

Solar Hydrothermal Processing of Biomass: Influence of Temperature and Pressure on the Fuels

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Abstract

Before the extended use of fossil fuels, biomass was the main source of energy. Nowadays, there is an interest for its use in the production of different energetic materials, as well as added value substances. In order to obtain these products, biomass has to be transformed through different conversion process. Thermochemical biomass transformation presents an attractive option due to its ability to produce fuels quickly, along with the potential to decompose most biomass compounds, such as lignin. Hydrothermal processing (HTP) is a promising technology for being carried out at lower temperatures than pyrolysis and gasification and utilizing wet material up to 70% humidity content, saving biomass drying. However, one concern is that HTP typically uses fossil-generated electricity for heating. Therefore, to reduce its environmental impact, concentrated solar energy has been proposed as a heat source. In the present work, hydrothermal liquefaction of agave bagasse was performed in a solar furnace of 25kW. The experiments were carried out in a solar reactor specifically designed to work at maximum conditions of 220 bar and 500°C. The experiments were carried out with heating rate of 2°C/min. They considered different operational parameters of temperature (150, 250 and 300°C), initial pressure (10, 30 and 50 bar), residence time (0 and 60 min). The main results indicate that at lower temperatures of 250°C, a bio-oil with better energetic properties than that obtained by conventional pyrolysis at 450°C can be accomplished.

Keywords: Solar hydrothermal processing, solar thermochemical conversion of biomass, solar hydrothermal liquefaction.

1. Introduction

Thermochemical conversion processes are attractive alternatives for the biomass transformation due to their faculty to be performed in a short period of time (hours, minutes or even seconds), and the complete transformation of biomass compounds, for instance lignin. Thermochemical processes can be classified in three main routes: pyrolysis, gasification and hydrothermal processing (HTP) (Zhang et al., 2010). Nevertheless, the only one with the capability to be carried out with high moisture content biomass is the HTP (Guo et al., 2015).

One of the main drawbacks in HTP is the energy requirement to heat the process (Gasafi et al., 2008). According to previous studies (Giaconia et al., 2017), the use of a concentrating solar system to provide heat to a hydrothermal plant can reduce the energy demand of the process by 54%.

Xiao et al., 2019 performed an exergetic analysis of microalgae at hydrothermal processing conditions (160 °C and 20 bar) for anaerobic digestion and gas production. In this study, authors compared the exergy efficiency of biogas production by conventional hydrothermal processing technology and solar-driven hydrothermal treatment, the main results found that the exergy efficiency improves by around 5% by carrying out the solar-driven process

(40.85%), in contrast with the conventional hydrothermal treatment (35.98%). This was attributed to the renewable solar energy that deleted the internal exergy loss, which results in improving methane production, compared to the conventional hydrothermal system. Although solar hydrothermal liquefaction of biomass is economically unattractive for its similarity in prices with conventional heating systems of hydrothermal liquefaction, solar hydrothermal processing presents higher thermal efficiencies. Giaconia et al., 2017 and Pearce et al., 2016 reported thermal efficiencies of 0.741 and 0.9, respectively. Meanwhile the work of Jiang et al., 2019 calculated one of 0.56. Proving major thermal capacities of concentrated solar technologies compared to conventional heating systems. Consequently, concentrated solar technologies have been proposed as an option for improving thermal efficiency, as well as reducing the environmental impact (Ayala-Cortés et al., 2020; Jiang et al., 2019).

2. Methodology

2.1 Solar reactor prototype

A solar reactor prototype of 644 mL was especially designed to operate at high radiative flux and high pressures. This solar batch reactor was used to perform the hydrothermal processing experiments. The head of the reactor has two standard fittings, where one type “K” thermocouple is placed to be in direct contact with the slurry. Additionally, a pressure transducer, a PT-100, a relief valve and system of inlet and outlet valves were used (Fig. 1). The reactor was placed in front of the concentrator, in the focal zone of the IER-UNAM solar furnace. The main characteristics of the IER-UNAM solar furnace can be found in a previous work (Ayala-Cortés et al., 2019).

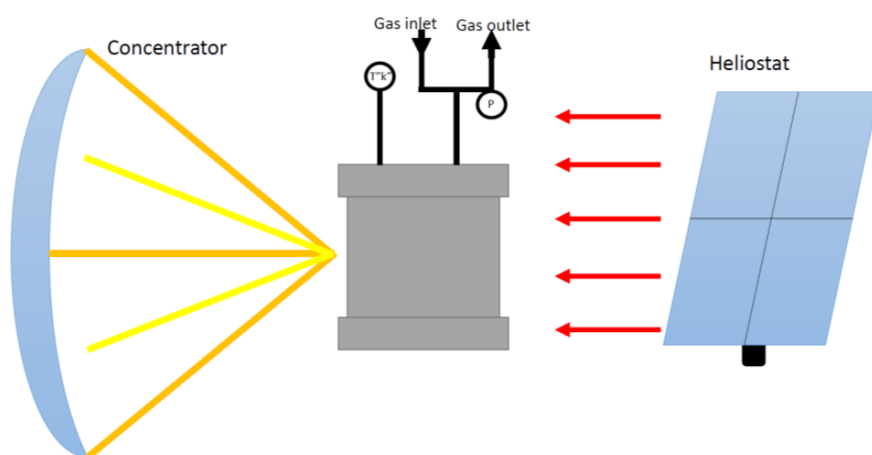


Fig. 1: Diagram of the solar batch-reactor for hydrothermal processing of biomass.

Fibers of *agave angustifolia* bagasse were collected from the state of Guerrero, Mexico, where the plant grows and is used in the production of mezcal. In the cooking and distillation process most liquids are extracted from the plant, and at the end of the process residual biomass that has no use and usually ends on the ground, representing an important industrial waste. 20 g of bagasse fibers were added in the reactor with deionized water at a solid concentration of 10 wt.%. Once the reactor was sealed, Argon gas was injected three times to the system to remove the oxygen and achieve an inert atmosphere.

In the course of the solar HTP experiments, four type “K” thermocouples were placed in the irradiated face of the reactor. Experiments were performed at 150, 250 and 300 °C, with an average heating rate (HR_{av}) of 1.7 °C/min, residence time (τ) of 0 and 60 min, solid concentration of 10 wt.% and initial pressure of 10, 30 and 50 bar at ambient temperature. It is important to point out that the residence time is defined as the time that the target temperature is maintained.

2.2 Separation products

After the residence time has passed and the heating is finished, the reactor cools down at room temperature. Then, the outlet valves are slowly opened to reduce the internal pressure in the reactor. The gas products are vented to the atmosphere and the remaining product is collected without adding any extra solvents, this product consists in a mixture of aqueous phase, bio-oil and char. The separation process of the different products was accomplished

according to Fig. 2, after venting gas, the product goes through a filtration process to separate the aqueous phase. Next, the mix of char and oil are separated by Soxhlet extraction in acetone for 12 h. Then, both products, char and bio-oil in acetone are dried at 60 °C to remove the remaining acetone.

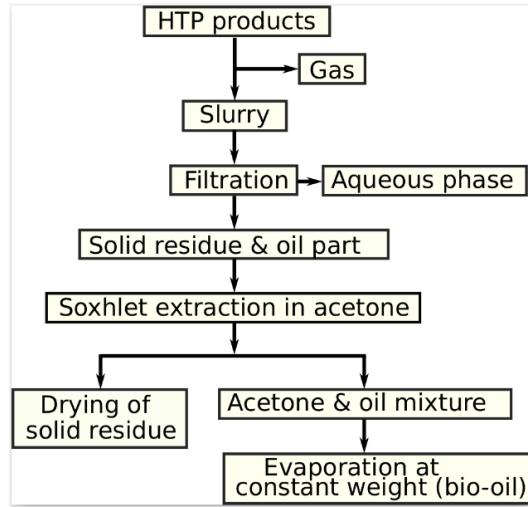


Fig. 2: Diagram of the separation methodology of the solar hydrothermal products.

The yield calculation uses the atomic carbon balance of each phase according to Eqs. (1) (2) and (3),

$$Y_{GasAq.phase}(\%) = (1 - Y_{Bio-oil} - Y_{Char}) \times 100 \quad (1)$$

$$Y_{Bio-oil}(\%) = \frac{m_{Bio-oil} \#C}{m_{Bagasse} \#C} \times 100 \quad (2)$$

$$Y_{Char}(\%) = \frac{m_{Char} \#C}{m_{Bagasse} \#C} \times 100 \quad (3)$$

Where $Y_{GasAq.phase}$ is the yield of the gas and aqueous phase obtained by difference, $Y_{Bio-oil}$ is the bio-oil yield, Y_{Char} is the char yield, $m_{Bio-oil} \#C$ is the carbon content in the bio-oil mass at constant weight, $m_{Char} \#C$, is the carbon content in the char mass and $m_{Bagasse} \#C$ is the carbon content in the raw biomass mass.

Additionally, high heating values (HHV) of char and bio-oil were calculated by Eq. 4 (Channiwala et al., 2002), as well as the energy recovery, ER, (Eq. 5) (Seehar et al., 2021).

$$HHV(MJ/kg) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211Ash \quad (4)$$

$$ER(\%) = \frac{HHV_{product}}{HHV_{biomass}} \times Y_i \quad (5)$$

3. Results

3.1 Effect of the solvent extraction

In order to separate and recover most oil product after the hydrothermal process a solvent is required. Nevertheless, previous studies have found that the type of extraction solvent has a direct impact on the product yields (Watson et al., 2019; Lu et al., 2019). Consequently, two different solvents, Dichloromethane (DCM) and acetone, were used during the separation process. Figure 3 shows the oil and char yields obtained with DCM and acetone, both experiments were performed at 250 °C, with an initial pressure of 50 bar, 10 wt.% solid

concentration and 60 min of residence time. The aqueous and gas phases were not included in this analysis because they do not have contact with the solvent extraction, as showed in the separation diagram (Fig. 2). Results indicate that DCM achieved a higher char yield than acetone (29% compared to 21%). However, there is a reduction in the oil yield (15% for DCM compared to 17% for acetone). This behavior has been previously reported by Lu et al., 2019, where different model compounds were used during HTP, such as cellulose, lignin and xylose. The authors suggest that some products of these model compounds are composed of ketones and phenol groups, and as acetone is also a ketone with the same polarity, it is easier to extract these substances. In the present work, the enhancement of using acetone during the oil recovery was around 13% in contrast with DCM. Therefore, acetone was used as extraction solvent during the product recovery process.

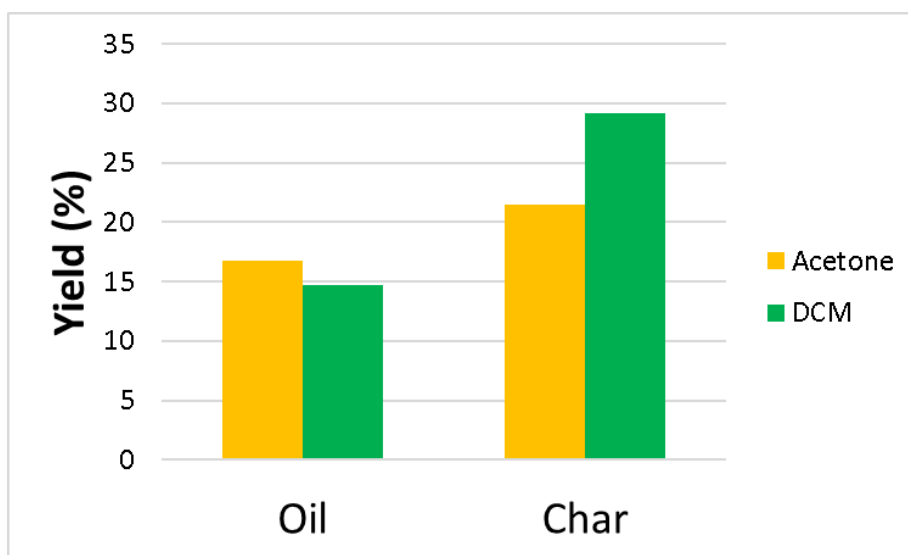


Fig. 3: Effect of solvent extraction (acetone and dichloromethane) during oil recovery. Operational parameters of the experiments: 250 °C, initial pressure of 50 bar, 10 wt% biomass concentration, heating rate of 1.7 °C/min and 60 min of residence time.

3.2 Effect of temperature

Table 1 shows the operational conditions of the different HTP experiments performed, where temperature and pressure are the analyzed parameters. Figure 4a) shows the influence of temperature on the yields, at 0 min of time residence, 10 wt.% solid concentration and 50 bar of initial pressure. It can be noticed that an increase of temperature reduced drastically the solid product, from 57 to 29%. In contrast, gas & aqueous phase along with oil yields are improved with temperature. Bio-oil yield increased from 9% at 150 °C, to 28% at 300 °C. Literature reports the same trend with lignocellulosic biomass. At lower temperatures, biomass starts to decompose and molecules break and to reorganize into lighter compounds [18]. In addition, most favorable oil yield is found near the critical point of water, in the range of temperature of 250-375 °C (De Caprariis et al., 2017; Guo et al., 2015; Zhang et al., 2010).

In the chemical content of the char and oil products (Table 2), it was observed that temperature increases carbon content from 56 to 69% in the oil, meanwhile, the oxygen is reduced from 52 to 45%, which directly impacts on the HHV of the crudes, being 23 MJ/kg at 150 °C and 28 MJ/kg at 300 °C, same behavior is also reported by Xue et al.; 2016. By comparing bio-oils from different thermochemical conversion processes, it was found that the oil produced in the present work shows and improvement against a typical bio-oil from pyrolysis process at 450 °C, due to pyrolysis bio-oils can have higher amount of moisture compared to bio-oils from HTP (Mohan et al., 2006), which have a negative effect on the HHV. Moreover, energy recovery reached its highest value for the char at 150 °C (65%), and the highest for oil at 300 °C (53%), which is related to the major yields of both products at these conditions, at lower temperatures superior amounts of char are expected, and by increasing temperature char decomposes and forms bio-oil.

Tab. 1: Operational conditions of the different solar HTP experiments

N	Conc. (wt. %)	τ (min)	T (°C)	P _i /P _f (bar)	HR _{av} (°C/min)
1	10	0	150	52/71	1.3
2	10	0	300	52/117	1.8
3	10	60	250	11/46	1.9
4	10	60	250	32/82	1.7
5	10	60	250	51/102	1.6

3.3 Effect of pressure

Pressure is an important parameter that allows to maintain water under liquid state in the hydrothermal process (Ayala-Cortés et al., 2020). The highest pressure that can be obtained during HTP experiments is directly related to the initial pressure, therefore, in this work different initial pressures were studied (10, 30 and 50 bar). Once the target temperature (250°C) was reached the pressure inside the reactor increases up to 46, 82 and 102 bar, for an initial pressure of 10, 30 and 50 bar respectively. Figure 4b) shows that the most significant change is related to the gas and aqueous phase, which increases from 41 to 54%, whereas bio-oil and char yields tend to decrease, from 27 to 23% and from 32 to 23%, respectively. The decrease of char and bio-oil yields could be related to secondary reactions. As reported by Xue et al., 2015 a rise of pressure tends to form intermediates that decrease the oil production. Additionally, solar reactor has high temperature gradients, which could reduce biomass conversion and therefore increasing this negative effect on the char and oil production.

Table 2 shows that initial pressure has a minor effect on the bio-oil composition. On the other hand, the chars at 10 and 30 bar have comparable chemical content between them, but at 50 bar there is a decrease on the carbon content and an increase of oxygen, which results in a lower HHV. In this respect, it could be proposed that higher initial pressures are not necessary to obtain bio-oils with similar chemical characteristics. This reduces the pumping demand which could represent saving costs in a higher commercial scale. In terms of energy recovery of bio-oil, at 10 bar, energy recovery showed the highest value (56%), as pressure increases, energy recovery tends to decrease. On the other hand, the ER for the char is similar at 10 and 30 bar. However, at 50 bar the ER from the char decreases almost half compared to the one at 10 and 30 bar.

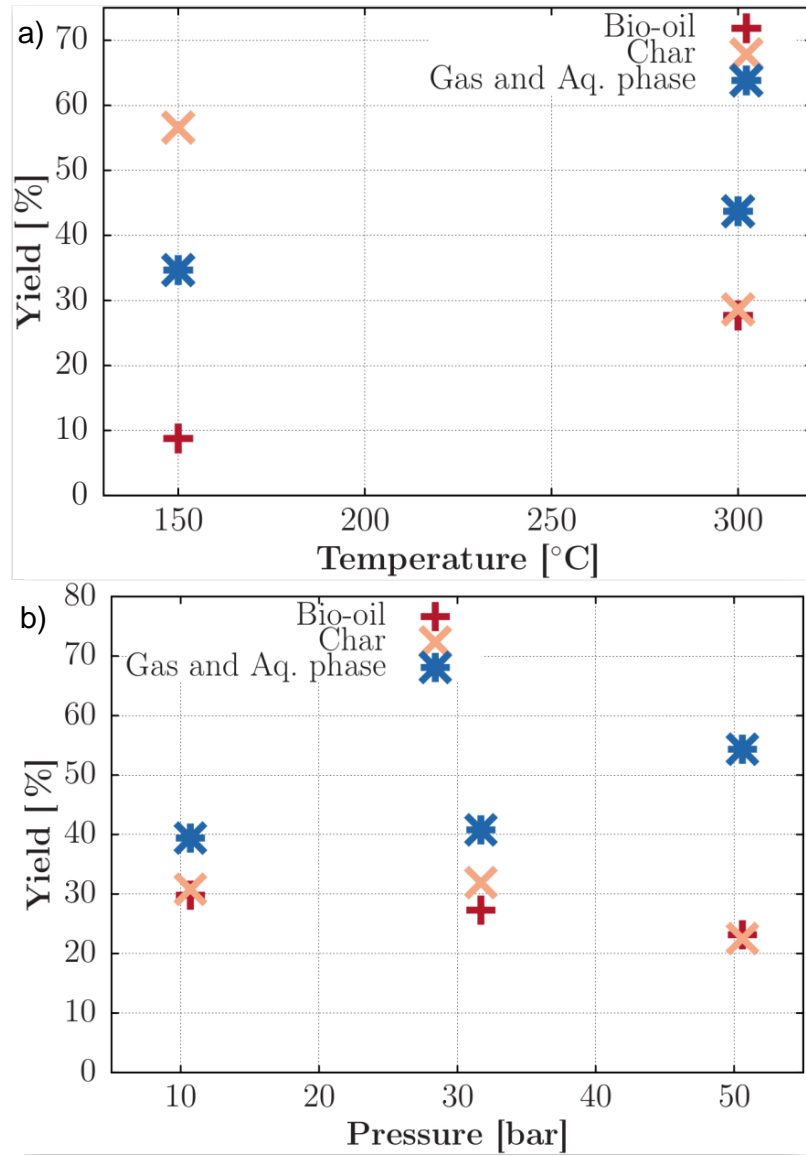


Fig. 4: Influence of the experimental conditions on yields as function of a) temperature ($P_o = 51.5$ bar/ $P_{out} = 92.1$ bar, $\tau = 0$ min, $HR_{av} = 1.6$ °C/min and 10 wt% solid concentration) and b) initial pressure ($T_{av} = 258$ °C, $\tau = 60$ min, $HR_{av} = 1.6$ °C/min and 10 wt% solid concentration).

Tab. 2: Chemical composition of the char/bio-oil at different operational conditions.

N	C (wt. %)	H (wt. %)	O (wt. %)	HHV (MJ/kg)	ER (%)
1	43/56	5/6	52/37	16/23	65/14
2	52/69	4/6	45/25	17/28	33/53
3	57/68	4/6	39/26	20/28	42/56
4	57/69	4/6	39/25	20/28	43/52
5	52/69	4/6	44/25	18/28	26/44

Raw biomass	45	5	49	16	Ash 11%
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4. Conclusion

Solar hydrothermal processing of biomass was successfully performed to analyze the influence of the operational parameters on the yields. Main results indicate that using acetone as solvent extraction can improve the bio-oil recovery up to 13% compared to dichloromethane. Additionally, it was found that bio-oil yields up to 28% can be obtained at 300 °C with residence time of 0 min. At the same time, it was found that an initial pressure of 50 bar tends to reduce the bio-oil yield, which indicates that lower initial pressures are better to improve yields. Furthermore, a decrease in the initial pressure can lead to save costs on a further commercial scale.

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