Procesamiento hidrotermal solar de biomasa: operación de reactor y características de los productos

Solar driven hydrothermal processing of biomass: reactor operation and products characteristics

Alejandro Ayala-Cortés[1], Heidi Isabel Villafán-Vidales[2*], Pedro Arcelus-Arrillaga[3], Camilo A. Arancibia-Bulnes[2], Patricio J. Valadés-Pelayo[2] and A. Longoria[4]

[1] Instituto de Carboquímica, CSIC. Miguel Luesma Castán 4, CP 50018, Zaragoza, Spain

[2] Instituto de Energías Renovables, UNAM. Priv. Xochicalco S/N. Col. Centro, Temixco, 62588, Morelos, Mexico

[3] Department of Chemical Engineering, Faculty of Engineering and Informatics. University of Bradford, Bradford, West of Yorkshire BD7 1DP, UK

[4] CICATA Unidad Morelos, Instituto Politécnico Nacional, Boulevard de la Tecnología, 1036 Z-1T P 2/2, Atlacholoaya, 62790, Morelos, Mexico

**Corresponding author: hivv@ier.unam.mx.*

Abstract

The use of concentrated solar energy to provide heat in the hydrothermal liquefaction is an attractive method to transform biomass into valuable products reducing the environmental impact. However, the coupling of both technologies requires further research. This work analyses the effect of solar fluctuations on the yields, and main characteristics of products obtained in a solar reactor with direct heating method. Results indicate that by direct heating in a solar furnace, at sustained reaction temperatures of 250 ºC, produced a bio-oil and char yield up 24 and 33%, respectively. The results are consistent with conventional heating systems, however direct heating results in higher temperature gradients between the frontal and non-irradiated walls (above 200 ºC), which results in an unstable system, especially at high heating rates and temperatures above 300 ºC, therefore, at the end of this work a modified solar reactor was proposed.

Resumen

El uso de energía solar concentrada para suministrar calor en el procesamiento hidrotermal de biomasa representa una alternativa atractiva para la transformación de biomasa en productos valiosos con menor impacto ambiental. Sin embargo, el acoplamiento de ambas tecnologías requiere más investigación en el tema. Este trabajo analiza el efecto de las variaciones en la irradiancia solar en los rendimientos y composición de los productos. Los principales resultados muestran rendimientos en el bioaceite y carbón de hasta 24 y 33%, respectivamente. Adicionalmente, se encontró que el tiempo de residencia entre 30-60 min favorece la formación superficial de una estructura porosa en el carbón. Los resultados obtenidos son consistentes con los sistemas de calentamiento convencional, sin embargo, el calentamiento directo del reactor solar genera grandes gradientes térmicos entre la pared frontal y la pared no irradiada (arriba de 200 ºC), lo que resulta en un sistema inestable, especialmente con rampas de calentamiento rápidas y temperaturas arriba de 300 ºC, por lo tanto, al final de este trabajo se propone un reactor mejorado.

Keywords

Thermochemical solar process, Bio-oil, Solar furnace, Solar fuels.

1. Introduction

Biofuels appear as an attractive option to reduce dependence on fossil fuels that results in important environmental and economic benefits by increasing renewability and supporting energy security [1]. There are different thermochemical routes for transforming biomass into fuels, which include: pyrolysis, gasification and hydrothermal processing. Pyrolysis and gasification are processes usually carried out at low pressures (up to 50 bar) and high temperatures (>600 °C) [2]. However, these methods use dry feedstock that represents a high energy penalty and increases the costs on major scale operations. According to Guo *et al*. [2], about 50% of the energy required to produce liquid fuels from wet biomass is consumed during the drying and distillation processes. On the other hand, hydrothermal processing is performed at lower temperatures (<400 °C) and high pressures (up to 300 bar) [3], and can employ wet biomass as feedstock, preventing the above-mentioned energy intensive pre-drying process. This ability on hydrothermal processing of biomass makes it attractive to produce a variety of different products, such as, hydrogen, methane, bio-oils, char and platform chemicals. Nevertheless, one of the main challenges of hydrothermal processing is that it requires a large amount of energy, normally from fossil fuels sources, to provide the process heat. In order to mitigate the impact of using conventional energy sources in the hydrothermal process, concentrated solar technologies have emerged as an option [3]. Some works have analyzed the supercritical domain where biomass gasification takes place [3], others have paid attention on coupling concentrated solar technologies to perform the hydrothermal liquefaction. Although it has been successfully proven that the implementation of concentrated solar technologies to hydrothermal treatment is possible [3], a study to analyze the effect of solar fluctuations on the yields, and nature of the products obtained is required. In the present work, different experiments of solar hydrothermal processing of agave were carried out in a solar reactor where the yield and chemical characteristics were evaluated. These results were used to propose a modified solar reactor capable to operate at higher temperatures and heating rates.

2. Methodology

A solar batch reactor capable of operating at high pressures with concentrated solar energy heating was built. This prototype is a stainless-steel cylinder with an internal volume of 644 ml and 4.2 cm of wall thickness (total weight of 80 kg). The reactor was installed near the focal zone of the IER-UNAM Solar Furnace (5 cm behind focal point), and was equipped with a pressure transducer, nine type "K" thermocouples (one to measure the slurry temperature and eight to measure the reactor wall's temperature), a relief valve and a gas inlet and outlet valves (Fig. 1).

Experiments were performed with a Direct Normal Irradiation (DNI) above 600 W/m^2, operating slurry temperatures (T_{Slurry}) of around 250 °C, 0, 30, 60 and 90 min of residence time (τ), 10 wt % of initial biomass loading, heating rates (HR) of around 2 °C/min and an initial argon pressure at ambient temperature (P_i) of 50 bar (Table 1). Zero-minute residence time is defined as the time that it takes for the reactor to reach the desired experiment temperature. The slurry temperature, heating rate and final pressure are governed by the concentrated solar flux that receives the frontal external wall of the reactor, although the shutter controls the flux there are small variations in final values.

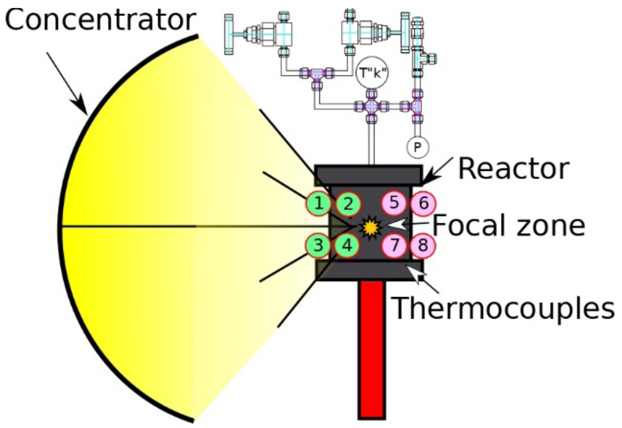

Figure 1. Experimental scheme and solar hydrothermal reactor in an experiment.

Figura 1. Esquema experimental y fotografía del reactor solar para procesamiento hidrotermal.

Table 1. Operational parameters of solar experiments.

Tabla 1. Parámetros operacionales de los experimentos solares.

No. Exp	T_{slurry} (ºC)	$T_{ext.walls}$ (ºC)	P_i/P_f (bar)	τ (min)	HR (ºC/min)
1	258	376	51/132	60	1.6
2	256	375	52/133	60	1.5
3	250	289	52/98	0	1.8
4	260	263	51/94	30	2.3
5	260	363	53/110	90	1.8

After reaction, the system was depressurized and the products were collected. Reaction products are a mixture of solid, oil and aqueous (water with some soluble organics) phases. This mixture is separated in each phase through a solvent extraction process. Chemical conversion and yields to each phase were calculated through an atomic carbon balance, and the HHV with the elemental composition of char and bio-oil:

$$Y_{oil}(\%) = \frac{m_{C,oil}}{m_{C,B}} x100 \quad \textbf{(1)}$$

$$Y_{char}(\%) = \frac{m_{C,char}}{m_{C,B}} x100 \quad \textbf{(2)}$$

$$Conversion(\%) = \frac{m_{C,B} - m_{C,char}}{m_{C,B}} x100 \quad \textbf{(3)}$$

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0{,}021Ash \quad \textbf{(4)}$$

Where , are the oil and char yields, respectively; , , are the carbon content in the mass of oil, bagasse, and char, respectively; HHV is the higher heating value and biomass conversion was calculated with Eq. 3 [4].

3. Results

3.1 Effect of solar radiation variations on the products

Direct heating of the reactor produces high temperature gradients between the frontal and non-irradiated wall (above 200 ºC), which results in an unstable system. This is especially evident at high heating rates and temperatures above 300 ºC. To reach a slurry temperature of 250 ºC, the frontal wall requires temperatures above 400 ºC, whereas the temperature in the non-irradiated remains low around 150 ºC. The high thermal inertia of the reactor promotes pressure stability when small DNI fluctuations occur during the solar operation. However, the system needs large heating times to reach reaction temperature (Fig. 2).

Regarding the impact of DNI fluctuation in the , , conversion and HHV in experiment 1 and 2, it can be seen that there are minor variations in the yield and chemical properties of the main products (Table 2). On the other hand, an increase in reaction time improves chemical conversion and carbon content in the bio-oil. Moreover, oxygen content in the bio-oil is reduced, which results in high HHV. However, char yield increases due to secondary reactions where there is thermal cracking of bio-oil [5,6].

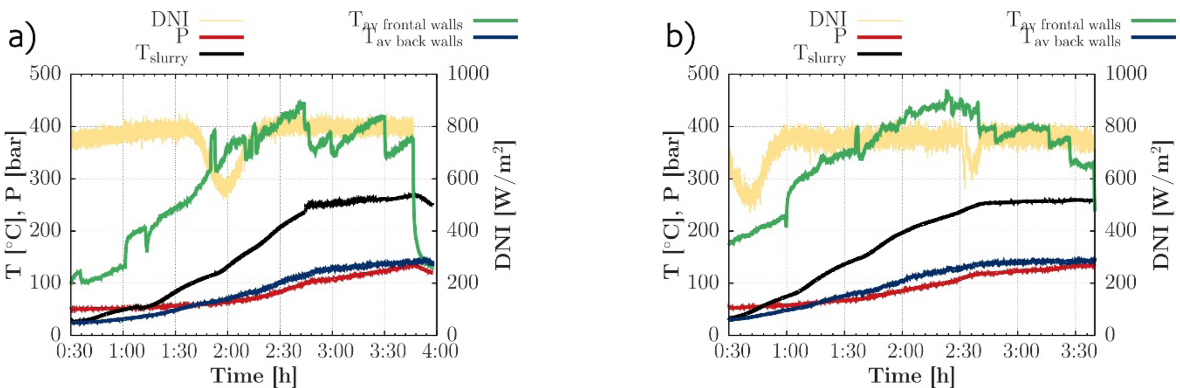

Figure 2. DNI, temperature and pressure distributions of experiment 1 and 2.

Figura 2. Distribución de la radiación solar directa (DNI), temperatura y presión de los experimentos 1 y 2.

Table 2. Experimental results of char and bio-oil.

Tabla 2. Resultados experimentales del carbón y bioaceite.

No. Exp	Y_{oil} (%)	Y_{char} (%)	Conv. (%)	HHV_{oil} (MJ/kg)	HHV_{char} (MJ/kg)	$C_{oil/char}$ (wt%)	$H_{oil/char}$ (wt%)	$O_{oil/char}$ (wt%)
1	23	22	80.5	28	18	69/52	6/4	25/44
2	22	23	80.4	27	18	66/53	6/4	28/43
3	21	33	70	24	19	60/50	6/5	34/45
4	21	23	81	23	19	59/54	6/4	35/42
5	24	30	80	28	20	67/57	6/4	27/39

According to its chemical content and HHV, the bio-oils produced are attractive as liquid fuel, as a result of the minor impact that associated to renewable and solar fuels. However, its high oxygen content would limit its direct application in engine motors combustion, along with thermal/chemical instability and corrosion. Therefore, an upgrading treatment to hydrodeoxygenate the bio-oils would be required. On the other hand, the chars can reach yields up to 33%, which represent considerable losses in major scale. Consequently, different ways to make use of this waste should be addressed. In Fig. 3 the Van Krevelen Diagram is employed as a tool to compare the chemical characteristics of different chars with raw biomass, it can be appreciated that after hydrothermal processing, the chars tend to reduce its O/C and H/C ratio. This direction is connected with dominant dehydration reactions [7]. Residence time also had an important effect on the chemical properties of the chars obtained. An increase from 0 to 30 or 60 min reaction time resulted in a reduction in O/C ratio. Then, a further increment from 60 to 90 min reduced slightly the O/C ratio to around 0.5.

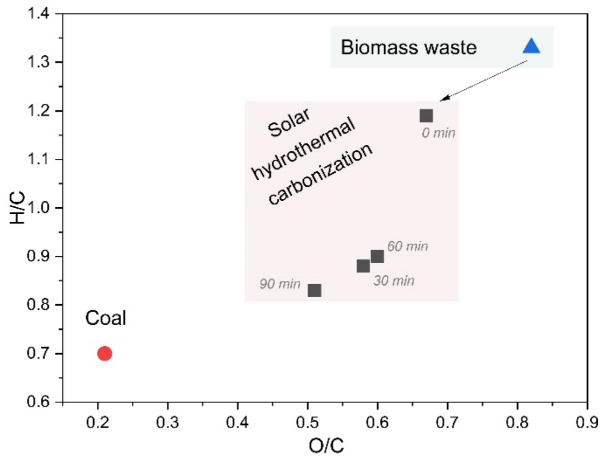

Figure 3. Van Krevelen diagram of raw biomass and chars.

Figura 3. Diagrama Van Krevelen de la biomasa inicial y carbones.

3.2 Effect of residence time on the morphology surface

Raw biomass and char morphologies at different retention times are shown in Fig. 4. The fibrous form of agave bagasse as a long and continuous structure can be appreciated in Fig. 4a). When biomass is treated at 0 minutes residence time, the surface starts a degradation process, where some superficial cavities appear as a result of cell wall destruction (Fig. 4b). An increase in reaction time of 30 minutes at similar experimental conditions, produces a rupture of the bagasse fiber structure that results in the formation of cavities (Fig. 4c). After 60 and 90 minutes of reaction, the cavities disappear and there is a formation of a multiple arrangement of small fibers (Fig. 4d, 4e). These observations are in good agreement with the work of Fang et al. [8], where the porosity of chars is affected by a pore blockage due to a constant decomposition of products on the superficial structure.

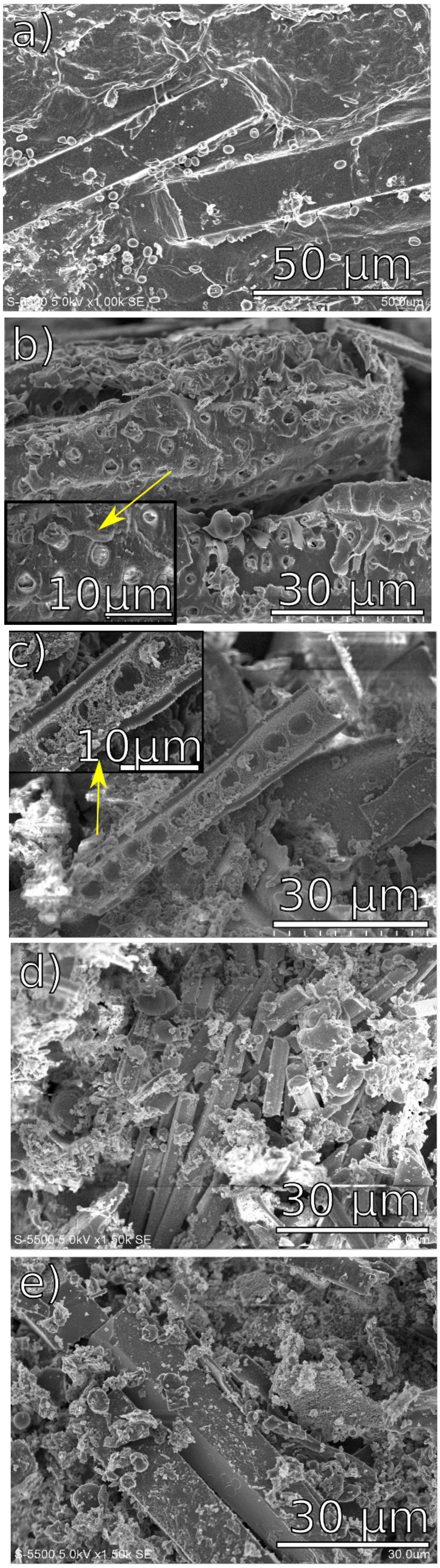

Figure 4. a) Raw biomass, and char micrographs at different residence time b) 0 min, c) 30 min, d) 60 min and e) 90 min.

Figura 4. a) Micrografías de la biomasa y de los carbones a diferentes tiempos de residencia b) 0 min, c) 30 min, d) 60 min and e) 90 min.

3.3 A modified solar hydrothermal reactor

The high thermal inertia of the system limits the maximal operation temperature (up to 300 ºC), and heating rates (up to 3 ºC/min) therefore a modified solar reactor was proposed. The design of this reactor is based on a highly simplified membrane stress study, where it is suggested that the tube wall thickness is proportional to the internal diameter of a tube. Therefore, a reactor with 35 mm of internal diameter (i.d) is considered. Based on the above, a stress analysis was carried out, where the Lame's equations for a thick-cylindrical vessel was used. In the analysis, the thickness of the wall was modified obtaining the radial and tangential stresses for each case. The results of this analysis indicate that a reactor of 35 mm internal diameter, with a wall thickness of 10 mm shows tangential and radial stresses up to 82 MPa and 3.5 MPa. Both parameters are below the elastic limit of 316 stainless-steel at 500 ºC (92 MPa), therefore a solar reactor of 35 mm-i.d. with wall thickness of 15 mm and 160 mm-length was proposed (Fig. 5). It is expected that this reactor allows to reach more homogeneous temperatures and higher heating rates than the previous version. It is important to point out that the Lame´s analysis is a highly simplified study. However, it is necessary to perform a complete analysis of the modified version that includes the equivalent stress in the system with a non-homogeneous temperature distribution.

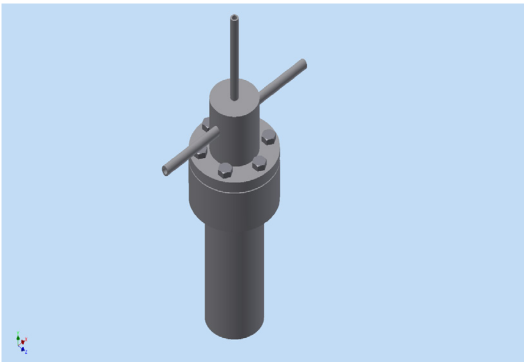

Figure 5. Modified solar reactor.

Figura 5. Reactor solar modificado.

4. Future applications for the solar chars

A solar reactor prototype to perform hydrothermal processing of agave bagasse was successfully used to produce bio-oil with yields of up to 24% and HHV of 28 MJ/kg and chars yield up to 33% and 20 MJ/kg. On one hand, it was also found that an increase in the residence time increases chemical conversion and improves bio-oil properties. On the other hand, during the period of residence time of 30-60 min, chars seem to form a porous structure result of the biomass degradation. Therefore, further studies should focus on the physicochemical properties of the char, such as surface area. In order to address the possible paths in which the char can be employed. Its direct use in energy storage such as electrode material for supercapacitors or as activated carbon in pollutant removal, might be compromised for the low temperature in which was produced. In any case, in order to maximize its possible uses a physic or chemical activation treatment would be required to improve its structural properties.

Acknowledgement

Authors would like to acknowledge J.J. Quiñones-Aguilar for the design of the modified solar reactor, and the financial support received from Fondo Sectorial CONACYT-SENER-Sustentabilidad Energética through Grant 207450, "Centro Mexicano de Innovación en Energía Solar (CeMIE-Sol)", within strategic project No. 120 "Tecnología solar para obtención de productos con valor agregado mediante procesamiento hidrotermal" and DGAPA-PAPIIT-UNAM Project number IN107923: Licuefacción hidrotérmica solar de biomasa residual.

References

Artículos en revistas científicas

[1] A. Demirbas. "Political, economic and environmental impacts of biofuels: A review", Applied energy, vol. 86, Supplement 1,pp. S108-S117, 2009. https://doi.org/10.1016/j.apenergy.2009.04.036.

[2] Y. Guo, T. Yeh, W. Song, D. Xu, S. Wang, "A review of bio-oil production from hydrothermal liquefaction of algae", Renewable and Sustainable Energy Reviews, Vol. 48, 2015, pp. 776-790, https://doi.org/10.1016/j.rser.2015.04.049.

[3] A. Ayala-Cortés, P. Arcelus-Arrillaga, M. Millan, C.A. Arancibia-Bulnes, P.J. Valadés-Pelayo, H.I. Villafán-Vidales, "Solar integrated hydrothermal processes: A review. Renewable and Sustainable Energy Reviews, Vol. 139, 2021, pp. 110575, *https://doi.org/10.1016/j.rser.2020.110575*.

[4] Channiwala, S. A., & Parikh, P. P. (2002). A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel*, *81*(8), 1051-1063.

Comunicaciones congresos

[5] A. Ayala-Cortés, P. Arcelus-Arrillaga, D.E. Pacheco-Catalán, C.A. Arancibia-Bulnes, H.I. Villafán-Vidales, "Solar hydrothermal liquefaction: Effect of the operational parameters on the fuels", MRS Advances Vol. 7, 2022, pp. 24–27, *https://doi.org/10.1557/s43580-021-00204-z*

Artículos en revistas científicas

[6] T. Hussain Seehar, S. Sohail Toor, K. Sharma, A. Haaning Nielsen, T. Helmer Pedersena, L. Aistrup Rosendahl, "Influence of process conditions on hydrothermal liquefaction of eucalyptus biomass for biocrude production and investigation of the inorganics distribution". Sustainable Energy Fuels, Vol. 5, 2021, pp. 477, doi: 10.1039/d0se01634a.

[7] Cai, J., Li, B., Chen, C., Wang, J., Zhao, M., & Zhang, K. (2016). Hydrothermal carbonization of tobacco stalk for fuel application. *Bioresource Technology*, *220*, 305-311.

[8] J. Fang, L. Zhan, Y. S. Ok, B. Gao, "Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass". Journal of Industrial and Engineering Chemistry, Vol. 57, 2018, pp. 15-21. https://doi.org/10.1016/j.jiec.2017.08.026.