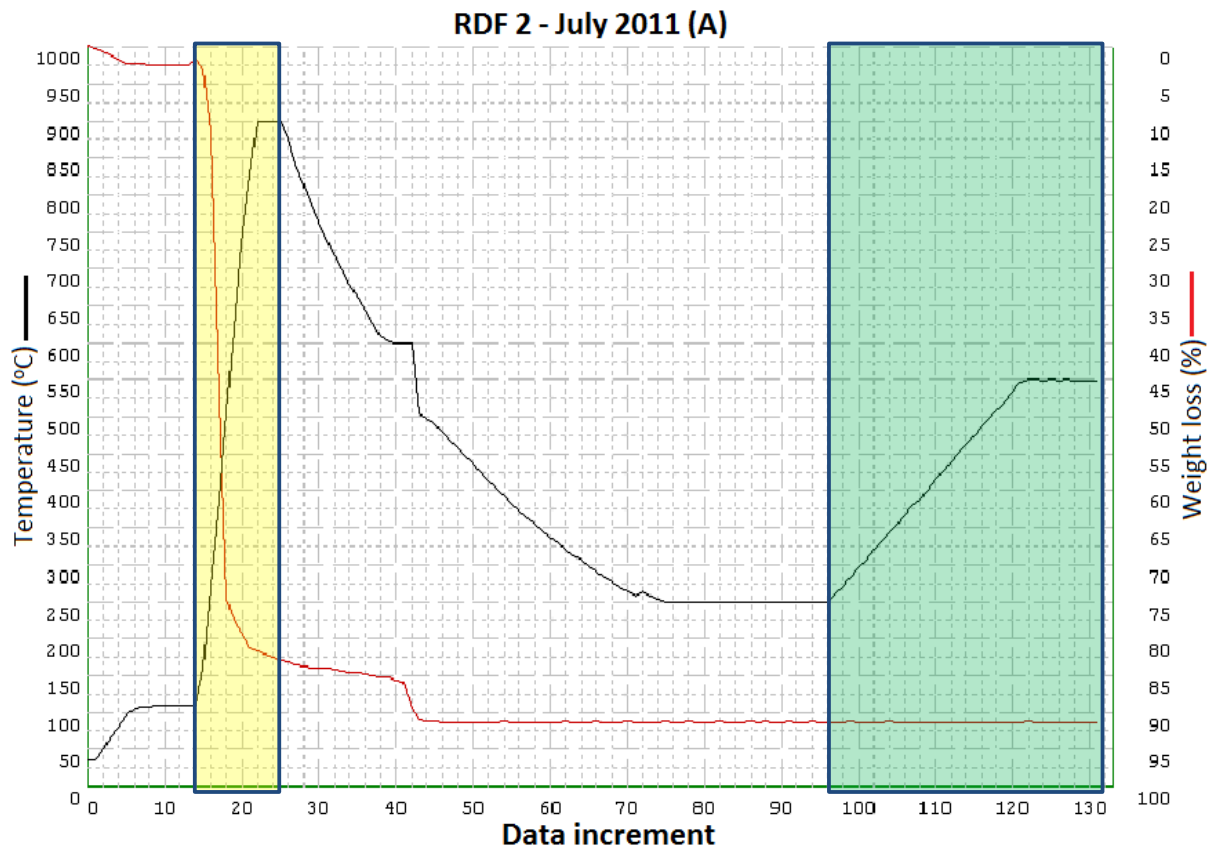


Figure 6: RDF 1 (A) – Complete thermogravimetric analysis

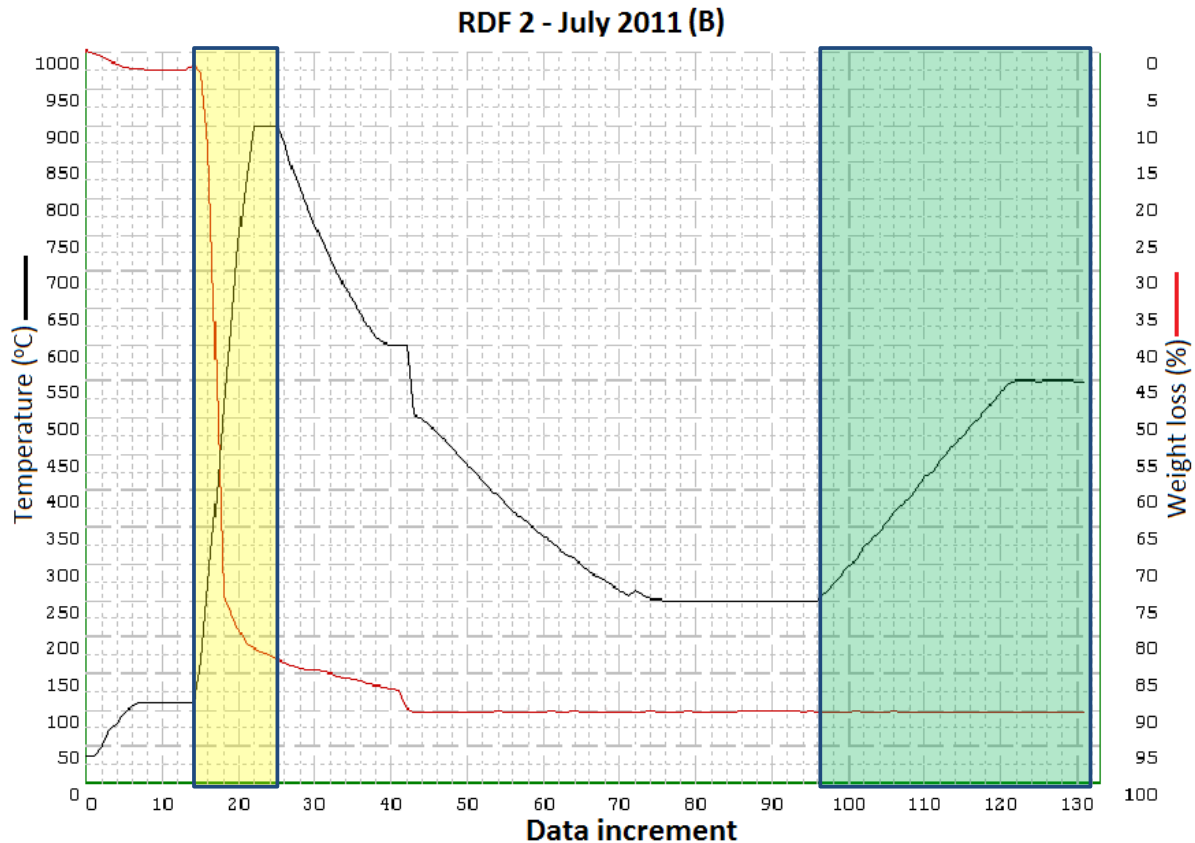


Figure 7: RDF 1 (B) – Complete thermogravimetric analysis

In all samples it is observed from the yellow region that there is a very high rate of mass reduction as the temperature rises. Moreover, even after letting the sample at high temperature for a designated time, it still loses mass, at the cooling phase. This indicates that maybe it should be left for a longer time at the designated temperature. From the green region it is shown that no significant mass losses are observed during the char combustion phase.

More specifically the second step of the procedure (devolatilization) is of particular interest for the analysis. For that reason the data of the temperatures ranging from 109 – 900 °C are isolated and presented in the following figures (figures 8-10).

Due to the lack of a plethora of data, it was found difficult to calculate a representative weight derivative. For that case, the following differentiation scheme was used:

$$\left(\frac{\partial y}{\partial x}\right)_i = \frac{1}{\Delta x_i + \Delta x_{i+1}} \cdot \left[\frac{\Delta x_i}{\Delta x_{i+1}} \cdot (y_{i+1} - y_i) + \frac{\Delta x_{i+1}}{\Delta x_i} \cdot (y_i - y_{i-1}) \right] - \frac{\Delta x_i \cdot \Delta x_{i+1}}{6} \cdot \frac{\partial^3 y}{\partial x^3}$$

The used equation produces the first derivative as a function of the previous and the next set of data, thus giving a more representative value.

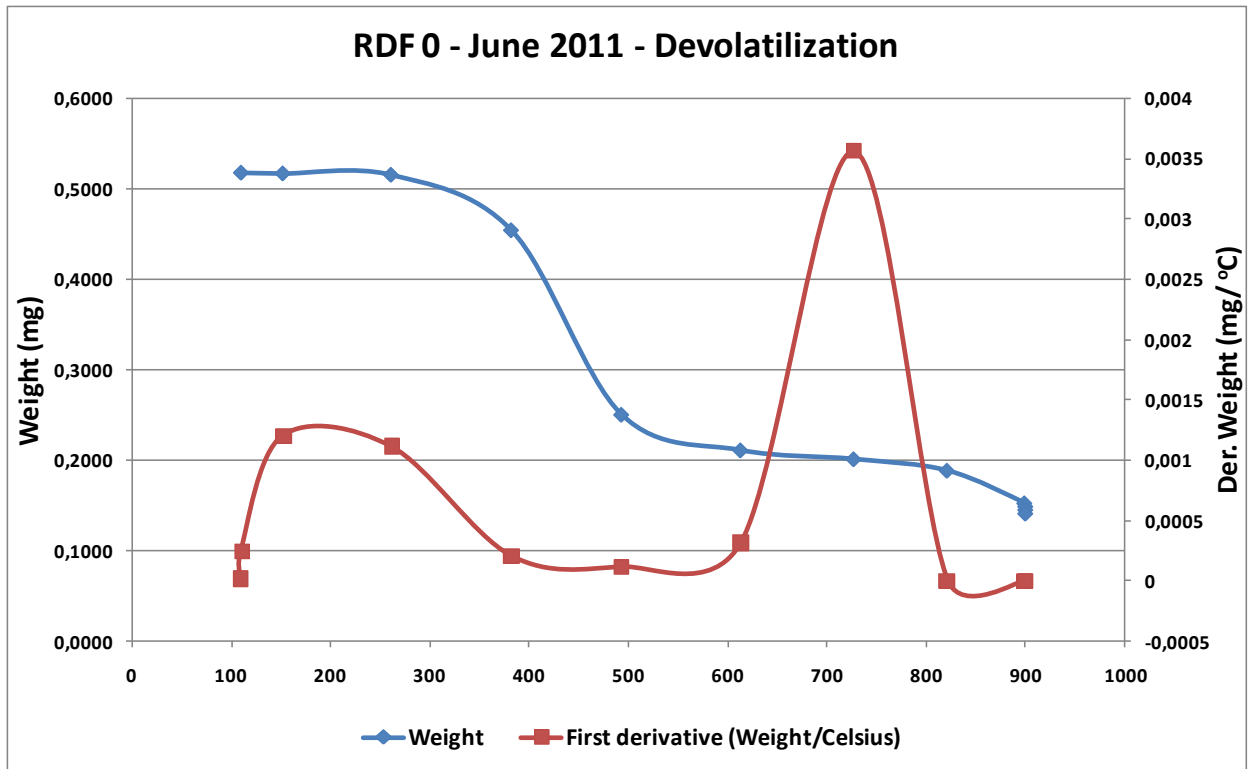


Figure 8: RDF 0 – Thermogravimetric analysis of the devolatilization step

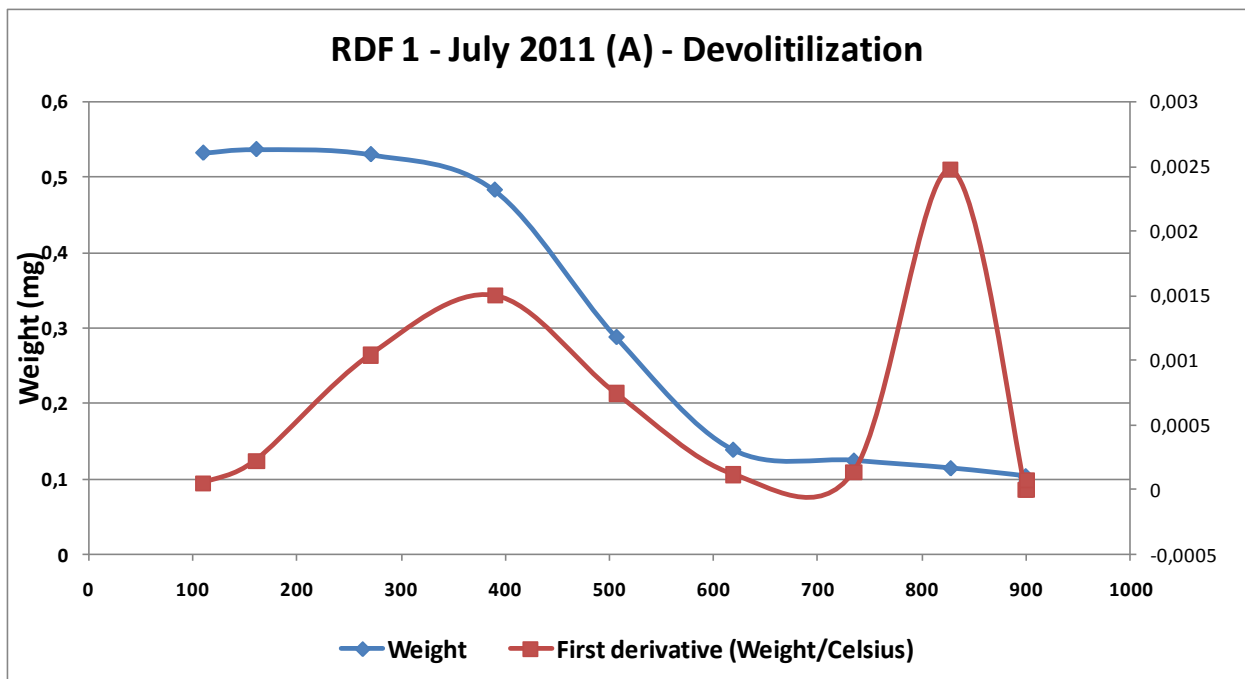


Figure 9: RDF 1 (A) – Thermogravimetric analysis of the devolatilization step

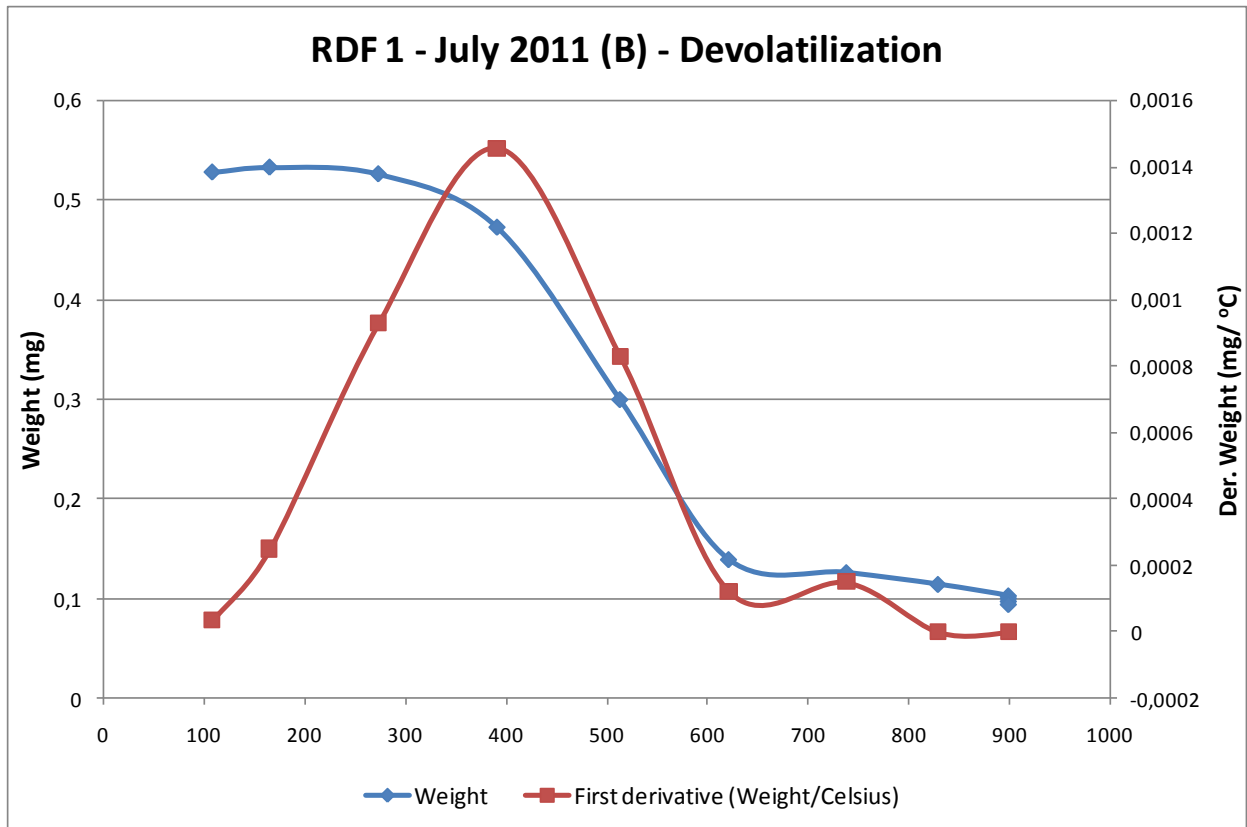


Figure 10: RDF 1 (B) – Thermogravimetric analysis of the devolatilization step

By observing the first two figures (figs 8, 9) it is noted that the TG/DTG curves are similar to the ones of tetra pack, but with the second shoulder moved slightly to the right. The first DTG shoulder for all three figures appears between the temperatures 250°C and 620°C, which is matched to the papers lignin, cellulose and hemicellulose degradation and to the plastics pyrolysis. Moreover the highest degradation rate is observed at the temperatures between 380-400°C.

4 Results: RDF gasification modeling

4.1 Model description

The process flowsheet is shown in the figure 11. Here we focus only at the gasification process. The main points investigated are

- the parameters to achieve autothermal operation,
- the effect of parameters equivalence rate, steam injection, drying on the product gas quality process efficiency.

The inlet fuel properties are determined by its Proximate and Ultimate analysis. A first pre drying step can be employed through a “RSTOIC unit operation model”. A FORTRAN statement has been set in order to specify the rate of this pre-drying. In the SEPARATOR block that follows, the evaporated water is removed from the main fuel stream.

In the next stage fuel decomposition is modeled by a RYILED unit operation model. This is used since the particular fuel is considered as a non-conventional fuel. This model yields elements out of the fuel. With a help of a Fortan calculator these yields the exact balance of the elements that are reported in the Ultimate and Proximate analysis of the fuel. As a next step, the main gasification process is modeled by the RGIBBS unit operation model, which is based on the minimization of Gibbs free energy function of defined products.

The Gibbs energy function G is given by:

$$G = H - T \cdot S \quad 2$$

where the enthalpy function H is

$$H(T) = \Delta H_{f,298} + \int_{298}^T C_p dT \quad 3$$

and the entropy function S

$$S(T) = \Delta S_{f,298} + \int_{298}^T \frac{C_p}{T} dT \quad 4$$

The specific heat capacity as a function of temperature is

$$C_p(T) = A + B \cdot T + \frac{C}{T^2} + D \cdot T^2 \quad 5$$

The Gibbs free energy minimization method for the C-H-O atom blend of the fuel and oxidant mixture is applied for predicting the thermodynamic equilibrium composition of waste gasification in major components: H_2 , CO , CH_4 , CO_2 , H_2O , N_2 , as well as char, which is modeled as solid graphite C_s .

The above methodology underestimates methane which derived from the pyrolysis step. This is corrected by taking into account non-equilibrium corrections to bring these product gas components closer to experimental values from fluidized bed

gasifiers. The unreacted char is assumed to consist only of carbon and 2% of the total carbon in the fuel [27]. This char (carbon) does not participate in the thermodynamic equilibrium calculations. Similarly, CH₄ content (mostly deriving from the pyrolysis) was assumed to 3% v/v in the final nitrogen free and dry product gas [28]. In the current model, tar formation is neglected.

The equilibrium product, the char and ash as well as the methane is mixed as the gasifier outlet - prior to the separation of solids from gaseous products which modeled with a separating cyclone. The produced raw syngas is cooled down to 525°C before it is combusted in a flare. The cooling medium is the air that is used for gasification and combustion.

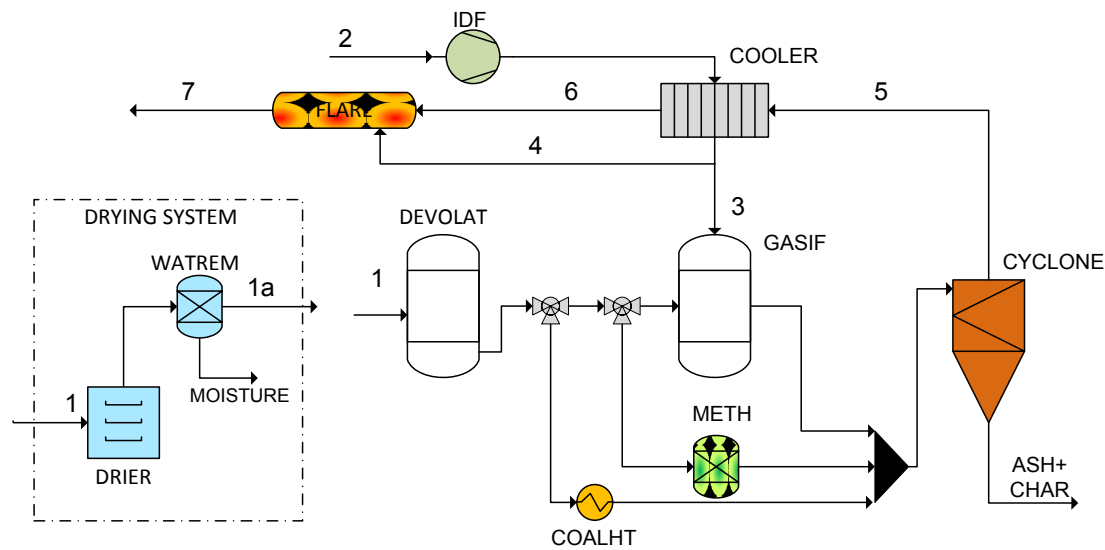


Figure 11. Flowsheet diagram of the process model

A detailed description of the process modeling blocks used in the particular simulation is presented in Table 4 whereas the corresponding flowsheet diagram is displayed at Figure 11.

Table 4: Description of process modeling blocks used

Block	ASPEN component	Brief description
DRIER	RSTOIC	a fraction of the fuel moisture is evaporated (specified by the user).
WATREM	SEPARATOR	evaporated moisture removal
DEVOLAT	RYIELD	the fuel is decomposed into its constituting components (C, H, O, N, S, Cl)
SEPAR	SEPARATOR	The amount of carbon that is not considered to react is separated from the total fuel
METH	RSTOIC	Production of CH ₄ that cannot be predicted by the equilibrium according to real value
GASIF	RGIBBS	The main part of gasification process, where the products prediction is based on minimization of free Gibbs energy.
COALHT	HEATER	In order to be consistent with energy balance in the gasifier, the heating of unreacted char up to equilibrium temperature should be taken into account

CYCLONE	SEPARATOR	The solids (ash, tars, unreacted carbon) are separated from the gaseous products
COOLER	MHEATX	A multi- stream heat exchanger where the produced syngas is cooled – heating off the air used for the gasification and combustion
IDF	COMPRESSOR	Delivers air to the gasifier with the required pressurization.
FLARE	RGIBBS	The produced syngas is combusted in a flare: modeled again as minimization of free Gibbs energy.

The gasification efficiency is most commonly expressed as cold gas efficiency, neglecting the sensible heat of the gas and char produced [11]:

$$CGE = \frac{LHV \text{ in cold product gas}}{LHV \text{ in feedstock}} \cdot 100\% \quad 6$$

Three representative diverse fuels will be investigated (see Table 5). Fuel A differs from fuel B at the moisture content only whereas fuel C has quite twice times more ash. This makes fuel C be less qualitative than fuel A.

Table 5: RDF composition

	Fuel A	Fuel B	Fuel C
Proximate analysis (wet basis)			
moisture	26.8	15.0	15.0
fixed carbon	2.4	2.8	4.7
volatiles	64.9	75.4	66.2
ash	5.9	6.9	14.1
Ultimate analysis (dry basis)			
C	45.77	45.77	43.99
H	5.96	5.96	6.36
N	1.16	1.16	1.30
O	38.56	38.56	31.09
S	0.05	0.05	0.58
Cl	0.43	0.43	0.05
calorific values			
HHV (dry) kJ/kg	19281.8	19281.8	17960.9
LHV (raw) kJ/kg	12515.2	14917.7	13720.8

The specifications of the base case model are exposure at the next table:

Table 6: Base case model assumptions

RDF fuel	fuel A
fuel mass flow rate	30 kg/hr
fuel drying	no
steam injection	no
gasification temperature	800 °C
pressure	1.01 bar
air preheating	200°C
equivalence ratio	0.31

maximum carbon conversion	98%
methane in dry syngas (v/v)	3%

Under these conditions the operation of the gasifier is slightly autothermal.

4.2 Results

Similar works for comparison of the current results can be found on [12], [29] for Municipal Solid Waste (MSW) and [30] Refused Derived Fuels (RDF).

Under the abovementioned assumptions the produced syngas has a typical composition (v/v dry basis):

Table 7: Syngas composition (% v/v, dry)

	wet	dry
H ₂ O	14.43	-
CO ₂	11.62	13.58
CO	16.56	19.36
H ₂	21.82	25.50
N ₂	32.50	37.99
CH ₄	2.57	3.00
H ₂ S	0.01	0.01
Ar	$3.8 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$
HCl	$1.0 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$
LHV (kJ/kg ³)	5388	6099

The basic streams of the pilot plant with their corresponding characteristics are given in Table 8:

Table 8. Stream results of the base case study ($T=800^{\circ}\text{C}$, $p=1\text{bar}$, $\lambda=0.30$)

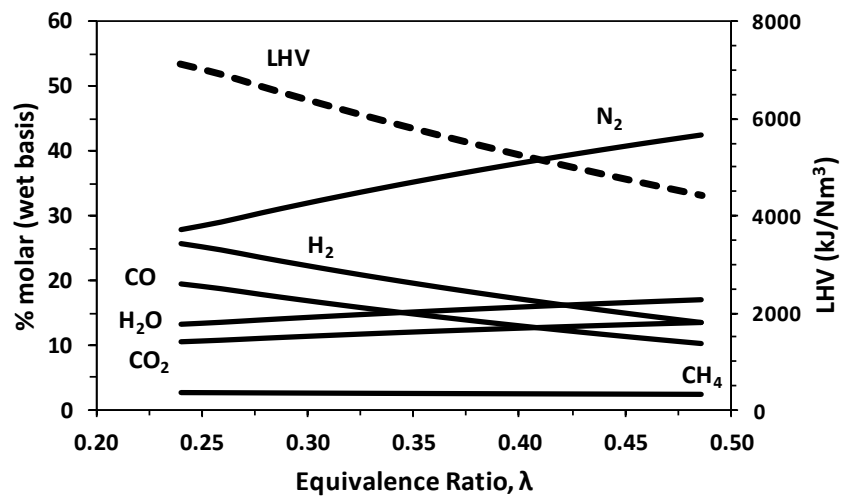
	1	2	3	4	5	6	7	
mass flow kg/hr	30.0	6.31	1.32	4.99	2.87	2.87	7.22	
mole flow kmol/sec	-	0.011	0.011	0.040	0.018	0.018	0.058	
Temperature °C	15.0	15.0	174.5	174.5	800.0	525.0	180.0	
molar composition %	see Table 5	H ₂ O	0.010	0.010	0.010	0.083	0.083	0.155
		CO ₂	$3.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$	0.080	0.080	0.127
		CO	0	0	0	0.211	0.211	0
		H ₂	0	0	0	0.232	0.232	0
		O ₂	0.207	0.207	0.207	0	0	0.032
		N ₂	0.773	0.773	0.773	0.360	0.360	0.677
		Ar	$9.2 \cdot 10^{-3}$	$9.2 \cdot 10^{-3}$	$9.2 \cdot 10^{-3}$	$4.2 \cdot 10^{-3}$	$4.2 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$
		CH ₄	0	0	0	0.027	0.027	0
		SO ₃	0	0	0	0	0	$6.4 \cdot 10^{-4}$
		HCl	0	0	0	$1.3 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$5.0 \cdot 10^{-5}$
		NH ₃	0	0	0	$2.8 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$	0
		COS	0	0	0	$4.5 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	0
		H ₂ S	0	0	0	$1.6 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	0

Table 9 summary of the energy balance of the pilot plant for the base case study:

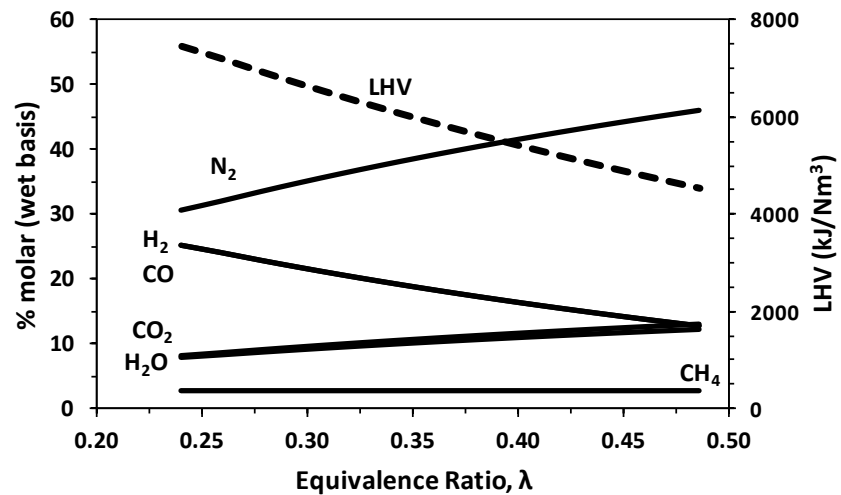
fuel heat input	kW_{th}	104.3
syngas heat input	kW_{th}	85.1
drying	kW_{th}	-5.1
fan	kW_{e}	-0.4

a- Equivalence rate & drying

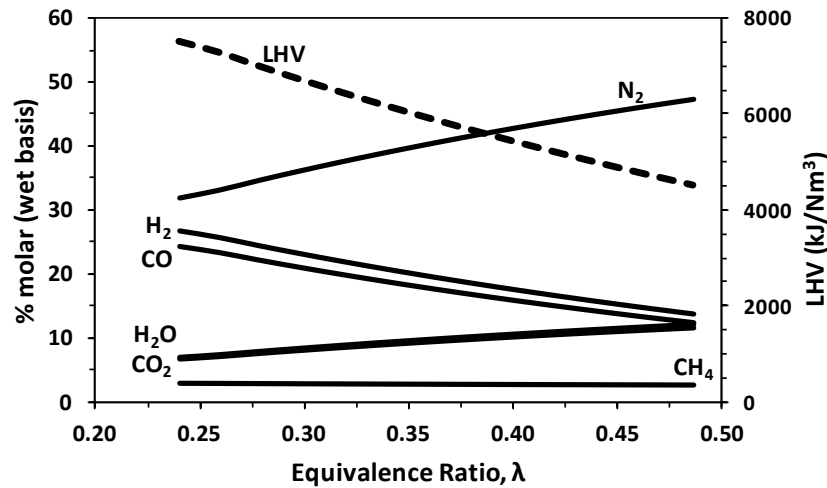
The effect of oxidant quantity on syngas composition is shown in the following figure. The trends of each component are similar with corresponding trends of other syngas derived from waste or biomass [12], [29], [30].



a



b



c

Figure 12. Effect of air gasification on raw syngas composition for the three fuel types (a: fuel A, b: fuel B, c: fuel C)

Figure 12 presents the distribution of syngas (wet) composition versus the equivalence ratio. As the oxidizing agent increases, more H_2O and CO_2 are produced, from the H_2 and CO oxidation respectively. Hence the calorific value of the gas is reduced. On the other hand, Figure 13 demonstrates the lower limit of the air requirement for gasification. Values below zero imply the requirement of heat for the proper operation of the gasifier. Values greater than zero imply the excess of heat production that is rejected to the ambient. For instance, fuel A can be gasified under autothermal conditions at 800°C with equivalence ratio 0.31.

The comparison of the curves of fuel A and B shows the effect of drying rate to the process operation. Reducing the moisture content of the fuel, autothermal condition can be met for lower air flow rates ($\lambda=0.275$ for fuel B case). In addition, as the quality of the fuel deteriorates (more ash content, less gross calorific value, see Table 5) more oxygen is needed for autothermal operation.

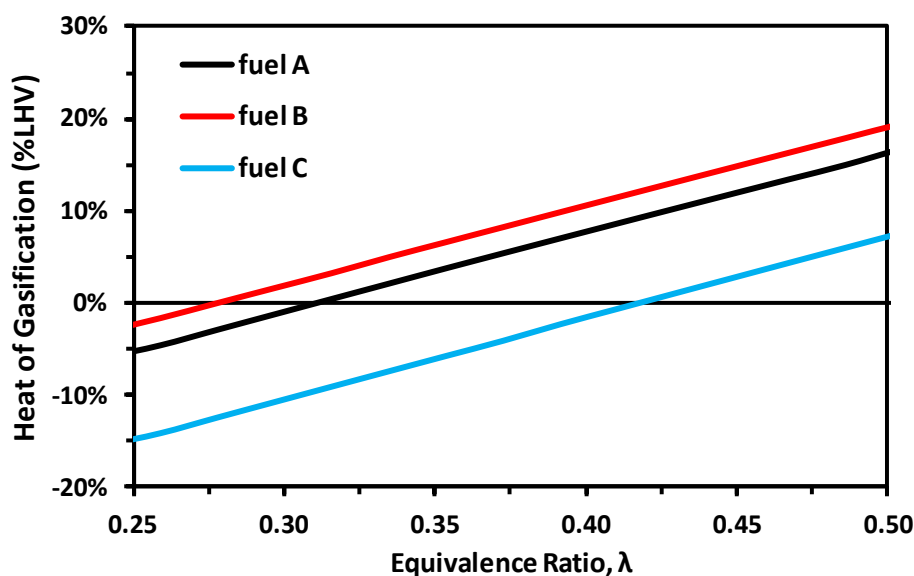


Figure 13. Gasifier required or rejected heat for maintaining the operation at 800°C .

Figure 14 correlates what is previously discussed as far as the efficiency is concerned. The bullets indicate the points where there is autothermal conditions. Curves of LHV and CGE for three cases are almost the same. However, for $\lambda=0.31$ fuel B is gasified without requiring heat, fuel C need around 10% of total heat input and fuel A yields 5% heat.

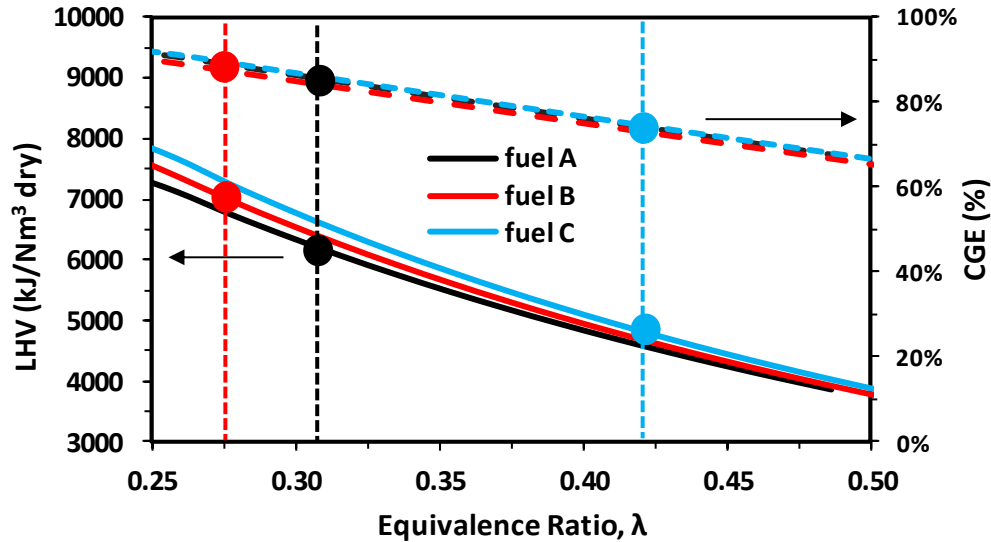
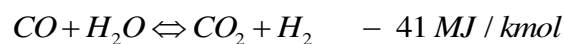


Figure 14. LHV of dry syngas and cold gas efficiency for three types of fuel (the bullets indicate the points where there is autothermal conditions)

b- Temperature effect

Gasification temperature does not have considerable effect on the thermodynamic of syngas composition (Figure 15). In that case the validity of assuming a constant methane composition has to be revised and checked. A principle reaction that determines syngas composition is Water Gas Shift reaction:



As the temperature rises the reaction equilibrium shifts at the right side and benefits CO and H₂O production. Hence, heating value increases at elevated temperatures.

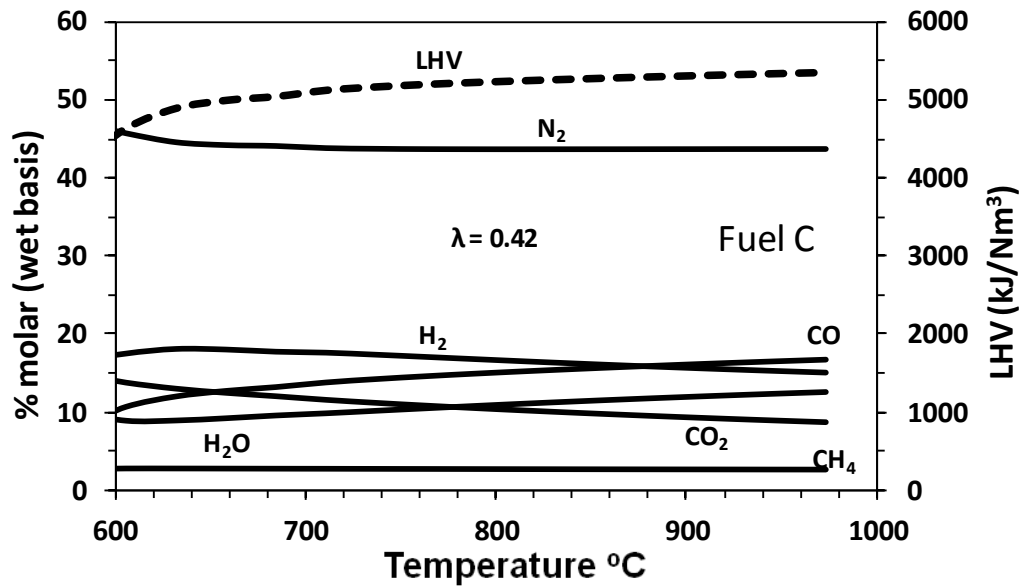


Figure 15. Effect of temperature of syngas quality (Fuel C, autothermal conditions)

The process efficiency is affected by the operating gasifier temperature. Lowering the reactor temperature, autothermal conditions can be achieved with less oxidant (air) flow rates (Figure 16). However, special attention should be paid for ensuring complete char gasification. Thus, an acceptable range for operational temperature would be 850-900 °C.

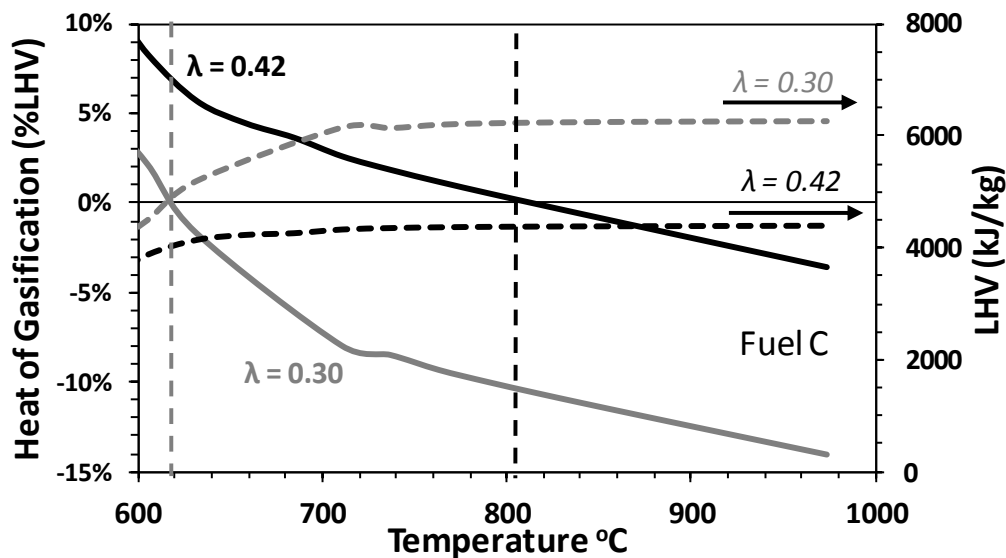
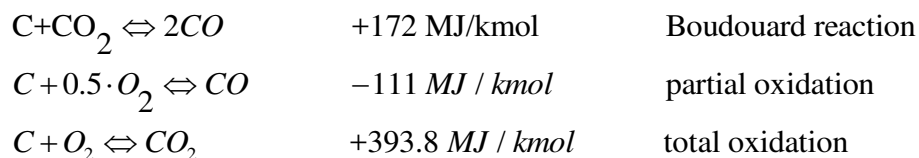


Figure 16. Heat of gasification (required or rejected) and raw syngas LHV (fuel C)

The efficiency of the process is tightly related with the rate of solid carbon conversion i.e. the fixed carbon that is gasified. The major reactions that carbon solids take part are the Boudouard reaction and the reactions with oxygen:



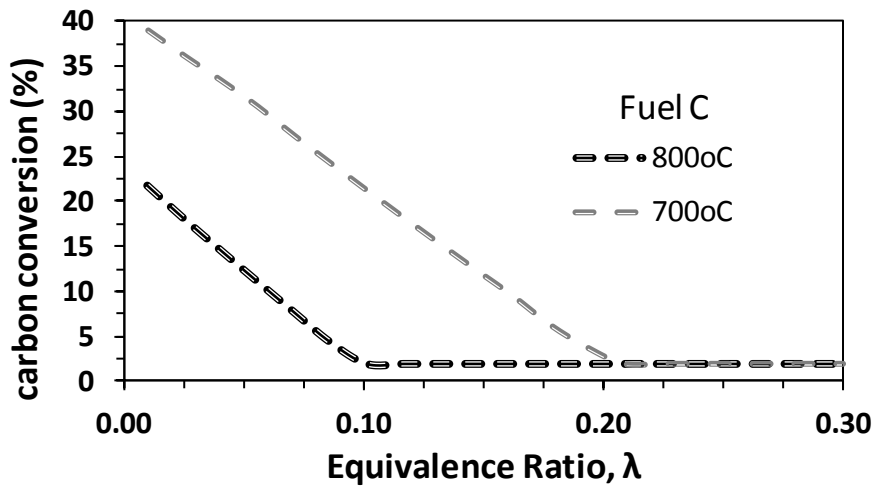


Figure 17: Effect of temperature on the carbon conversion efficiency (Fuel C)

Figure 17 shows the effect of these low equivalence ratios as well as temperature on the carbon conversion. In case of fuel C, thermodynamic equilibrium predicts that carbon solids can be gasified for equivalence ratio rates greater than 0.2. Lowering the operational temperature the corresponding critical values reduces, too. However, the demand for autothermal conditions in the reactor pushes this value up. Several other factors also contribute to the solid carbon gasification like kinetic rates, fluid dynamics of the flow, etc. that in this analysis are not taken into account but for assuming maximum carbon conversion efficiency equal to 98%.

c- Air preheating

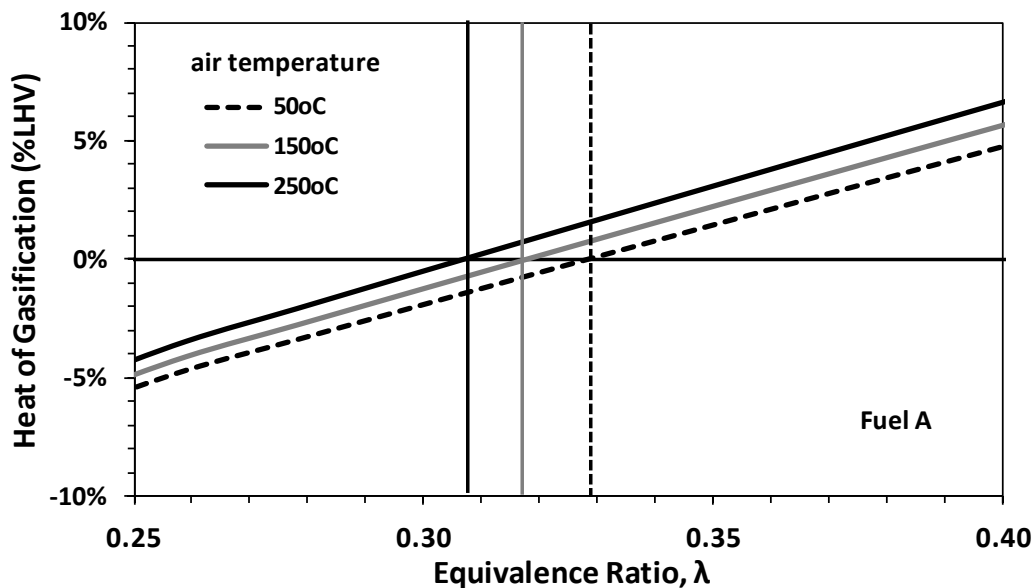


Figure 18: Effect of air preheating on process operation

Figure 18 shows that air preheating can reduce the required quantity of air for isothermal conditions up to 2%. For constant gasification temperature and provided that maximum of carbon conversion is achieved, the less the oxidizing agent enters to the reactor, the higher the heating value of the produced gas. High preheating rates can be achieved recovering heat from the hot raw syngas. However, assuming constant gasification temperature, the change in air temperature inlet does not have effect on CGE.

5 Conclusions

- From the proximate analysis it is found that magazine paper has a high percentage of ash concentration in contrast with other types of paper. The existence of magazine paper in the RDF influences the percentage of ash measured. On the contrary, the plastic fraction of the RDF contains very low percent of ash. The ash percentage measured does not impose a factor that will create a critical problem during the gasification tests.
- From the proximate analysis and regarding the moisture, RDF presents an increased percentage of total moisture measured in all types of paper and plastic. This may be caused due to the existence of other materials high in moisture, in RDF.
- High moisture content in the input fuel leads to low heating value. By assuming a constant mass insertion rate of the fuel, a need for increased thermal input in order to keep constant the total thermal input
- No specific conclusions can be conducted from volatiles and fixed carbon concentrations calculated, since the volatiles can be constituted from different kinds of simple and complex hydrocarbons, which influence differently the chemical equilibrium of the reactions taking place during the gasification procedure.
- According to the ultimate analysis of the RDF, carbon and hydrogen measured is closer to the percentage concentration of paper. As far as nitrogen is concerned, the measured concentration is several times more than the ones measured in all papers and plastic, except Polyamide (PA).
- The chlorine (Cl) concentration calculated is believed to originate mainly from PVC, a plastic with high chloride concentration, while the quantity measured is not believed to cause any significant technical disorders or environmental problems.
- Regarding HHV, it is closer to the paper's, a fact, which depicts that the paper fraction is considerably higher than the plastic fraction. Moreover the average value of the lower heating value is higher than that of the tetra packs in dry basis, while in as received basis it is notably lower.
- From the gasification analysis it is found that fuel drying has positive effects on the process so a drying system should be added, in case of the utilization of refused derived fuels with increased moisture content.
- Moreover, fuel quality has considerable effect on process specification. This is represented by how the increase of content in ash requires greater equivalence ratio

- As studied in a process modeling scenario, heat recovery from raw syngas cooling for air preheating will increase process efficiency
- The optimal operational temperature, regarding carbon conversion and gasification efficiency should be around 700-800°C based on the process simulation results

6 Literature

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