



## Investigating the Valorisation of Refused Derived Fuel for Energetic Uses Through Its Co-Gasification with Woody Wastes

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### ABSTRACT

The present study aimed to investigate the valorization of Refused Derived Fuel (RDF) produced from solid waste management units for energetic uses, through its co-gasification with agricultural or forest wastes and carbon dioxide agents. Experiments were conducted using a fixed bed reactor and a thermal analysis system. The thermal behavior, the reactivity, the conversion, and the cold gas efficiency up to 950°C were evaluated based on the structural characteristics and inherent minerals of the materials, as well as on the basis of alkali catalysts and bio-oils admixed. Kinetic analysis of the co-gasification process was performed by developing an independent parallel reactions model. Blending RDF with the woody wastes at mass ratios 30:70 increased the conversion from 55% up to 86.4%. Gasification reactivity followed the order cotton stems>sunflower>pine cones>RDF. The addition of alkali compounds at low loadings as external catalysts enhanced conversion up to 100% and the process, in general, took place at much lower temperatures. The catalytic activity followed the order: CaO> Li<sub>2</sub>CO<sub>3</sub>>K<sub>2</sub>CO<sub>3</sub>. The addition of bio-oil at ratios 1:1 increased the conversion up to values 85-92%. The kinetic model applied was proven very successful, with deviation values below 5%. In presence of 10% wt, CaO the activation energy values of biochars were lowered from 148-252 kJ/mol to 138-201 kJ/mol, implying a better performance.

**Keywords:** RDF, co-gasification, Carbon dioxide, Alkali, Kinetics

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### INTRODUCTION

The generation of urban wastes has increased tremendously in recent years, due to the rising population and industrialization around the world. Accumulation in landfills is a major issue, due to the limited number of available sites, the high cost, and the environmental restrictions (Bondarczuk *et al.*, 2016). Thus, thermal treatment of these wastes for energy production, destroying pathogens and other pollutants, seems an attractive solution, in view also of global crisis. It has been estimated that urban wastes could contribute to energy consumption from 1 to 3 EJ/y worldwide (Vamvuka, 2009).

The majority of waste-to-energy systems are based on combustion. However, air pollution from incineration plants was the driving force for the development of gasification technologies, which offer the advantages of higher efficiency, reduced emissions, and greater flexibility in terms of scaling, feedstocks, and end products (Vamvuka & Sfakiotakis, 2015; Hla *et al.*, 2016). A two-stage process in fixed bed appliances, where the first step is pyrolysis of wastes and the second step reaction of char with carbon dioxide as the gasifying agent, presents several benefits. Bio-oil and gases produced during the first step can be used as sources of chemicals and energy (Policella *et al.*, 2019), leaving a highly reactive bio-carbon to be converted to fuel gas free of tar (Vamvuka & Sfakiotakis, 2015). Furthermore, the use of the principal constituent of industrial flue gases

causing global warming, as a post-treatment technique, gives a potential solution to the greenhouse gas effect.

The reaction of char with carbon dioxide, the so-called Boudouard reaction, is a slow process proceeding at high temperatures. For the design of gasifiers, kinetic analysis is required. Nth order kinetics has been commonly applied for particle sizes below 1mm when the reaction is chemically controlled (Lahijani *et al.*, 2015; Sathwani *et al.*, 2016). Various models have been employed, such as iso-conversional models (Zhao *et al.*, 2017; He *et al.*, 2021), the volume reactor model (Xu *et al.*, 2016; Diedhiou *et al.*, 2019), the shrinking core model (Sathwani *et al.*, 2016; Xu *et al.*, 2016; Diedhiou *et al.*, 2019) and the random pore model (Xu *et al.*, 2016; Diedhiou *et al.*, 2019; He *et al.*, 2021). Isoconversional methods introduce approximations, whereas the random pore model has been proven quite successful, however, it is very complex.

The reactivity of char in the above models accounts for temperature, partial pressure of reactant, and structural characteristics. Other factors found to affect reactivity are the conditions of the pyrolysis step (Min *et al.*, 2011; Li *et al.*, 2017) and the composition of fuel ash. Inherent mineral matter, such as K, Na, Ca, and Fe compounds, have been reported (Bouraoui *et al.*, 2016; Naidu *et al.*, 2016) to improve gasification reactivity. Thus, carbonates, oxides, or chlorides of these metals were used as effective external catalysts (Vamvuka *et al.*, 2012; Lahijani *et al.*, 2015; Sathwani *et al.*, 2016).

Urban solid waste streams are highly heterogeneous, making their thermal treatment difficult (Mohammadi *et al.*, 2020). Their high moisture content and ash content, lowering the calorific value, and the presence of hazardous species (Vamvuka

et al., 2018) may pose serious limitations in energy enterprises. Therefore, blending with higher quality woody residues is often mandatory, to accelerate their promotion for energy recovery. There is insufficient data throughout the literature on the gasification behavior of urban wastes or their kinetics, while there is a lack of information on their co-gasification with woody agricultural or forest residues. In a previous study (Kwon et al., 2010) the gasification of municipal solid wastes (MSW) under various concentrations of carbon dioxide was investigated and the effects of waste-to-polymer ratios on product yields were explored. Some authors (Arafat & Jijakli, 2013; Alruwaili et al., 2022) developed a simple equilibrium model to examine the effects of operating temperature and different MSW compositions on the performance of the process, without considering reaction kinetics, whereas others (Hla et al., 2016) calculated intrinsic reaction rates. More recently, the characteristics of hydrogen and syngas formation were determined for MSW (Zheng et al., 2018) at different carbon dioxide/steam ratios and gasification temperatures. According to the above discussion, the present study aimed to investigate the valorization of refused-derived fuel (RDF), produced from urban solid waste management units, for energetic uses, through its co-gasification with agro- or forest wastes and carbon dioxide agents. (Shihab et al., 2019). The thermal behavior, the reactivity, the conversion, and the cold gas efficiency were evaluated based on the structural characteristics and inherent minerals of the materials, as well as on the basis of alkali catalysts and bio-oils admixed. Kinetic analysis of the co-gasification process was performed by developing an independent parallel reactions model.

## MATERIALS AND METHODS

### Selected waste materials

Aiming to improve the gasification reactivity of the municipal solid waste material of this study, a variety of biomass fuels, abundantly found in Greece and Mediterranean countries in general, were selected. These were Sunflower or Helianthus annuus L. (SUN) a short rotation coppice crop provided by Pettas A.E. Company, one agro-industrial waste Cotton stems (CST) provided by a cotton ginning factory, as well as a forest waste Pine cones (PCO), collected from a local forest in Crete island. Refused Derived Fuel (RDF) was obtained from the solid waste management company of Chania, Crete, named DEDISA. After air drying, all samples were riffled and ground in a cutting mill to a particle size below 1 mm. Representative samples were characterized in terms of proximate and ultimate analysis, following European standards CEN/TC335. Structural characteristics were determined according to the BET method, using an analyzer model Nova 2200 of Quantachrome. Prior to tests, materials were out-gassed overnight at 110 °C, under vacuum. Mineral species were identified by an X-ray fluorescence spectrometer, model S2 Ranger/EDS of Bruker AXS.

### Preparation of biochars

Raw materials and mixtures of agricultural and forestry wastes with RDF at mass ratios 70:30 were devolatilized in a fixed bed unit (Tefiki, 2021). The reactor was charged with about 15 g of sample, flushed with nitrogen (flow rate 200 mL/min) for 30 min at room temperature, and heated up to 600°C, with a

heating rate of 10°C/min. Volatiles were passed through isopropanol, ice-cooled baths, to collect liquid fractions, from which bio-oil was collected after centrifugation at 6000 rpm for 20 min from the top layer. Following a retention time of 30 min at 600°C, the reactor was cooled under nitrogen and the solid biochar was weighed and characterized with the same methods as for raw fuels. Also, each biochar, before being used in the gasification tests, was ground to a particle size below 200 µm, to conduct the experiments under a kinetic regime.

### Gasification tests

Gasification experiments were carried out in a TG/DTG thermobalance of Perkin Elmer, with temperature precision ±2 °C and sensitivity <5 µg. About 15 mg of each biochar was gasified in a carbon dioxide atmosphere of flow rate 35 mL/min up to 950°C, with a heating rate of 10°C/min, until a constant weight was reached. Two to three replicates confirmed the high reproducibility of the results, expressed by the relative standard deviation RSD reported below.

External catalysts were purchased by Sigma-Aldrich company and consisted of pure carbonates of calcium, potassium, and lithium. Calcium carbonate was calcined at 1000°C, to avoid interference with DTG curves at high temperatures, due to its decomposition above 700°C. Catalyst loading was performed according to the incipient wetness method and ranged from 0.1 to 0.5 gMe/gC in char (Vamvuka et al., 2012; Sadhwani et al., 2016). For mixtures of biochars with the bio-oils, a mass ratio of 1:1 was chosen.

From processing of weight loss (TG) and rate of weight loss (DTG) curves as a function of temperature, the initial ( $T_i$ ) and peak inflection ( $T_{max}$ ) temperatures, as well as the peak reaction rate ( $R_{max}$ ) were determined, whereas gasification reactivity was defined according to the equation:

$$R_r = R_{max} / (T_{max}) \times 100 \text{ (min}^{-1}/^{\circ}\text{C)} \quad (1)$$

Gasification efficiency was expressed by:

$$CCE = \frac{m_{CO}}{m_{bioch}} \times 100(\%) \quad (2)$$

where  $m_{CO}$  and  $m_{bioch}$  are the masses of product gas CO and initial biochar, respectively.

The cold gas efficiency was calculated as follows:

$$CGE = \frac{m_{CO} LHV_{CO}}{m_{bioch} LHV_{bioch}} \times 100(\%) \quad (3)$$

where  $LHV_{CO}$  and  $LHV_{bioch}$  are the lower heating values of CO gas and biochar in MJ/kg, respectively.

### Mathematical modeling of kinetics

The independent parallel reactions model (IPR) was developed for the kinetic analysis of the carbon dioxide gasification of the materials studied. The decomposition of the various pseudo-components was described by parallel reactions so that the overall conversion was the sum of all partial values for k reactions:

$$\frac{d\alpha}{dt} = \sum_i c_i \frac{d\alpha_i}{dt} \quad i=1,2,3\dots k \quad (4)$$

where  $c_i$  is the contribution factor of each pseudo-component. The conversion rate of each reaction  $i$  was expressed as follows:

$$\frac{da_i}{dt} = A_i \exp\left(\frac{E_i}{RT}\right) P_{CO_2}^{\nu} f(\alpha_i) \quad (5)$$

where  $\alpha_i$  the degree of conversion,  $t$  the time,  $A_i$  the pre-exponential factor,  $E_i$  the activation energy,  $R$  the universal gas constant,  $T$  the absolute temperature,  $P_{CO_2}$  the partial pressure of carbon dioxide,  $\nu$  the reaction order and  $f(\alpha_i)$  a function of fractional conversion reflecting the change of reactivity:

$$f(\alpha_i) = (1 - \alpha_i)^{n_i} \quad (6)$$

where  $n_i$  is the reaction order with respect to char conversion.

The optimal parameters, that minimized the difference between experimental and calculated rate, were derived from the development of an algorithm in Matlab® code (gradient-based minimization function `fmincon`):

$$OF = \min \sum_{j=1}^N \left[ \left( \frac{d\alpha_j}{dt} \right)_{\text{exp}} - \left( \frac{d\alpha_j}{dt} \right)_{\text{cal}} \right]^2 \quad (7)$$

where  $(d\alpha/dt)_{\text{exp}}$  and  $(d\alpha/dt)_{\text{cal}}$  are the experimental and calculated conversion rates, respectively, and  $N$  is the number of experimental points.

The deviation between experimental and calculated DTG curves by the model was determined by the following equation:

$$dev(\%) = 100 \frac{\sqrt{OF(N-Z)}}{\max\left(\frac{d\alpha}{dt}\right)_{\text{exp}}} \quad (8)$$

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

## RESULTS AND DISCUSSION

### Proximate and ultimate analyses of raw materials and biochars

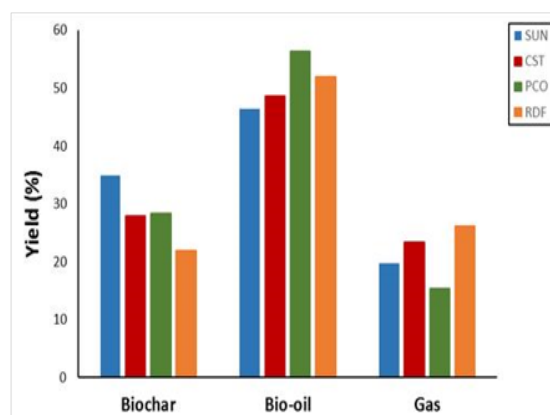
From the proximate and ultimate analysis results in **Table 1**, it can be seen that the volatile percentage of biomass materials varied between 73% and 77% (at 950°C), whereas that of ash was between 5% and 9%. RDF presented the highest volatile content (85%) and a very low concentration of fixed carbon. The increased carbon and hydrogen content of this municipal solid waste, in conjunction with the lower oxygen content in comparison to the other samples, resulted in a higher calorific value. The amount of sulfur was low for all fuels, implying insignificant emissions during the process. On the other hand, the amount of nitrogen was low for CST, PCO, and RDF, but rather high for SUN, implying the evolution of some nitrogenous species during thermal treatment.

**Table 1.** Proximate and ultimate analysis of raw materials and biochars (% dry weight)

	Volatiles	Fixed carbon	Ash	C	H	N	S	O	HHV <sup>a</sup> (MJ/kg)
SUN	72.8	20.1	7.1	43.1	6.3	2.7	0.2	40.6	18.4
SUN <sub>b</sub>		79.0	21.0	58.6	1.7	1.7	-	17.0	24.9
CST	76.0	15.3	8.7	42.2	6.1	1.0	0.2	41.8	18.0
CST <sub>b</sub>		72.4	27.6	64.8	1.8	0.6	-	5.2	32.6
PCO	77.0	17.6	5.4	47.9	6.7	0.2	0.06	39.7	21.2
PCO <sub>b</sub>		81.2	18.8	62.2	1.8	1.0	-	16.2	26.1
RDF	85.0	0.05	15.0	52.9	8.3	0.3	-	23.7	30.9
RDF <sub>b</sub>		45.9	54.1	33.9	0.8	0.2	-	10.0	25.7

<sup>a</sup> Higher heating value (dry-ash-free) <sub>b</sub> Biochar

After devolatilization at 600°C, RDF material emitted ~26% of gaseous volatiles and 52% of condensable volatiles, thus producing a lower amount of biochar ~22%. **Figure 1** compares the yield of pyrolysis products of all samples. Furthermore, from **Table 1** it can be noticed that after the evolution of H-, O-, N- and S- bearing compounds by thermal decomposition, the concentrations of these elements were greatly reduced, leaving a solid material enriched in carbon and minerals. The higher heating value was in principle enhanced, especially for CST biochar, reaching a value of 32.6 MJ/kg. Therefore, produced biochars were upgraded and cleaner fuels were obtained with respect to raw materials. However, as can be seen, RDF did not follow this trend. Its carbon content and accordingly its higher heating value was decreased upon pyrolysis because in this case carbon was bound in volatile species.

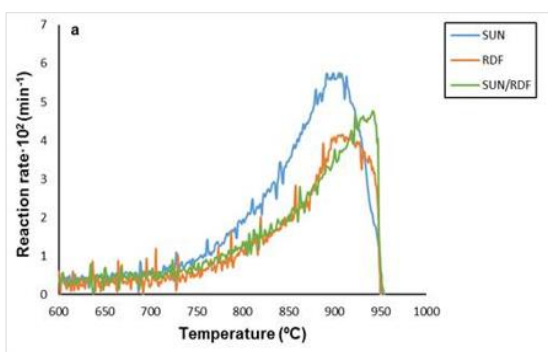


**Figure 1.** Yield of pyrolysis products of raw materials

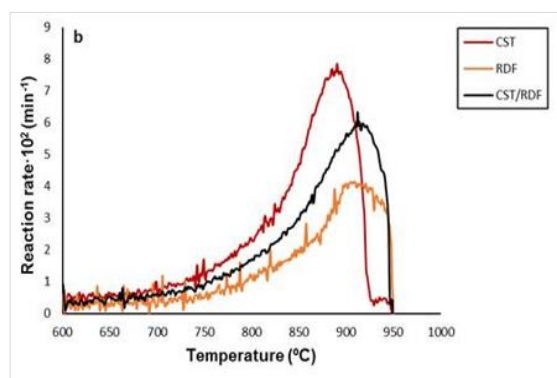
### Gasification characteristics

**Figure 2** compares the DTG gasification profiles of the biochars under study and their blends with RDF material, whereas **Table**

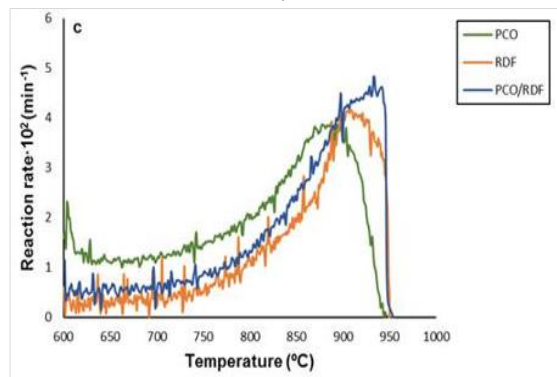
2 summarizes the characteristic parameters of the process. For all fuels, the Boudouard reaction took place above 650°C. Peak inflection temperature occurred around 890°C for PCO and CST samples and around 905°C for SUN and RDF samples. Reactivity  $R_r$  followed the order: CST>SUN>PCO>RDF. Conversion to carbon monoxide ranged between 55% and 95%, while cold gas efficiency between 42% and 54%, agreeing with earlier data for MSW and waste tires biochars, 30-63% (Zheng *et al.*, 2018) and 62.6% (Policella *et al.*, 2019; An *et al.*, 2022), respectively. The highest reactivity and conversion were achieved in the case of CST fuel. When RDF was mixed with the agricultural and forest waste chars, both reactivity and conversion were enhanced, the latter by ~35% to 57%, reaching a value of 86.4% for the CST/RDF mixture. Furthermore, as **Figure 2** shows, the DTG curves of the blends lied between the curves of the individual components, however, peak position was displayed to a higher value (16-38°C) than the expected theoretical value. Taking into consideration that the RSD between replicate experiments was below 2%, this behavior implies some mutual interactions between component fuels, as they reacted within a similar temperature regime.



a)



b)



c)

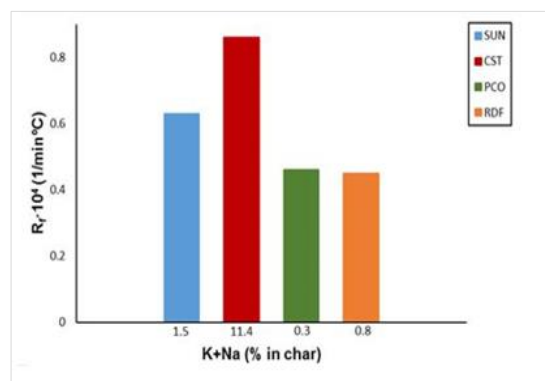
**Figure 2.** DTG gasification profiles of (a) SUN, RDF, SUN/RDF (b) CST, RDF, CST/RDF and (c) PCO, RDF, PCO/RDF fuels (RSD=0.4-1.4%)

**Table 2.** Characteristic parameters of gasification of biochars and RDF blends with catalysts

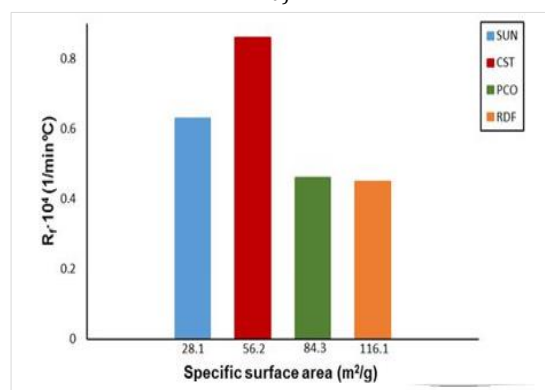
Sample	Catalyst	Catalyst Loading (%)	T <sub>i</sub> (°C)	T <sub>max</sub> (°C)	R <sub>max</sub> (10 <sup>2</sup> /min)	R <sub>r</sub> (10 <sup>2</sup> /min°C)	CCE/CGE (%)	
SUN	-	-	670	906	5.7	0.63	81.0/43.5	
		CaO	10	670	876	4.6	0.52	89.0
		20	670	876	4.3	0.49	100.0	
		30	660	875	4.2	0.48	100.0	
	K <sub>2</sub> CO <sub>3</sub>	10	645	847	4.2	0.49	88.0	
		20	645	811	3.2	0.39	92.0	
		30	635	806	3.2	0.39	95.5	
	Li <sub>2</sub> CO <sub>3</sub>	20	650	872	3.1	0.36	92.0	
		30	650	849	2.7	0.32	100.0	
	Biooil	50	690	940	1.9	0.20	92.0	
CST	-	-	660	891	7.7	0.86	95.0/42.1	
		CaO	10	680	908	4.1	0.45	100.0
		20	-	-	-	-	-	-
		30	-	-	-	-	-	-
	K <sub>2</sub> CO <sub>3</sub>	10	600	898	3.5	0.39	93.4	
		20	600	847	3.0	0.35	95.3	
		30	600	815	2.6	0.32	100.0	
	Li <sub>2</sub> CO <sub>3</sub>	20	600	840	3.5	0.42	99.6	
		30	-	-	-	-	-	
	Biooil	50	690	940	1.8	0.19	87.8	

PCO	CaO	-	670	887	4.1	0.46	86.0/42.8
		10	675	889	4.2	0.47	93.0
		20	675	893	3.2	0.36	100.0
		30	-	-	-	-	-
	K <sub>2</sub> CO <sub>3</sub>	10	600	857	4.4	0.51	88.0
		20	600	819	3.3	0.40	89.1
		30	600	785	2.6	0.33	94.8
	Li <sub>2</sub> CO <sub>3</sub>	20	620	824	3.4	0.41	93.0
		30	600	813	3.2	0.39	100.0
	Biooil	50	600	940	2.1	0.22	91.0
RDF	CaO	-	705	907	4.1	0.45	55.1/49.2
		10	690	853	3.6	0.42	69.0
		20	690	862	3.4	0.39	77.6
		30	690	875	3.4	0.39	96.8
	K <sub>2</sub> CO <sub>3</sub>	10	600	848	3.5	0.41	57.8
		20	600	796	3.3	0.41	58.0
		30	600	791	2.5	0.32	58.3
	Li <sub>2</sub> CO <sub>3</sub>	20	700	800	2.1	0.26	69.2
		30	700	749	1.7	0.23	73.2
	Biooil	50	685	891	1.4	0.16	84.8
SUN/RDF	CaO	-	700	940	4.8	0.51	74.5/54.1
		10	700	877	3.6	0.41	84.6
CST/RDF	CaO	-	696	912	6.3	0.69	86.4/43.6
		10	672	867	5.8	0.67	89.3
PCO/RDF	CaO	-	705	932	4.8	0.52	79.6/42.3
		10	685	911	5.2	0.57	89.9

As discussed in the introduction section, among the many factors affecting gasification reactivity of chars are inherent alkali metals, particularly K and Na, as well as porosity and surface area. In current tests, pyrolysis and gasification conditions were kept the same, so that the effects of the physical and chemical composition of the fuels on reactivity changes could be examined. A plot of reactivity versus alkali K and Na in char, in **Figure 3a**, clearly indicates that the higher reactivity of CST biochar could be assigned to its great content in these metals. The rest of the samples had a very low K and Na concentration. Additionally, plotting reactivity versus specific surface area of biochars in **Figure 3b**, a direct relationship was not observed. From a previous work by the authors (Teftiki, 2021; Enwa *et al.*, 2022) it can be inferred that although the elemental composition of SUN and PCO was similar and the specific surface area of PCO was higher, the latter contained alcohols or carboxylic acids, presenting lower carbonization and aromaticity than SUN biochar, which could affect negatively the gasification rate. On the other hand, RDF fuel although had the highest specific surface area among the samples studied, not only consisted of alcohols and carboxylic acids (Zhang *et al.*, 2017) but also had a very high amount of ash, which presented a physical barrier to the gasifying agent, leading to a drop in rate and reactivity.



a)



b)

**Figure 3.** Reactivity of SUN, CST, PCO and RDF biochars versus (a) alkali K and Na in char and (b) specific surface area

*Influence of external catalysts*

The influence of external catalysts used on conversion and characteristic gasification parameters is illustrated in **Table 2**. As can be observed, for agricultural and forest wastes at catalyst loading 20% wt conversion level reached values between 89% and 100%. For CST biochar, the addition of 10% wt CaO was enough for complete conversion. In the case of  $\text{Li}_2\text{CO}_3$ , a higher amount of catalyst was necessary to achieve loadings of 0.1-0.5 gMe/gC in char. According to the mechanisms of catalytic gasification proposed (Lahijani *et al.*, 2015; Sathwani *et al.*, 2016), alkaline compounds increase the number of active sites or alter the identity and reactivity of the surface intermediates. Moreover, **Table 2** shows that in the presence of all catalysts used (except for CaO added to CST and PCO) the process took place at much lower temperatures, which is very important for reducing slagging/fouling tendencies in gasifiers and at the same time the overall cost (Vamvuka *et al.*, 2012). Initial and peak inflection temperatures were shifted to 30-160°C lower values. In terms of conversion and reactivity, the catalytic activity of alkali compounds under study followed the order:  $\text{CaO} > \text{Li}_2\text{CO}_3 > \text{K}_2\text{CO}_3$ . These findings are in agreement with literature data, including the authors (Vamvuka *et al.*, 2012; Sathwani *et al.*, 2016).

Concerning the mixtures of RDF with SUN, PCO, and CST biochars, it can be noticed that upon addition of 10% wt CaO, which presented a better performance, the gasification process also took place at lower temperatures and the yield of carbon monoxide produced was increased up to 10%.

As already mentioned, one of the objectives of the present work was to investigate the valorization of bio-oil produced from the pyrolysis of biomass materials, through its co-gasification with the biochars. The benefits could be not only economic,

contributing to energy recovery, but environmental too, due to some pollutant oxygenated aliphatic and aromatic compounds contained in these oils (Vamvuka, 2009). **Table 2** clearly indicates that although the gasification rate of biochar/bio-oil blends at high temperatures was lower with respect to biochars, due to thermal decomposition at temperatures between 200°C and 450°C (assigned to acids, alcohols, and phenols) (Zhang *et al.*, 2017), the conversion was significantly increased up to 85-92%.

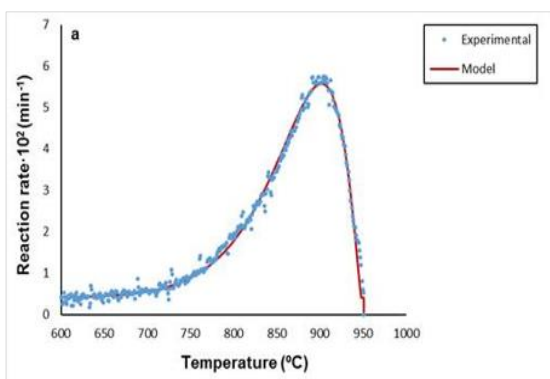
Overall, the above results demonstrate that the gasification efficiency of RDF from a value of 55% was enhanced up to 86.4% when this waste was blended with higher quality agricultural or forest residues or bio-oils and up to 90% when a low amount of CaO external catalyst was also added.

*Kinetic modeling results*

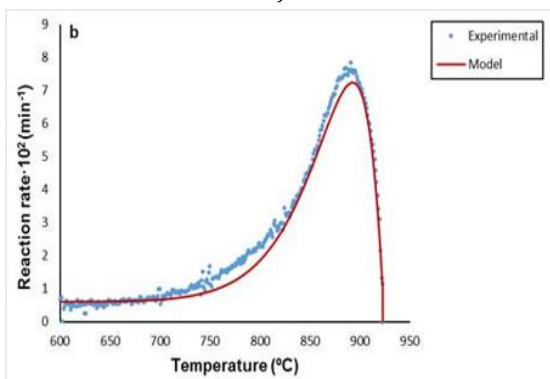
Kinetic analysis results and deviation between experimental and model thermogravimetric curves are represented in **Table 3**. **Figure 4** shows the good fit between the experimental data and model predictions, which varied between 2.3% and 5.4%. All samples were successfully modelled by one pseudo-component. Activation energy values of individual chars were quite high, ranging between 148 kJ/mol and 252 kJ/mol, due to increased aromaticity and thermal stability of the chars after the evolution of volatile species at high temperatures. CST, which was the biochar with the greater reactivity, presented the lowest activation energy value. In reference to the mixtures, from **Table 3** it can be observed that the kinetic parameters varied between those of component fuels. Present results are in agreement with those reported in the literature for agricultural wastes (Vamvuka & Sfakiotakis, 2015; Sathwani *et al.*, 2016; Xu *et al.*, 2016; Edreis *et al.*, 2018; He *et al.*, 2021).

**Table 3.** Kinetic parameters of gasification of of biochars and RDF blends with catalysts

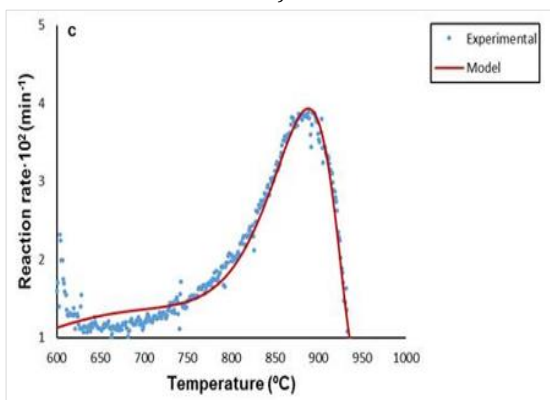
Sample	Catalyst	$E_i$ (kJ/mol)	A ( $\text{s}^{-1}$ )	n	c	Dev (%)
SUN	-	200	$1.6 \times 10^8$	0.5	1	2.3
SUN	CaO	149	$1.0 \times 10^6$	0.8	1	4.9
SUN	Bio-oil	160	$6.3 \times 10^2$	0.6	0.75	4.9
SUN/RDF	-	227	$1.5 \times 10^9$	1.5	1	4.2
SUN/RDF	CaO	210	$1.4 \times 10^9$	0.4	1	2.7
CST	-	148	$5.5 \times 10^5$	0.3	1	5.4
CST	CaO	138	$1.5 \times 10^5$	0.6	1	4.9
CST	Bio-oil	142	$6.0 \times 10^2$	0.6	0.45	1.9
CST/RDF	-	159	$1.4 \times 10^6$	0.40	1	3.1
CST/RDF	CaO	150	$1.4 \times 10^6$	0.60	1	2.5
PCO	-	252	$4.4 \times 10^{10}$	0.7	1	3.4
PCO	CaO	201	$1.7 \times 10^6$	1	1	3.9
PCO	Bio-oil	155	$6.7 \times 10^2$	1	0.45	1.5
PCO/RDF	-	250	$3.2 \times 10^{10}$	0.9	1	4.9
PCO/RDF	CaO	155	$3.0 \times 10^{10}$	0.6	1	2.5
RDF	-	236	$4.6 \times 10^9$	0.5	1	4.4
RDF	CaO	147	$4.3 \times 10^9$	0.9	1	3.7
RDF	Bio-oil	148	$6.7 \times 10^3$	0.6	0.65	4.6



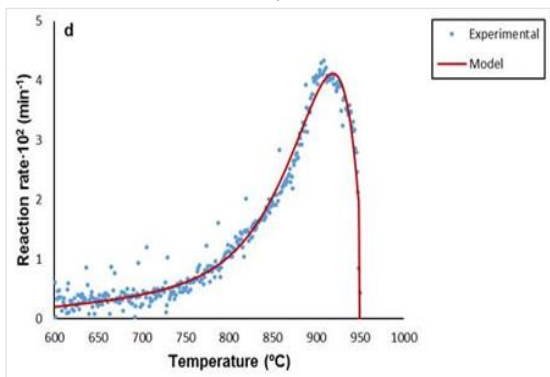
a)



b)



c)



d)

**Figure 4.** Modeling of gasification rate of (a) SUN (b) CST (c) PCO and (d) RDF biochars

Kinetic analysis was also performed for the gasification of biochars studied in presence of the most effective catalyst CaO as shown above, at a low percentage of 10% wt, as well as for the gasification of biochar/bio-oil blends at ratios 1:1. The kinetic parameters are included in **Table 3**. As can be noticed, both addition of external catalysts or bio-oil resulted in a significant reduction in activation energy, which for RDF material was 38%. Activation energy values of raw biochars were lowered from 148-252 kJ/mol to 138-201 kJ/mol. On the other hand, reaction orders of raw biochars were increased from 0.3-0.5 to 0.6-1, revealing a greater dependence of gasification rate on conversion when external catalysts were used. Current data are in line with literature for chemically controlled gasification processes (Sadhvani *et al.*, 2016; Edreis *et al.*, 2018; He *et al.*, 2021).

## CONCLUSION

Conversion of RDF material to carbon monoxide at 950°C was 55%, while that of agricultural and forest wastes was 81-95%. Blending RDF with these wastes at mass ratios 30:70 increased its conversion up to 86.4%. Peak inflection temperature occurred between 890°C and 940°C. Gasification reactivity followed the order CST>SUN>PCO>RDF. In the case of CST biochar, it was correlated to its inherent alkali metals.

The addition of alkali compounds as external catalysts enhanced conversion at low loadings up to 100% and the process, in general, took place at much lower temperatures. The catalytic activity followed the order: CaO> Li<sub>2</sub>CO<sub>3</sub>>K<sub>2</sub>CO<sub>3</sub>. The addition of bio-oil at ratios 1:1 increased the conversion up to values 85-92%. The gasification efficiency of RDF material blended with the woody fuels and 10% wt CaO as catalyst reached values 85-90%.

The kinetic model applied was proven very successful, with deviation values below 5%. In presence of 10% wt, CaO the activation energy values of biochars were lowered from 148-252 kJ/mol to 138-201 kJ/mol, implying a better performance.

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