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 staintless 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 ºC/min to the final pyrolysis temperature of 550 ºC. The reaction time considered to ensure the pyrolysis process was set to 30 min. A condenser (ice-cooled trap) using a water reflux at 3ºC 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.

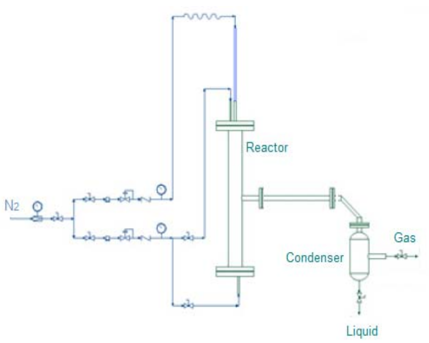

Figure 1. Fixed-bed reactor scheme used for catalytic co-pyrolysis experiments

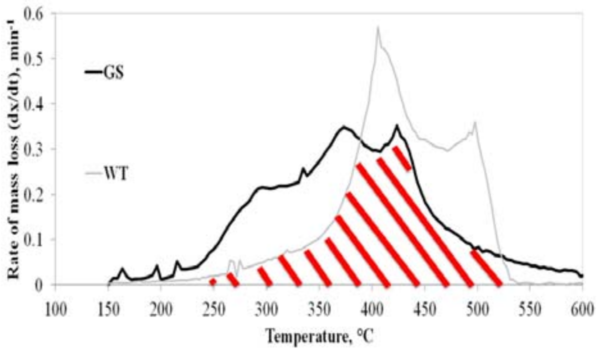

Figure 2. Simulated-rate of mass loss of grape seeds and polystyrene at heating rate 100 °C/min.

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 CO_2 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.%).

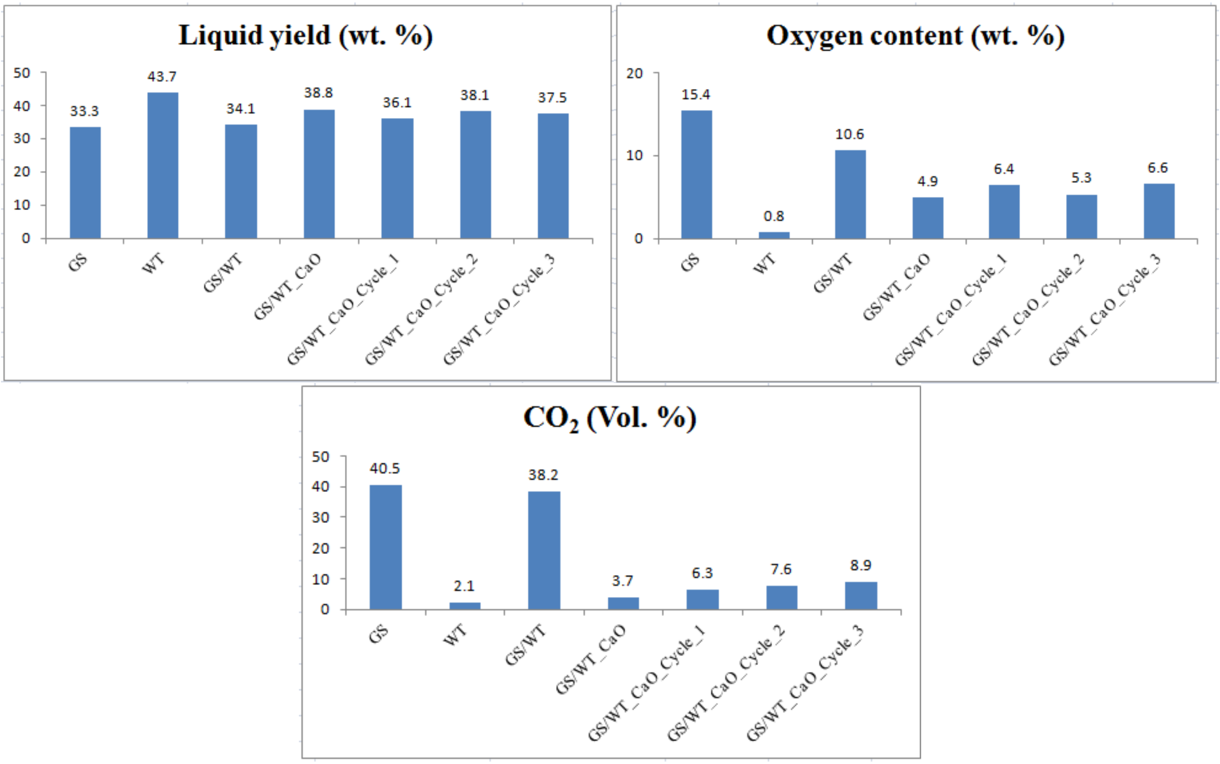

Figure 1. Outstanding results after the catalytic co-pyrolysis of GS and WT

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

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Keywords
Bio-oil, catalytic co-pyrolysis, biomass, waste tires.

Curriculum vitae

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University Education

18/05/2012 University of Zaragoza — **Zaragoza, Spain**
Chemical Engineer / Enviromental Option

3/10/2014 University of Zaragoza — **Zaragoza, Spain**
Master´s degree / Renewable Energies

24/11/2016 University of Zaragoza – Instituto de Carboquímica — **Zaragoza, Spain**
phD: Production of second generation biofuels from lignocellullosic biomass.

Complementary Education

2003,2008	Engineering and environment conferences.DIR Europa. University of Zaragoza.
2005	Industrial engineering conferences. University of Zaragoza.
2007	Course: Residues in soils and water. Program "Genetics, Enviroment and Society". University of Zaragoza.
2013	ER100 : Introduction to Renewable Energies. Solar Energy International.
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 CO_2. 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 copyrolysis of biomass and waste tyres.

16/11/2011-31/12/2015

Position: Chemical Engineer 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.

Projects (3): Second generation biofuels by catalytic biomass pyrolysi; 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

Position: Chemical Engineer 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.

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 acepted) 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 pyrolisis" and "biosystems engeneering.

Scientific publications

- Demonstration of the waste tire pyrolysis process on pilot scale in a continuous auger react Journal of Hazardous Materials Volume 261, 5 October 2013, Pages 637-645.

- Co-pyrolysis of biomass with waste tyres: Upgrading of liquid bio-fuel. Fuel Process Technology Volume 119, March 2014, Pages 263-271.

- Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based cataly Bioresource Technology, 2014, 162: 250-258.

- Production of upgraded bio-oils by biomass catalytic pyrolysis in an auger reactor using low cost materials. Fuel Volume 141, 1 February 2015, Pages 17-22.

- Catalytic upgrading of biomass derived pyrolysis vapors over metal-loaded ZSM-5 zeolites: Effect of different metal cations on the bio-oil final properties. Microporous and Mesopor Materials Volume 209, 1 June 2015, Pages 189-196 .

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

- Promoting Deoxygenation of Bio-Oil by Metal-Loaded Hierarchical ZSM-5 Zeolites.A Sustainable Chem. Eng. Volume 4, January 2016, Pages 1653-1660.

- An integrated process for the production of lignocellulosic biomass pyrolysis oils using calcined limestone as a heat carrier with catalytic properties. Fuel Volume 181, 1 October 2016, Pages 430-437.

- Garcia T, Veses A, Lopez JM, Puértolas B, Perez-Ramirez J, Callén MS. Determining Bio-oil Composition via Chemometric Tools based on Infrared Spectroscopy. ACS Sustainable Chemistry & Engineering. Acepted september 2017

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 biocombstibles líquidos obtenidos a partir de la pirolisis 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 propiedades 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.