Catalytic Gasification of Waste Biomass Blends with Carbon Dioxide

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Abstract— Co-gasification of waste biomass materials was studied under carbon dioxide atmosphere up to 1000°C, using the thermal analysis technique. The influence of physical and chemical composition of biochars and calcium and lithium catalysts on thermal behavior, reactivity, conversion and cold gas efficiency was examined. The gasification process occurred above 650°C. At 950°C conversion varied between 85% and 100% and cold gas efficiency between 41% and 69%. Reactivity was correlated to either inherent alkali in char or/and to the porous structure of char. Blending of forest and agricultural wastes with an industrial waste resulted in complete conversion at 950°C. Impregnation of biochars with CaO or Li_2CO_3 at loadings 0.1-0.2 gMe/gC in char increased the yield of CO achieving 100% conversion, whereas in the case of Li_2CO_3 it reduced significantly the onset and peak inflection temperatures of the process.

Keywords— *co-gasification; waste biomass; catalysts*

I. INTRODUCTION

Forest, agricultural and industrial wastes are readily available in large amounts around the world [1]. Given the European Union policies for recycling, reuse and valorization of wastes [2], as well as market needs for diversification in view of global energy crisis, their thermal treatment for energy recovery and reduction of greenhouse gas emissions seems very attractive.

Gasification of solid wastes is a promising process with superior environmental performance to incineration, which produces hazardous air pollutants [3-7]. A two-stage process, where the first step is devolatilization generating bio-oil and gas as sources of energy and chemicals [4,6], and the second step is the reaction of charcoal with a gasifying agent, could be advantageous, because of the lack of tar in product gas and the higher reactivity of biochar [3] and could be combined with advanced technologies, such as solid oxide fuel cells [8]. When carbon dioxide from flue gases is used as the reactant gas instead of being directed for sequestration, the process offers a potential solution to the greenhouse gas problem [9].

Conversion of char by carbon dioxide to carbon monoxide, the so called Boudouard reaction, is a slow process requiring a high temperature to proceed. The pyrolysis conditions of char preparation [10,11], the physical and chemical properties of chars [3,4,6,12,13], as well as the gasification temperature and pressure, are all factors that greatly affect the reactivity. A high pore volume [3,4,6] and inherent mineral matter, such as alkali and alkaline earth compounds [10,12,14,15], have been found to increase the gasification rate. Thus, various oxides, chlorides or carbonates of these metals have been used as external catalysts to improve conversion [8,16,17].

Thermal analysis techniques are widely used to study the Boudouard reaction. The gasification of woody [7,11,16,17] and municipal solid waste [8,9,18] materials has been conducted under both isothermal [19] or non-isothermal [11,20-22] conditions. Mixtures of biomass with coal have also been investigated [5,23,24]. However, co-gasification of waste materials, covering uncertainties in biomass availability with concomitant reduction of the carbon footprint to the environment, has been scarcely documented [21].

Accordingly, this work aimed to investigate the exploitation of waste materials and their blends for energetic uses, via carbon dioxide gasification. The objective was to study the influence of the physical and chemical composition of chars and calcium and lithium catalysts on thermal behavior, reactivity, conversion and cold gas efficiency.

II. EXPERIMENTAL

Biomass materials studied were pine needles (PIN) and sawdust (SAW), collected from a local forest and a furniture manufacturing company in West Crete, respectively, as well as cotton residues (COT) from a ginning factory in North Greece. After air drying, raw materials were riffled and ground in a cutting mill to a particle size of < 1mm. CEN/TC335 European standards were adopted for fuel characterization.

Specific surface area and micropore volume were measured by a volumetric apparatus model Nova 2200 of Quantachrome, using liquid nitrogen, and were determined according to the BET method. Samples were out-gassed overnight at 110°C, under vacuum.

Pyrolysis experiments for production of biochars were carried out in a lab-scale stainless steel fixed bed reactor, equipped with a programmable furnace and a Ni-Cr-Ni thermocouple in contact with the sample bed. After charging the reactor with about 15 g of biomass sample onto a stainless steel grid basket supported by a rod, the reactor was flushed with nitrogen for 30 min with a flow rate of 150 mL/min. Then the furnace was set to 600°C at a heating rate of 10°C/min and retention time of 30 min. Condensable volatiles were collected in two iso-propanol, ice-cooled baths. Following cooling under nitrogen, the biochar was weighed and ground to a particle size ≤ 200μm, in order to eliminate heat and mass transfer limitations in subsequent gasification tests and it was characterized by the same methods as for the raw material. Additionally, each biochar was analyzed for inorganic species by an X-ray fluorescence spectrometer, model S2 Ranger/EDS of Bruker AXS.

Gasification experiments were performed for biochars and mixtures of PIN and COT with SAW biochar, at mass ratios 70:30. Also, improvement of gasification reactivity was investigated by addition of CaO or Li_2CO_3 to biochars as catalysts, at percentages 10-20% wt (corresponding to 0.1-0.2 gMe/gC in char), following the incipient wetness impregnation method [8]. A differential thermogravimetric analyzer TG/DTG of Perkin Elmer, with temperature precision ±2°C and microbalance sensitivity <5 μg, was used for the tests. About 15 mg of sample was heated up to 950°C, with a heating rate of 10°C/min, under carbon dioxide of flow rate 35 mL/min, until a constant weight was reached and it was cooled by nitrogen. The weight loss and the rate of weight loss were recorded continuously as functions of temperature or time. Reproducibility was very good, as expressed by the relative standard deviation RSD reported below.

Gasification reactivity was calculated from the DTG thermograms as follows:

$$R_f = R_{max}/(T_{max}) \times 100 \ (min^{-1}/°C) \qquad (1)$$

where T_{max} and R_{max} are the peak decomposition temperature and rate of weight loss, respectively.

Gasification efficiency was calculated on the basis of CO evolution from the Boudouard reaction, according to the following equation:

$$CCE = \frac{m_{CO}}{m_{bioch}} x100(\%) \qquad (2)$$

where m_{CO} and m_{bioch} are the masses of CO produced and initial biochar sample, respectively.

The cold gas efficiency was expressed as follows:

$$CGE = \frac{m_{CO}LHV_{CO}}{m_{bioch}LHV_{bioch}} x100(\%) \qquad (3)$$

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

The alkali index, which is widely used to evaluate gasification reactivity [3,15,25], was defined as:

$$AI = ash(\%) \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + Al_2O_3 + TiO_2} (\%) \qquad (4)$$

III. RESULTS AND DISCUSSION

A. Materials Characterization

From Table 1, representing the proximate and ultimate analysis of raw materials and biochars, it can be seen that the content of volatiles in raw fuels was high, ranging between 75% and 85%, whereas the content of ash was low and for sawdust sample it was only 0.5%. The concentrations of sulfur and nitrogen were also low to undetectable in all samples, revealing insignificant emissions during the gasification process. The calorific value of PIN was higher, due to its lower ash and oxygen contents.

After pyrolysis, it can be observed that the percentages of hydrogen and oxygen were greatly reduced, due to dehydration, dehydroxylation and decarboxylation [26,27] with thermal treatment, thus resulting in an enrichment of materials in carbon and minerals. The calorific value of PIN and COT biochars was significantly increased as compared to raw fuels, while that of SAW was slightly decreased due to its high oxygen content. Fig. 1 shows that the yield of biochar was similar for PIN and COT (~28% wt). On the other hand, for SAW sample the yield of biochar was lower (~23% wt) at the expense of that of condensate.

TABLE I. PROXIMATE AND ULTIMATE ANALYSES OF THE FUELS (% DRY WEIGHT)

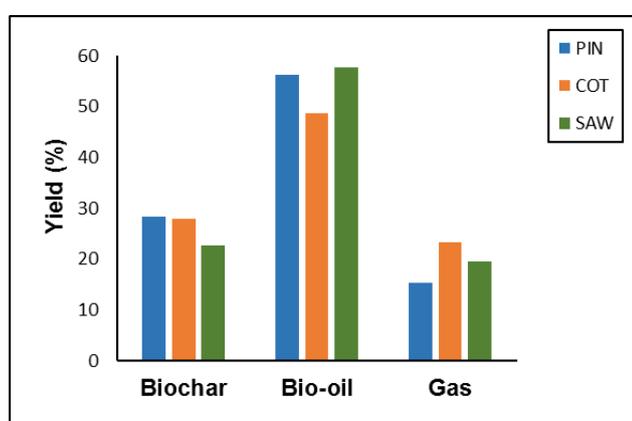|	Raw materials			Biochars		
	PIN	**COT**	**SAW**	**PIN**	**COT**	**SAW**
Volatiles	76.7	75.4	84.8			
Fixed carbon	17.4	15.7	14.7	79.2	73.0	97.8
Ash	5.9	8.9	0.5	20.8	27.0	2.2
C	47.7	41.5	46.2	63.2	65.6	56.3
H	6.8	6.0	6.4	1.8	1.8	2.0
N	0.2	1.1	-	1.0	0.6	-
O	39.3	42.3	46.9	13.2	5.0	39.5
S	0.07	0.24	-	-	-	-
GCV^a (MJ/kg)	21.1	17.8	17.4	27.7	32.8	16.1

[a] Gross calorific value

Fig. 1. *Yield of pyrolysis products of biomass fuels*

B. Gasification Characteristics of Biochars and their Blends

The DTG curves of biochars and their mixtures as a function of temperature are compared in Fig. 2. The characteristic gasification parameters derived from the processing of these curves are reprsented in Table 2. It can be noticed that the Boudouard reaction occurred above 650°C, reaching a peak rate around 890°C for PIN and COT biochars and around 950°C for SAW biochar. Reactivity order followed the sequence: COT>SAW>PIN, while conversion, ranging between 85% and 100% and cold gas efficiency followed the sequence: SAW>COT>PIN.

The behaviour of the mixtures of PIN and COT with SAW biochar was different. From Fig. 2 and Table 2 it can be observed that for PIN/SAW mixture peak position was practically the same as that of SAW, but its height, representing the maximum reaction rate was higher than the expected theoretical one from the contribution of each fuel. Reactivity was increased with respect to PIN and conversion was complete, revealing mutual interactions between PIN and SAW materials during the gasification process. On the other hand, for COT/SAW mixture it is clearly shown that the DTG
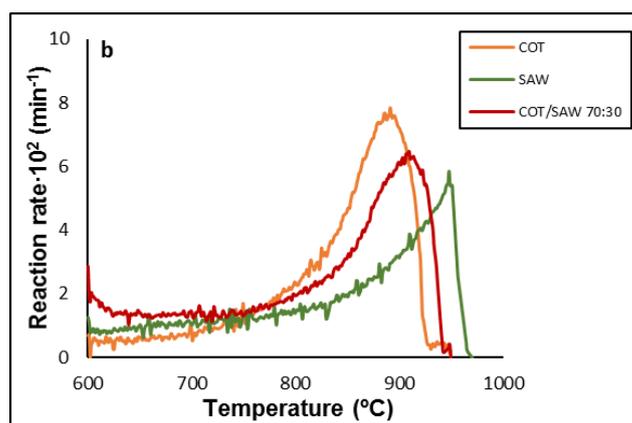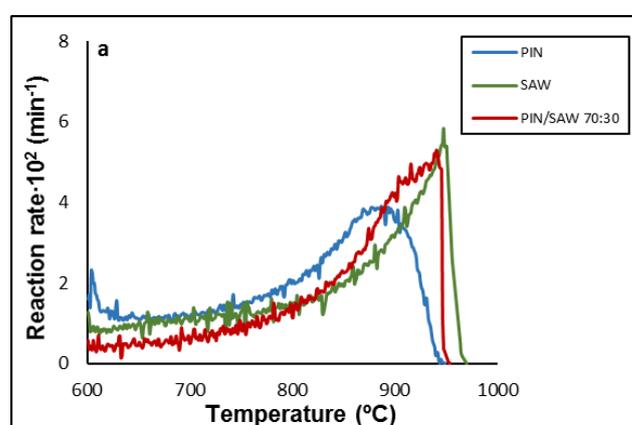

Fig. 2. *DTG gasification profiles of biochars (a) PIN, SAW and their blends and (b) COT, SAW and their blends (RSD=0.4-0.6%)*

Table II. GASIFICATION CHARACTERISTICS OF BIOCHARS WITH CATALYSTS

Sample	*Catalyst*	*Catalyst loading (%)*	T_i (°C)	T_{max} (°C)	R_{max} (10^2/min)	R_f (10^2/min°C)	*CCE (%)*	*CGE (%)*
PIN		-	674	888	3.9	0.44	85.3	41.0
	CaO	10	675	890	4.1	0.46	92.4	
		20	675	895	3.1	0.35	100.0	
	Li_2CO_3	20	615	825	3.3	0.40	92.4	
COT		-	657	891	7.9	0.88	94.1	41.1
	CaO	10	690	909	4.0	0.44	100.0	
		20	-	-	-	-	-	
	Li_2CO_3	20	600	841	3.4	0.40	99.3	
SAW		-	750	948	6.0	0.63	100.0	69.2
PIN/SAW		-	678	941	5.4	0.57	100.0	51.8
COT/SAW		-	750	909	6.5	0.71	100.0	45.9

curve lied between the curves of the two components, whereas peak temperature, maximum rate and reactivity values were found close to weighed average ones. Hence, COT and SAW biochars presented an additive behaviour.

In order to explain the different reactivity behaviour of the materials studied, the alkali index AI, commonly used to indicate any catalytic activity of alkaline (K and Na) and alkaline earth (Ca and Mg) metals of fuel ashes and the specific surface area of raw and pyrolyzed samples were determined. A plot of reactivity versus AI and percentage of alkali in char, in Fig. 3 and 4 and versus specific surface area in Fig. 5 shows that the higher gasification reactivity of COT biochar was attributed to its great content in K and Na. On the other hand, it can be observed that there was a direct relationship of reactivity with surface area for PIN and SAW biochars, the alkali concentration of which was low (specific surface area of raw materials was for PIN: 0.9 m^2/g, COT: 2.1 m^2/g, SAW: 2.4 m^2/g). Specific surface area of SAW sample after devolatilization was increased by 190 times.
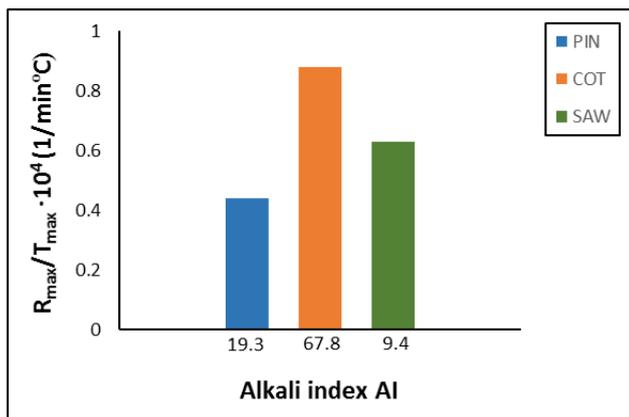

Fig. 3. *Reactivity of biochars versus alkali index*

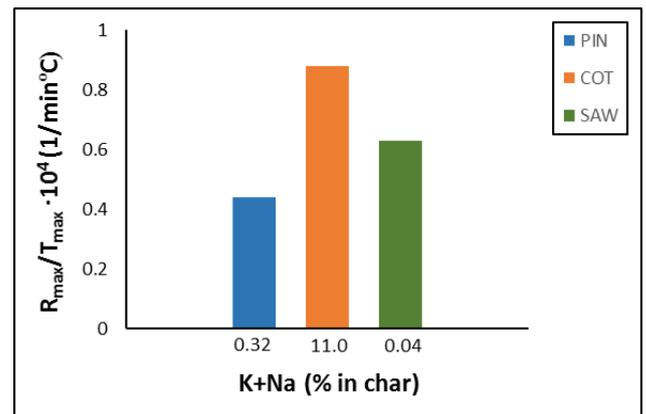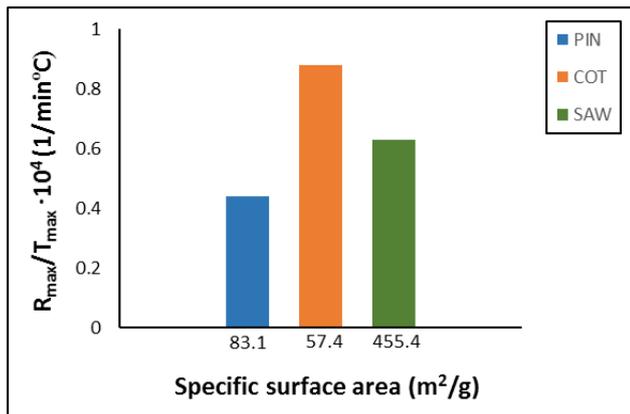

Fig. 4. *Reactivity of biochars versus alkali in char*

Fig. 5. *Reactivity of biochars versus specific surface area*

C. Influence of Catalysts on Gasification of Biochar

The effect of catalyst addition on conversion and characteristic parameters of gasification is represented in Table 2. Complete conversion was achieved at catalyst loading 20% wt or even lower in the case of CaO. For Li_2CO_3, in order to achieve a loading of 0.1-0.5gMe/gC in char, a higher amount of catalyst was added. The reactive intermediate was lithium oxide or hydroxide, as confirmed in a previous work by the authors [8].

The influence of the two catalysts used on the temperature profile of the process was different. In presence of Li_2CO_3 the onset gasification temperature and peak inflection temperature were shifted to significantly lower values, about 60°C and 50-63°C, respectively, while in presence of CaO they were slightly increased. Carrying out the gasification process at a lower temperature is very advantageous in terms of operating problems, such as slagging/fouling and cost [4,8]. Therefore, it can be speculated that Li_2CO_3 presented a better overall catalytic performance in comparison to CaO.

IV. CONCLUSIONS

The gasification process occurred above 650°C. At 950°C conversion varied between 85% and 100% and cold gas efficiency between 41% and 69%. Reactivity was highly correlated to the alkali content of cotton residue biochar, whereas to the specific surface area of pine needles and sawdust biochars and followed the order: COT>SAW>PIN. Blending pine needles or cotton residue with sawdust at mass ratios 70:30 resulted in complete conversion at 950°C.

Impregnation of biochars with CaO or Li_2CO_3 at loadings 0.1-0.2 gMe/gC in char increased the yield of CO achieving 100% conversion, whereas in the case Li_2CO_3 it reduced significantly the onset and peak inflection temperatures of the process.

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