Exploitation of Refused Derived Fuel for energetic uses via gasification and recycling of CO₂ streams

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Abstract

The aim of this work was to investigate the possibility of exploitation of RDF to energetic uses, via gasification with agricultural and forestry residues and recycling of CO_2 streams. The efficiency of the process, the reaction rate and the reactivity of raw materials and their mixtures with RDF were evaluated. A kinetic model was developed for predicting the characteristic kinetic parameters of the chars. The samples were gasified in a thermogravimetric analyzer, using CO_2 as the gasifying agent. The obtained data were modeled for kinetic study, employing an independent parallel reaction's (IPR) model.

The gasification took place above 600°C for all samples. RDF was found to have the lowest reaction rate, reactivity and conversion to CO, while its mixture with pine needles had the highest values of these parameters among mixtures. Activation energy values and reaction order varied between 166-280 kJ/mole and 0.50-1.06, respectively. The kinetic model fitted the experimental results accurately.

Keywords: Municipal wastes, Gasification, Carbon dioxide, Kinetics

1. Introduction

Nowadays, energy consumption and the output of wastes have rapidly increased, due to population growth and economic development. The handling and disposal of these wastes is of vital importance, because of their impact on the environment and human health [1]. Thermal treatment is a very appealing method that can replace other waste management techniques such as ocean dumping, landfill disposal and incineration and can be used in order to produce energy.

Municipal Solid Wastes (MSW) are generated by virtually every activity of modern industrial society. Refused Derived Fuel (RDF) is a fraction of municipal solid waste, consisting of components such as synthetic and natural polymers which are very challenging to manage, due to the fact that they demand very long time in order to degrade, as well as a big number of available sites for landfilling. However, it is a very efficient fuel for producing useful products. Methods such as pyrolysis and gasification can be utilized for retrieval of chemicals and energy from RDF.

Gasification is a green technology producing a fuel gas suitable for gas engines, gas turbines, synthesis of biofuels and chemicals and can contribute to the solution of the energy problem, due to its high thermal efficiency [2-5]. The gasification process in fixed bed units is based on three successive stages: a) drying of the biomass, b) devolatilization of biomass forming char and volatiles and c) gasification where the char reacts with the gasifying agent (CO₂, H₂O, O₂), producing synthesis gas rich in CO and H₂ [6-8]. Devolatilization and gasification should be examined together in order to understand the mechanisms of gasification. Gasification of char is the rate controlling step and the study of the kinetic parameters of this stage is of vital importance for developing new technologies, optimization of the process and designing of the gasifier [9-11].

Carbon dioxide gasification can be described by the Boudouard reaction, in which CO_2 reacts with carbon producing CO [12]. This reaction is endothermic and the equilibrium does not favor CO production, unless the temperature is above 700°C [13,14]. The Boudouard reaction can contribute to the mitigation of the greenhouse effect, as CO_2 which is the main greenhouse gas is being captured and used to produce fuel gas. Understanding the mechanism of the Boudouard reaction is very important, both for describing the phenomenon and for modeling of the process. Various theories have been formulated concerning the mechanism of the reaction [2,15-17].

The most widely used mechanism involves [18]:

 $C_f + CO_2 \leftrightarrows C(O) + CO$

 $\mathrm{CO} \rightarrow \mathrm{CO} + \mathrm{C_f}$

where C_f represents an active site and C(O) a carbon-oxygen complex. The presence of CO produces an inhibiting effect by lowering the steady state concentration of C(O). The first equation describes the oxygen exchange phenomenon, while the second one the conversion of carbon from solid to gas.

The aim of this work was to investigate the possibility of exploitation of RDF to energetic uses, via gasification with agricultural and forestry residues and recycling of CO_2 streams. The objective was to evaluate the efficiency of the process, the reaction rate and the reactivity of raw materials and their mixtures with RDF. Furthermore, a kinetic model was developed for predicting the characteristic kinetic parameters of the chars. The obtained data should be useful in designing and operating efficient gasification systems, to upgrade residual streams for energy production and concomitantly protect the environment.

2. Materials and Methods

2.1 Materials preparation and characterization

The materials used in the present study were: cotton residue (COT) from a cotton ginning factory, grape husks (GH) from a spirit making unit in the region of Apokorona in Crete, pine needles (PIN) from a forest in Crete and Refuse Derived Fuel (RDF) from the solid wastes management enterprise of the region of Chania, in Crete. RDF sample consisted of biodegradable organic materials, paper from magazines, newspapers, packaging and plastic.

The preparation procedure was as follows. Representative samples were taken in order to determine the initial moisture and then the materials were air-dried, homogenized, riffled, milled in a cutting mill and sieved to a particle size of $< 200 \mu m$. Mixtures of cotton residue, pine needles and grape husks with RDF, with a mass ratio of 70:30, were also prepared.

Each biomass sample was characterized according to European standards CENT/TC335. For proximate analysis programmable laboratory furnaces were used, while ultimate analysis was conducted using a Flash 2000 CHNS analyzer. For calorific value a Leco AC-300 calorimeter was used.

2.2 Gasification experiments and data processing

The experimental system used for the gasification tests was a TG/DTG thermogravimetric analyzer of Perkin Elmer. The precision of temperature measurement was $\pm 2^{\circ}$ C and the microbalance sensitivity was $<5\mu$ g. The weight loss and rate of weight loss were recorded continuously under dynamic conditions, as functions of time or temperature, in the range of 25°C-950°C. All experiments were carried out under nitrogen/CO₂ atmosphere, with a flow rate of 35ml/min. Small masses (25mg) of each material with particle sizes of -200 μ m were used for the experiments.

The experimental procedure was as follows. The sample under test was uniformly spread and weighed directly into the crucible. After flushing with nitrogen, which was used as a purge or cooling gas, the temperature was increased to 110°C and maintained at this value for 15 min, in order to dry out the sample completely. Then the temperature was increased to 350°C and held constant for 30 min, so as to achieve devolatilization. Following pyrolysis, the sample was gasified using carbon dioxide as the gasifying agent. For this purpose, the temperature was increased up to 950°C, until a constant weight was reached. The heating rate was 10°C/min.

From the thermograms obtained during the experiments, the initial and maximum decomposition temperatures T_i and T_{max} , as well as the temperature at the end of the gasification process (T_f) were determined. The maximum rate of weight loss (R_{max}) was defined, too. Gasification reactivity was calculated by the following equation:

$$R_f = \frac{R_{max}}{T_{max}({}^{\circ}K)} \times 100 \left(\frac{min^{-1}}{{}^{\circ}K}\right)$$
(1)

Yield of CO was calculated based on the sample's mass value at 600°C and 950°C:

$$CO Yield = \frac{m_{600} - m_{950}}{m_{600}} \times 100(\%)$$
⁽²⁾

2.3 Kinetic model

In this work, an independent parallel reaction's (IPR) model was developed for the kinetic analysis of the gasification process. According to this model, the decomposition of biomass is described by a number of independent parallel reactions. Thus, the rate of conversion of each reaction i was expressed by the following equation:

$$\frac{da_i}{dt} = A_i \exp(\frac{-E_i}{RT}) P_{CO_2}^{\nu} f(a_i)$$
(3)

where α_i is the reacted fraction, A_i the pre-exponential factor, E_i the activation energy, R the universal gas constant, T the absolute temperature, P_{CO2} the partial pressure of carbon dioxide, v the reaction order with respect to gas partial pressure and $f(\alpha_i)$ describes the change of surface reactivity as a function of the fractional conversion:

$$f(a_i) = (1 - \alpha_i)^{n_i} \tag{4}$$

where n is the reaction order with respect to char conversion.

To include the char heterogeneity into the model, it was assumed that a char sample was a mixture of components with different reactivities:

$$-\frac{dm}{dt} = \sum_{k} c_{k} \frac{da_{k}}{dt} \quad i = 1, 2, 3, \dots, N$$
(5)

where dm/dt is the mass loss rate, k the component, c_k the contribution of the partial reaction to the overall mass loss m_o-m_{char} and α_i the conversion rate $m_{o,i} - m_i/m_{o,i} - m_{char}$.

In the kinetic analysis the nonlinear least squares algorithm was used, which defines kinetic parameters that minimize the objective function:

$$O.F. = \sum \left[\left(\frac{dm}{dt}\right)^{exp} - \left(\frac{dm}{dt}\right)^{calc} \right]^2 \tag{6}$$

where (dm/dt)^{exp} and (dm/dt)^{calc} are the experimental and calculated curves, respectively.

The deviation between the experimental and calculated curves, at the optimal set of parameters, was calculated by the following equation:

$$Deviation (\%) = 100 \frac{\sqrt{0.F.(z-N)}}{\max(-\frac{dm}{dt})^{exp}}$$
(7)

where z is the number of data points and N is the number of parameters employed in the model.

3. Results and discussion

3.1 Characterization of fuels

The proximate and ultimate analyses, as well as the calorific values of the samples under study, are shown in Table 1. As can be seen, all samples were characterized by high amounts of volatile matter and low content of ash. RDF displayed the highest percentage of volatiles and ash and the lowest in fixed carbon. As for the ultimate analysis, the carbon and hydrogen contents were similar for all biomass materials, while RDF had the highest percentage in both cases. The percentages of nitrogen and sulfur were generally very low for all the samples. The higher carbon and hydrogen contents, in conjunction with the lower oxygen content of RDF, resulted in a higher calorific value, as compared to the other three samples.

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Sample	Volatiles	Ash	Fixed	С	Н	Ν	0	S	HHV ^a	
			Carbon						(MJ/kg)	
PIN	76.7	5.9	17.4	47.7	6.8	0.2	39.3	0.07	21.1	
COT	75.4	8.9	15.7	41.5	6.0	1.1	42.3	0.24	17.8	
GH	72.1	14.7	13.2	49.4	6.5	2.6	26.4	0.45	25.7	
RDF	85.0	15.0	0.05	52.9	8.3	0.3	23.7		30.9	

Table 1				
Proximate analysis,	ultimate analysis an	d calorific value	of raw materia	als (% dry weight)

^a Higher heating value

3.2 Thermal decomposition characteristics

The characteristic parameters of gasification for all raw materials and their mixtures, are represented in Table 2. The DTG curves of the biomass samples, are compared in Fig.1, while those comparing the raw materials with their mixtures with RDF, are presented in Fig.2.

As seen in Table 2, the gasification process started above 600°C for both raw materials and mixtures. The thermal decomposition of RDF started at a much higher temperature, as compared to the other samples. RDF presented the lowest values of maximum reaction rate, reactivity and yield of CO, while pine needles/RDF had the highest values of these parameters among the mixtures. Grape husks demonstrated the highest value of maximum reaction rate and yield of CO and was the most reactive in comparison to the other samples. However, the mixture grape husks/RDF had the lowest reaction rate, reactivity and CO conversion of all mixtures.

As can be observed, the initial reaction temperature of mixtures was almost identical to that of raw fuels, indicating that the thermal behavior of each component in the mixture was independent.

Sample	$T_i(^{\circ}C)$	T_{max}	R _{max}	$R_{\rm f}$	T_{f}	Yield of CO	
		(°C)	(10 ² /min)	(10 ² /minK)	(°C)	(%)	
PIN	679	871	4.7	1.31	950	75.2	
COT	690	837	4.5	1.18	912	66.8	
GH	668	864	5.7	1.58	906	82.3	
RDF	722	808	3.3	1.07	900	58.4	
PIN/RDF	679	854	4.7	1.39	920	77.9	
COT/RDF	685	837	4.3	1.22	912	70.9	
GH/RDF	668	816	3.9	1.08	906	68.2	

Table 2

Characteristic parameters of gasification



Fig. 1. DTG profiles of raw materials

3.3 Kinetics

The kinetic parameters calculated by the model are summarized in Table 3, both for all raw materials and mixtures. Fig.3 illustrates the good fit of the kinetic model to the experimental values obtained for grape husks. Similar fits were obtained for all samples.

As concerns the raw materials, the gasification process was described by one reaction for all samples, except for grape husks. Activation energy values and reaction orders varied between 166 and 280 kJ/mole and 0.50-1.06, respectively. Grape husks displayed the highest activation energy value, while pine needles the lowest.

Activation energy for mixtures was found to be between 193-225 kJ/mole and reaction order varied from 0.57 to 0.86. Cotton/RDF presented the highest activation energy among the mixtures, while pine needles/RDF displayed the lowest.

The values of kinetic parameters, for both raw materials and their mixtures with RDF, were within the limits suggested by literature [19,20] and were typical of CO_2 gasification of biomass materials.







Fig. 2. DTG profiles of mixtures: a) COT/RDF, b) PIN/RDF, c) GH/RDF in comparison to the raw componets

Sample	Kinetic parameters	Reaction 1	Reaction 2
PIN	A (1/min)	6.76·10 ⁶	
	E (kJ/mole)	166	
	c (%)	100	
	n (%)	0.50	
COT	A (1/min)	$1.40 \cdot 10^{11}$	
	E (kJ/mole)	250	
	c (%)	100	
	n (%)	0.78	
GH	A (1/min)	$5.55 \cdot 10^{10}$	$2.80 \cdot 10^{13}$
	E(kJ/mole)	246	280
	c (%)	68	32
	n (%)	0.50	1.06
PDF	Λ (1/min)	$1.02 \ 10^7$	
RDI	\mathbf{F} (l/molo)	1.02.10	
	C(%)	100	
	n (%)	0.50	
PIN/RDF	A (1/min)	$1.83 \cdot 10^{8}$	
	E (kJ/mole)	193	
	c (%)	100	
	n (%)	0.57	
COT/RDF	A (1/min)	$1.08 \cdot 10^{10}$	
	E (kJ/mole)	225	
	c (%)	100	
	n (%)	0.59	
GH/RDF	A(1/min)	254.10^9	
	F(kI/mole)	2.54 10	
		100	
	n (%)	0.86	
	()	0.00	

Table 3Kinetic parameters of gasification



Fig. 3. Kinetic evaluation for grape husks gasification

4. Conclusions

All biomass materials were characterized by high amounts of volatiles and low content of ash. RDF had the highest amounts of volatile matter, ash and calorific value and the lowest in fixed carbon.

The gasification process was initiated above 600°C for both raw materials and mixtures. RDF displayed the lowest values of reaction rate, reactivity and yield of CO. Pine needles/RDF was proved to be the most reactive among the three mixtures, in contrast to grape husks/RDF.

High activation energy values were required in order for the Boudouard reaction to take place, which ranged from 166 to 280 kJ/mole. The reaction order varied from 0.50 to 1.06. The kinetic model fitted the experimental results with great accuracy.

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