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Fe catalysis for lignocellulosic biomass conversion to fuels and materials via thermochemical processes

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ABSTRACT

Recently, international research is aiming at developing gasification and pyrolysis processes for the cost-effective thermochemical conversion of non-food biomass to biofuels. Gasification produces a mixture of carbon monoxide and hydrogen, known as syngas. Pyrolysis produces a liquid bio-oil. Both syngas and bio-oil can be used directly or can be converted to clean fuels and other valuable chemicals. Catalysis is central to achieving this aim. This study presents results from lignocellulosic biomass pyrolysis, air and steam gasification in the presence of Fe. Noncatalytic and catalytic pyrolysis and gasification experiments were carried out at temperature range of $T = 500–760\,^{\circ}C$ under an inert helium atmosphere for pyrolysis and at $T = 750–1050\,^{\circ}C$ with air and steam as the gasification agents for gasification. The effect of temperature (°C), heating rate (°C/min), gasification medium (steam or air), air ratio (λ), steam to biomass ratio (S/B) as well as the catalytic effect of Fe naturally dispersed in the biomass char were studied. The influence of the iron traces originated from the native biomass and ending up in the char residue is mostly studied. Moreover, experiments were performed and results discussed of Fe residues utilization mixed with the bed material to act as catalyst for the conversion of biomass. The results of the performed study showed that olive kernel pyrolytic char is highly reactive comparing to cellulosic biomass char, due to its porous structure, increased surface area and ash content rich in metals. In combination, the presence of metals in olive kernel ash (especially Fe metal) can play an active catalytic role in tar cracking. Additional results have also shown that the addition of Fe residue as in bed catalyst for upgrading non edible residual biomass, favorises the production of H_2 rich gas (syngas) due to Fe pronounced catalytic activity.

1. Introduction

Biomass, according to the biorefinery approach, seems to be a unique renewable source able to satisfy both needs of providing feedstocks for biofuel and high added value materials production [1]. Amongst other kinds of biomass, agricultural residues of lignocellulosic origin could contribute to the satisfaction of the local and seasonally increased energy demand with the avoidance of wasteful and environmentally damaging practices, such as open-field burning. Residual biomass can today contribute to the targets of green energy production and sustainable development in rural areas. Current agro residues availability estimates revealed that almost 5 gtons of agricultural residues are produced in an annual base all over the world [1]. Agricultural residues could be converted by thermo chemical methods (pyrolysis and gasification) and give useful products of commercial interest (H_2 rich gas and biofuels, chemicals or carbon materials).

Towards that direction the gasification seems to be the core of many advanced biomass exploitation technologies aiming at the production of electricity, hydrogen, liquid biofuels and chemicals of high added value. However, gasification faces a number of technical challenges in order to become a commercially feasible renewable energy technology. The main technical barrier in gasification systems remains the efficient destruction and removal of tars in favor of the produced syngas. Syngas produced during gasification contains tars that are contaminants, but these tars can be reformed to more syngas using tar-reforming catalysts. Catalysts are also used to convert synthesis gas into fuels and chemicals. Catalysis seems to play a significant role towards the efficient upgrading of the residual biomass. The development of efficient catalysts, able to in situ decompose and reform the produced tar from biomass gasification, represents an important stage when aiming at the production of a hydrogen-rich gas. Among other catalytic materials, pyrolysis char was noticed to present a good catalytic activity for tar removal.

Furthermore, scaling up material for pilot-scale testing with biomass-derived syngas and further commercial development needs improvement of the thermochemical conversion process as a whole. The goal today is to demonstrate pilot-scale performance for the cost-effective thermochemical conversion of biomass to

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biofuels. In a general approach of the optimization in cost and operation of gasification/pyrolysis processes and the optimum performance of small bioenergy systems, the exploitation of cheap materials (residues, wastes) and also low cost gasification bed material and catalysts are required.

Taking this in consideration, the ultimate aim of the present study was the investigation of sustainable performance of a small bioenergy system by using low cost biomass, available in Greece such as olive kernel, as feeding material and residue Fe to act as catalyst. This study is a part of a research carrying out at the Aristotle University of Thessaloniki (AUTh) and funded by a PENED03 project aiming at the development of a pilot fluidized bed gasification system for heat and power production in rural areas. Our main concern is the development of a cost effective and easy to operate small scale unit however not against its efficiency. For tar destruction and enhancement of H_2 rich gas production the incorporation of iron residue, a readily available, low-cost, and non-toxic material in olive kernel pyrolysis and gasification is considered.

2. Literature review

Olive kernel is a biomass found mostly in Mediterranean countries. Several studies have been reported in international literature and concern the effect of temperature (T), heating rate (°C/min) and lignin content (%, w/w) during *olive kernel* pyrolysis and gasification. Such works have been mainly accomplished by research groups from the Mediterranean Universities, since olive plantations are natively found around the Mediterranean sea.

Garcia Ibanez et al. [2] studied the devolatilization of olive kernel under three different heating rates (10, 20 and 50 °C/min) and concluded that the increase in heating rate had a positive effect on the devolatilization process. Blanco Lopez et al. [3] performed olive kernel pyrolysis and studied the produced gas composition. Similarly, Zanzi et al. [4] studied the fast pyrolysis of olive kernel in a type free fall reactor. They concluded that high lignin content of olive kernel led to the production of high amounts of char. Members of the authors' research group, Zabaniotou et al. [5], have also proved that fast pyrolysis of olive kernel in a captive sample reactor reduced char production while biomass moisture favoured the gas production.

Minkova et al. [6] studied the effect of steam presence during slow pyrolysis of agricultural residues and concluded that the olive kernel char proved very active in the adsorption of chemicals. Furthermore, Minkova et al. [7] studied the effect of steam in two reactor configurations: a rotary and a fixed bed reactor. They also measured the product yields of each process. They proved that exploitation of olive kernels in a rotary type reactor excelled due to the higher heating rate, achieving yields of gaseous products up to 70% (w/w), comparing with the yields achieved during biomass gasification in a fixed bed reactor (40%, w/w). Putun et al. [8] studied the slow pyrolysis of olive kernel under several atmospheres indicating that tar yield increased considerably in the presence of N_2 and steam, comparing to an atmosphere of only N_2.

Additionally, several studies can be also found in the international literature dealing with the *catalytic cracking* of tar by using cheap bed materials with considerable focus in Fe mainly contained in bed materials such as in olivine. Towards that direction Nordgreen et al. [9] used metallic iron and iron oxides in order to reform tar compounds during wood gasification in pilot scale. They performed experiments in the temperature range of T = 700–900 °C and low air ratios ($0 < \lambda < 0.2$), indicating the ability of adequate tar cracking at such low temperature conditions. Brage at al. [10] studied similarly the cracking of some basic constituents of tar produced by biomass pyrolysis in a bench scale, fixed bed reactor and proved the positive effect of raising the pyrolysis temperature, as well as the presence of steam towards tar cracking. Hu et al. [11] investigated the peach stone gasification with steam and used dolomite/olivine in order to maximize H_2 production in a laboratory scale, fixed bed reactor. They concluded that dolomite favored the production of H_2, due to the high Fe_2O_3 content while presence of CaO–MgO seemed to help in the capture of the produced undesirable CO_2.

Rui Neto et al. [12] studied the gasification of mixtures of olive oil waste with coal in both quartz and dolomite fluidized bed ending up at similar conclusions. Skoulou et al. [13] studied the air gasification of olive kernels in a 5 kW bench scale bubbling fluidized bed gasifier. The experimental results revealed that producer gas H_2 content increased at the temperature of T = 750 °C and ER = 0.2, resembling the high-temperature pyrolysis conditions. Members of the authors' research group, Skoulou et al. [14], have investigated also the effect of high temperature and steam presence in a high temperature fixed bed unit (HTSG) at KTH Sweden, with focus to hydrogen maximization in the produced gasification gas by using olive kernel from Greece. This study proved that olive kernel HTSG gasification could be an effective technology for a hydrogen-rich gas production by achieving ~40% (v/v) H_2 in the produced gasification gas at 1050 °C.

Zabaniotou et al. [15] have also indicated that pyrolysis could serve as an alternative method for the production of activated carbons from olive kernel. A two stage process (pyrolysis and physical and chemical activation) was performed. Towards the same direction Ioannidou et al. [16] studied the removal of Bromopropylate (BP) pesticide from water by activated carbons produced from several agricultural residues and amongst them olive kernels. The same team of researchers in their publication of Skoulou et al. [17] compared the results from laboratory fixed-bed air gasification of olive kernels and olive tree cuttings regarding their final conversion to fuels and carboneous materials of high added value. They showed that gasification with air at high temperatures (T = 950 °C) favored syngas gas yields. However, olive kernels produced more char with a higher content of fixed carbon than olive tree cuttings, reaching the conclusion that olive kernel gasification for fuels is competitive with olive kernel pyrolysis to materials.

The same team of researchers has proceeded with the modeling of the thermochemical process. Damartzis et al. [18] modeled the combined gasification process coupled with an internal combustion engine by using a comprehensive mathematical model based on the Aspen Plus®. This model was validated by using the experimental data obtained by the 5 kW_{th} pilot scale olive kernel gasification unit developed by Skoulou et al. [13] showing a very good validity.

A great number of studies have been also published dealing with the catalytic and non catalytic gasification of olive kernel, with different gasifying agents and in several reactor configurations [19], mainly due to the raising interest in agricultural residues alternative exploitation around the Mediterranean region and the necessity not only to operate effectively biomass plants [17], but also to promote more environmental friendly energy production methods.

Concerning questions arising about biomass pretreatment for higher thermochemical conversion yields, Skoulou et al. [20] showed that water leaching did not favor the steam reforming of tar, while at the same time, the H_2 yield in gas product decreased under air gasification conditions, due to the possible loss of the catalytic effect of ash that removed from olive kernel chars during water leaching.

Concluding, pyrolysis and gasification could be considered according to Bridgwater, [21], two complementary processes of biomass valorization into renewable energy and high added value products. The main advantage of thermochemical treatments, comparing to biochemical, seems to be the ability of thermo-chemically decompose the macro-molecules of lignin. Catalysis could then play a major role in both pyrolysis and steam gasification processes