Synergetic effects from catalytic co-pyrolysis of biomass and plastic residues

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Highlights
- Catalytic co-pyrolysis of grape seeds and waste tires is an environmental-attractive alternative to produce advanced liquid fuels.
- A specific-designed fixed-bed reactor eases positive synergetic effects during catalytic co-pyrolysis of biomass and waste tires.
- Oxygen content of liquid fuel remains in the same range after 3 consecutive cycles of pyrolysis-catalyst regeneration.

1. Introduction
Second-generation bio-fuels, those produced from lignocellulosic biomass, can be considered as an important renewable energy source in order to minimize the negative environmental impact caused by derived-fossil fuel. In this sense, the purpose of this second-generation bio-fuels are actual refineries and future bio-refineries but, in order to accomplish that target, it is necessary to improve its properties. Introducing catalysts at the same time as plastic materials seems to be an attractive solution [1]. This way, not only an improved bio-oil is obtained but also, a reduction of plastic residues in landfills is achieved. In order to obtain directly high quality bio-oils to be used as renewable energetic vectors, the implementation of catalytic co-pyrolysis process as a new, simple and low-cost strategy has been studied in this work.

2. Methods
Local agricultural wastes such as grape seeds (GS) were selected as lignocellulosic biomass and WT were selected as a plastic-type residue. On the other hand, CaO was selected as low-cost catalyst based on previous experiences by the group [1,2]. The catalytic co-pyrolysis process was carried out in a specific-designed fixed-bed reactor as shown in Figure 1. The installation consist of a stainless steel fixed-bed reactor (52.5 cm length and 5 cm internal diameter). This reactor has been designed specifically to carry out this process having the peculiarity that incorporates a vertical mobile liner to ensure higher heating rates needed for the process. Thus, samples were pyrolysed using nitrogen as carrier gas (300 ml/min). The reactor was heated externally with an electrical resistance at approximately 100 °C/min to the final pyrolysis temperature of 550 °C. The reaction time considered to ensure the pyrolysis process was set to 30 min. A condenser (ice-cooled trap) using a water reflux at 3°C was used to collect the liquids. Liquid and solid yields were obtained by weight, while the gas yield was calculated by the gas composition sampled in a gas bag. Thus, different feedstock mixtures on mass basis (up to 40 wt. % of WT) were studied and the influence of the impact of ratio catalyst to feedstock, lifetime of regenerated catalysts and product fraction properties were also analyzed.

Figure 1. Fixed-bed reactor scheme used for catalytic co-pyrolysis experiments

Figure 2. Simulated-rate of mass loss of grape seeds and polystyrene at heating rate 100 °C/min.
Moreover, previous thermogravimetric experiments have shown that there is a great common area during the devolatilisation of GS and WT (from 200 ºC to 550 ºC approximately) where radical interaction of both materials in order to produce synergetic effects on liquid fraction could be favored (see Figure 2).

3. Results and discussion
An improved organic phase is obtained after co-pyrolysis of GS and WT. As anticipated in TGA analyses, a positive synergetic effect occurs on the liquid fraction during the volatilization step and, at the same time, hydrogen-transfer reactions promoted by CaO, allows for the formation of a stable bio-oil with upgraded properties. This effect has been reflected by obtaining a more deoxygenated liquid (down to values of 4.9 wt. %) and in consequence, higher heating values associated to final liquid (up to 40.8 MJ/kg), values that can be considered in the same range of those by liquid derived from fossil fuels. As can be observed in Figure 3, although CO₂ production rises after 3 consecutive cycles of catalytic co-pyrolysis and regeneration of catalyst (850 ºC in air) keeping a catalyst to feedstock ratio 1 to 1 by weight, liquid yields stand approximately in the same range (38 wt. % approximately). Moreover, oxygen content in liquid fraction barley suffer any variation (oxygen content increase from 5.3 to 6.6 wt.%).

![Figure 1](image)

**Figure 1.** Outstanding results after the catalytic co-pyrolysis of GS and WT

4. Conclusions
The catalytic co-pyrolysis process of GS and WT results as a simple and economic way to improve the bio-oil obtained from catalytic pyrolysis of solely lignocellulosic biomass. Moreover, there are not remarkably changes on oxygen content when CaO regenerated is used up to 3 consecutive cycles.

References
[1]. X. Zhang, H. Lei, S. Chen, J. Wu. Green Chem 18 (2016); 4145-4169
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Curriculum vitae

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University Education

18/05/2012 University of Zaragoza
Chemical Engineer / Environmental Option
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3/10/2014 University of Zaragoza
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phD: Production of second generation biofuels from lignocellulosic biomass.
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Complementary Education

2005 Industrial engineering conferences. University of Zaragoza.
2007 Course: Residues in soils and water. Program “Genetics, Environment and Society”. University of Zaragoza.
2013 Energy 101, Georgia Institute of Technology (Coursera).
2013 Course: Advanced technologies on clean energy generation.Instituto de Carboquímica-Grupo Español del Carbón-University of Zaragoza.
2014 Conferences about capture, transport, storage and uses of CO₂. Fundación CIRCE.
2015 Course: Nano-structured materials for energy conversion and storage. Instituto de Carboquímica-Grupo Español del Carbón-University of Zaragoza.
2017 Course: Classical and advanced mass spectrometry strategies to chemical characterization of liquid products obtained by thermal conversion of biomass. University of Zaragoza.

Work Experience
19/09/2010- 19/09/2011

**Position:** Chemical Engineer internship Contract

**Name and address of employer:** Instituto de Carboquímica. Miguel Luesma Castán 4, 50018 Zaragoza, Spain (Environmental Research Group)

**Type of business or sector:** Research

**Project:** Production and characterization of liquid fuels by co-pyrolysis of biomass and waste tyres.

16/11/2011- 31/12/2015

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**Type of business or sector:** Research.

**Projects (3):** Second generation biofuels by catalytic biomass pyrolysis; Catalytic upgrading of bio-oils; Pyrolysis and dry processes of forestry and agricultural residual biomasses.

**Main activities and responsibilities:**
- Experimentation with a fixed-bed reactor in a small scale.
- Set up, operation and maintenance of a pyrolysis pilot plant driven by an auger reactor, with 15 kg/h of capacity.
- Analysis and interpretation of properties of obtained products (liquid, solid and gas).
- Utilization of several analytic techniques for measuring liquid fuel properties (pH, water content, Total Acid Number, viscosity, density, thin layer column...).
- Handling of different types of gas chromatographs for measuring gas composition
- Synthesis of different catalysts.
- Attendance to 3 national conferences (2 oral contribution and 2 poster contributions) and 4 international conferences (1 oral contribution and 2 poster contributions).

01/12/2016- 31/12/2018

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**Type of business or sector:** Research.

**Projects:** Low-cost strategies for the production of high-valuable second generation biofuels

**Main activities and responsibilities:**
- Experimentation and design of two different fixed-bed reactors at small scale.
- Design, set up, operation and maintenance of a pyrolysis pilot plant driven by an auger reactor, with 15 kg/h of capacity.
- Analysis and interpretation of properties from obtained products (liquid, solid and gas).
- Utilization of several analytic techniques for measuring liquid fuel properties (pH, water content, Total Acid Number, viscosity, density, thin layer column...).
- Handling of different types of gas chromatographs for measuring gas composition
- Synthesis of different catalysts.
- Conferences programmed: 1 national conference in November 2017 (poster contributions accepted) and 2 international conferences in December 2017 and September 2018 (oral contributions)
Languages

**English:** high level. **Spanish:** Mother tongue.

Computer skills and competences

Microsoft Office/ Advanced Level
Origin/ User Level
Hysis, Matlab, EES / User Level

Other skills and competences

- Driving license B.
- Regular reviewer of "Journal of analytical and applied pyrolysis" and "biosystems engineering."

Scientific publications


- Porosity-Acidity Interplay in Hierarchical ZSM-5 Zeolites for Pyrolysis Oil Valorization Aromatics. ChemSusChem Volume 8, Issue 19, 1 October 2015, Pages 3283-3293.


Citations: 235 citations by 192 documents

h-index: 7

Conferences attended
Title of the work: Production and characterization of biofuels by co-pyrolysis of biomass and waste tyres
Name of the conference: EU BC&E. 20th European Biomass Conference and Exhibition
City of event: Milan, Italy
Date of event: 18/06/2012
Authors: A. Veses; A. Artigues; N. Puy; J.D. Martínez; T. García; R. Murillo; J.M. López.
Type: Poster presentation.

Title of the work: Obtención de biocombustibles mejorados a partir de la co-pirólisis de biomasa y neumáticos fuera de uso
Name of the conference: XII Reunión del grupo español del carbon, GEC
City of event: Madrid, Spain,
Date of event: 29/10/2013
Authors: A. Veses; J.D Martínez; R. Murillo; T García.
Type: Poster presentation.

Title of the work: Evaluación del proceso de pirólisis de neumáticos fuera de uso en continuo escala piloto
Name of the conference: XII Reunión del grupo español del carbon, GEC
City of event: Madrid, Spain,
Date of event: 29/10/2013
Authors: J.D Martínez; R. Murillo; T García; A. Veses.
Type: Oral presentation.

Title of the work: Mejora catalítica de biocombustibles líquidos obtenidos a partir de la pirólisis de biomasa lignocelulósica.
Name of the conference: 6ª Jornada de Jóvenes investigadores de Química y Física en Aragón
City of event: Zaragoza, Spain
Date of event: 20/11/2014
Authors: A. Veses; J.M López; M.S Callén; T García
Type: Poster presentation

Title of the work: Effect of different cations in ZSM-5 zeolite in the catalytic upgrading of bio-oil
Name of the conference: COPS X
City of event: Granada, Spain
Date of event:14/05/2014
B Puértolas; A Veses; M.S Callén; J.M López; M.V Navarro; R Murillo; T García.
Type: Poster presentation.

Title of the work: Efecto de las propiedad ácidas y estructurales de zeolitas ZS jerarquizadas en el proceso de craqueo catalítico para la valorización de bio-aceites.
Name of the conference: XIII Reunión del Grupo Español del Carbón, GEC
City of event: Alicante, Spain
Date of event: 25/10/2015
Authors: A. Veses; B. Puértolas; T. García; R. Murillo.
Type: Oral presentation.

Title of the work: Valorización de neumáticos fuera de uso por pirólisis: rendimiento y propiedades de los productos usando un reactor de tipo auger.
Name of the conference: Congreso Nacional y V Internacional del Ciencia y Tecnología Carbón y Combustibles Alternativos
City of event: Medellín, Colombia
Date of event: 27/08/2015
Authors: J.D Martinez, M.L Betancourt, A. Veses; T. García; R. Murillo.
Type: Oral presentation.

Title of the work: Promoting the enhancement of bio-oil deoxygenation by metal cation impregnation of hierarchical ZSM-5 zeolites
Name of the conference: Catalysis for renewable sources: Fuel, Energy, Chemicals
City of event: Catania, Italy
Date of event: 06/09/2015
Authors: A. Veses; J.M López; M.S Callén; T García
Type: Oral presentation.