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Catalytic hydrothermal liquefaction of sugar cane leaf in an ethanol-water co-solvent

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Abstract. The sugar cane is one of the major agricultural plants in Thailand. Each year, 22 million tons of sugarcane leaves are left over in the field or burnt before harvesting. This causes environmental problems such as particle dust, smoke, smell, and global warming from the CO_2.It would be a great benefit if the sugar cane leaf can be utilized as an energy resource. The main purpose of this study is to investigate the effect of cosolvent on the yield of bio-oil from sugar cane leaf. The experiments carried out in a high-pressure autoclave batch reactor sized of 100 mL with a different volume ratio of ethanol to water (0:1, 1:10, 1:5, 1:2.5, and 1:1). 5 g of sugar cane leaves 5 g, 45 g of solvent and 0.5 g of Na_2CO_3 as a catalyst were loaded into the reactor. Reacting temperatures are in the ranges of 250℃ – 350℃ for the reaction time 60 minutes. The maximum yield of 34.8 % is obtained from 1:5 ethanol to water ratio, temperature 300℃. Finally, the maximum conversion is 89.36 % which is obtained from 1:.5 ethanol to water ratio and temperature of 350℃ reacting condition.

1. Introduction

The increase in global energy demand impels to find renewable sources.The thermochemical conversion process (TCC) is processed to convert solid biomass into the liquid and gaseous product. Moreover, TCC has been widely researching for more many years ago [1]. Nevertheless, due to low petroleum price, TCC was still deserted. The significant technologies of TCC are direct combustion, pyrolysis, gasification, hydrothermal liquefaction, and hydrothermal gasification. Gasification is processed for converting solid biomass into synthesis gas, mainly hydrogen, carbon dioxide, carbon monoxide, and methane [2]. Moreover, a product of both pyrolysis and hydrothermal liquefaction is bio-oil. However, a major problem of pyrolysis is needed dry feedstock before entering to process [3] and high oxygen content product [4]. In addition, typically pyrolysis temperature is rather high up to 350 °C – 700 °C [5].

Hydrothermal liquefaction (HTL) is a process to convert solid biomass into bio-oil, by dissolved organics compound in a subcritical solvent. Furthermore, HTL gives many advantages over another thermochemical process and have been widely investigating for crude bio-oil synthesis [6].This process does not require drying process for remove water from the feedstock [7, 8].The drying process takes an extension of energy and time that lead process had low efficiency.Moreover, HTL process used pressurized water as a solvent so let this process become an environmentally friendly process [9]. In recent years, there has been an increasing amount of literature on HTL with various types of feedstock [10]. Several high water content feedstock can be converted to bio-oil by HTL process [11-14].

Sugar canes (*Saccharum*) was planted about 1,884 million tons per year worldwide. Therefore sugar cane leaves about 263.76 million tons (14% of the sugar cane crop) were burned or abandoned [15]. As a result, burning of trash in the pre-harvest process is producing CO_2 about 2,600 - 4,500 kg/ha [16].There has a few study on sugarcane leaf pyrolysis, Josilaine A. C. et al.[17] reported a maximum yield of sugar cane pyrolysis is 63.2 % at pyrolysis temperature 900 °C, with a heating rate 15 °C/minute. Furthermore, K. Duanguppama and A. Pattiya [18] had been investigating properties of bio-oil and biochar from sugar cane leave fast pyrolysis, at temperature 550°C with a feed rate of 150 g/h; the result showed bio-oil yield is 53.34 % with a higher heating value of 15.77±1 MJ/kg.

A recent review of this topic found that the hydrothermal synthesis was studied wildly with many feedstocks. The composition and yield depend on the type of feedstock and process condition. Previous work has only focused on their local material [19-24], and some aquatic biomass [25-31] and a major difficulty of hydrothermal is high pressure and high temperature to reach a critical point of water. In order to reduce temperature and pressure of hydrothermal process, should use co-solvent include water blend with a liquid that has lower critical point such as methanol or ethanol [26, 32]. No previous study has investigated hydrothermal liquefaction of sugarcane leaves. Hence, this study is the first attempt to investigate the HTL with sugarcane leaf. This paper will focus on the effect of reaction temperature and ethanol/water ratio on bio-oil yield and conversion.

2. Material and methods

2.1 Feedstock

Fresh sugar cane leaves were obtained from a farm in Ubon Ratchathani province, Thailand. Before the experimental, sugarcane leave was died at 105 °C for 48 hr.Then, it is grounded in a rotary mill with a screen size of 0.25 mm. (60 mesh). The feedstock samples were analyzed according to ASTM D7582, ASTM D5373, ASTM D4239, and ASTM D5865 standard. The compositions and properties of feedstock are shown in Table 1 and Table 2 respectively.

Table 1 The elementary composition of sugarcane leaves

Composition	Amount (%)
Hydrogen	6.26
Carbon	44.45
Nitrogen	0.69
Oxygen	44.9
Sulphur	0.16

Table 2 Properties of sugarcane leaves

Analysis	Value	Unit
Moisture	6.26	%
Volatile matter	74.65	%
Fixed carbon	16.20	%
Ash	3.54	%
High heating value	4,130	kcal/kg

Note: Tested by Thailand Institute of Scientific and Technological Research

2.2 Experimental apparatus

HTL process was carried out with 100 mL reactor with 25 mm. internal diameter. The reactor supplied by Zhengzhou CY Scientific Instrument CO., Ltd. The 3.0 kW electric heater was employed to heat the reactor by automatics controller. Operating pressure has detected by the pressure sensor for monitoring and noticing for the overpressure releasing. The arrangement of equipment as shown in Figure 1.

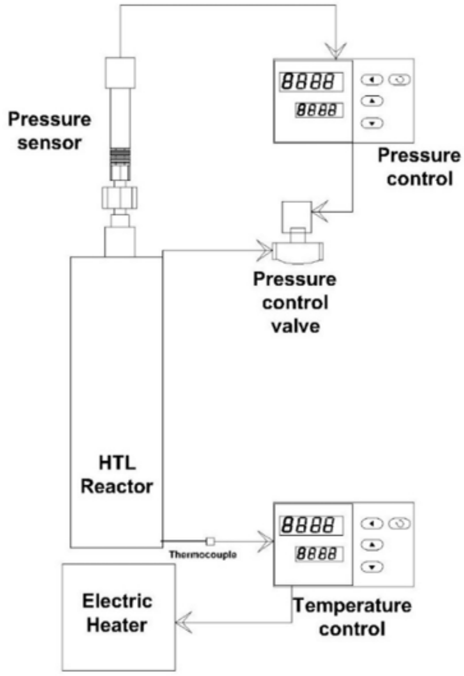

Figure 1 Hydrothermal reactor 100 mL and a temperature and a pressure controller.

2.3 HTL and separation procedures

The experiments were performed with mixed 5 g of sugarcane leaf with solvent 45 g (deionized water + ethanol). The ratios of ethanol to water were varied at 1:10, 1:5, 1:2.5, and 1:1 compared with the absence of ethanol. Firstly, reactants (solvent + biomass+ Na_2CO_3 10% w/w) were loaded to the non-stirred batch Ni-alloy reactor with 100 mL volume capacity. Secondly, the reactor was closed and tightening a bolt on the top. Next, Nitrogen gas was used for release the air by a purge for 5 minutes and give initial pressure to 1.0 MPa. Then, the controller has settled the reaction temperature at 250 °C, 300°C, and 350 °C. Moreover, the heating rate of all experiments were set at 10°C/minute. Thus, the pressure during the reaction is autogenous which is in the range of 6.0-10 MPa.

After reaching the reaction time 60 minute, the reactor will be cooled down rapidly by quenching in the water basin to ambient temperature. After that, the gaseous products were vented without further analysis.Then, the liquid and solid portion were removed from the reactor and separated by filter paper. Subsequently, the reactor was washed with dichloromethane 100 mL; this procedure was repeated three times.After that residue and liquid products were separated by filtration, the remaining solid from filter paper named solid residue (SR). Then, water product was separated from di-chloromethane soluble by a separatory funnel. Finally, the residue is dried at 105 °C for 48 hours. The dichloromethane was removed from bio-oil by rotary evaporator and weighed all product for yield calculation. The separation procedures are showed in Figure 2, and the conversion and yield will be calculated by Equation 1 – 2

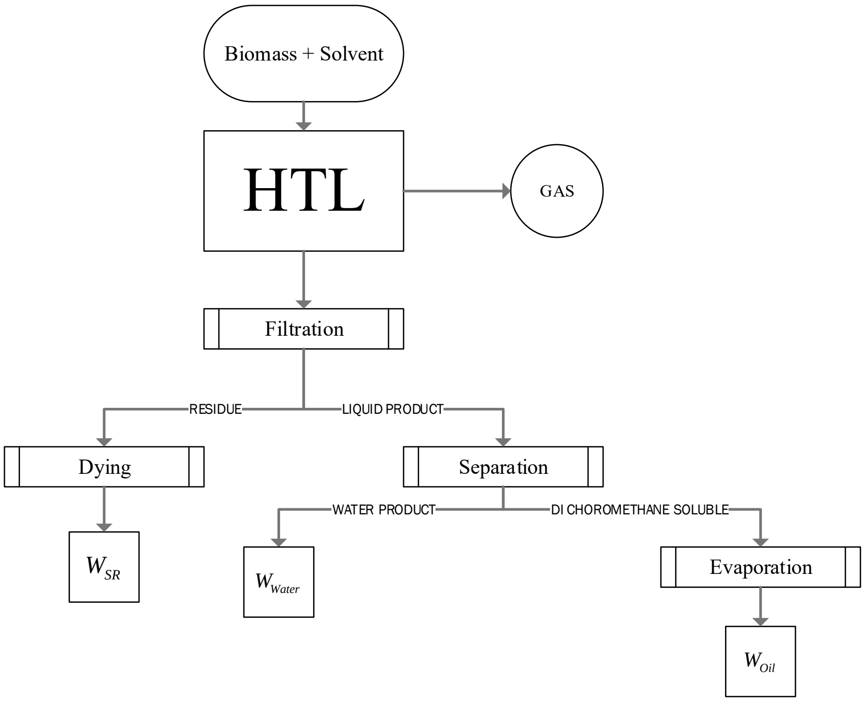

Figure 2 HTL separation procedure diagram.

$$Conversion(\%) = \left(1 - \frac{W_{SR}}{W_B}\right) \times 100 \quad (1)$$

$$Yield_{oil} = \left(\frac{W_{oil}}{W_B}\right) \times 100 \quad (2)$$

Where;

Conversion	is a conversion percentage of solid fuel to liquid and gaseous product (%)
$Yield_{oil}$	is a yield of bio-oil (wt %)
W_B	is a weight of biomass feedstock (g)
W_{oil}	is a weight of bio-oil (g)
W_{SR}	is a weight of solid residue (g)

3. Results and discussions

3.1 Effect of reaction temperature

Experiments were carried out at three reaction temperatures which are 250 °C, 300 °C, and 350 °C. The reaction time was controlled for 60 minutes in each run. Figure 3 illustrates a yield of crude bio-oil in case of using ethanol-water mixture in the range of 0:1 to 1:1 with different reaction temperature.We can see from data that, the bio-oil yield significantly increased when temperature rise from 250 °C to 300 °C, and then dropped slightly when raising temperature to 350 °C, bio-oil yield trend was observed and found similar to that in previous studies [33-35]. By contrast, for the E/W ratio1:5 and 1:2.5 the yield rise steadily. A possible explanation for this might be that bio-oil was cracking to gas when reaching a reaction temperature 350 °C. However, the result of the bio-oil yield of E/W ratio 1:5 and 1:2.5 had a different trend. The maximum bio-oil yield is 34.8 % obtained from E/W ration 1:5 at temperature 300 °C, these results match those observed in earlier algae hydrothermal study [36]. In Figure 4 there is a clear trend of increasing of conversion relates to rising of reaction temperature in all E/W ratio. The maximum conversion is 89.36 % obtained from E/W ration 1:2.5 at temperature 350 °C. Moreover, the minimum conversion was founded from E/W ration 1:1 at temperature 250 °C.

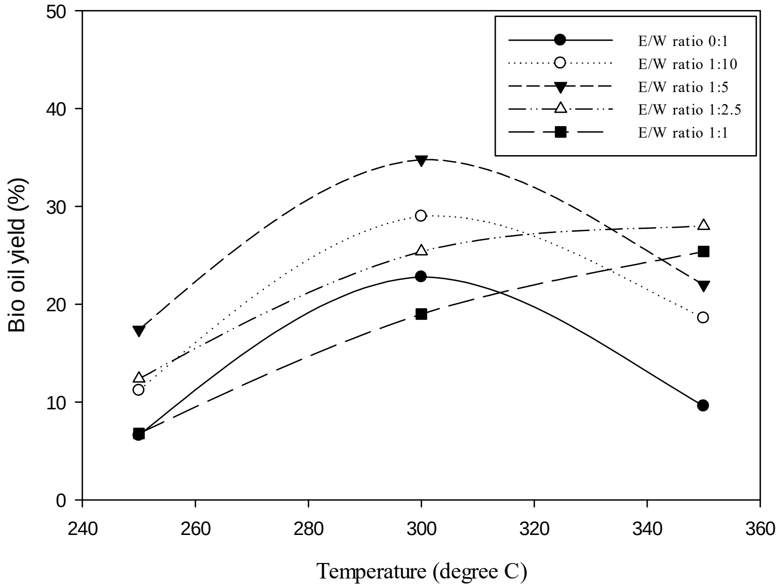

Figure 3 Yield of crude bio-oil with different ethanol/water (E/W) ratio of various reaction temperatures.

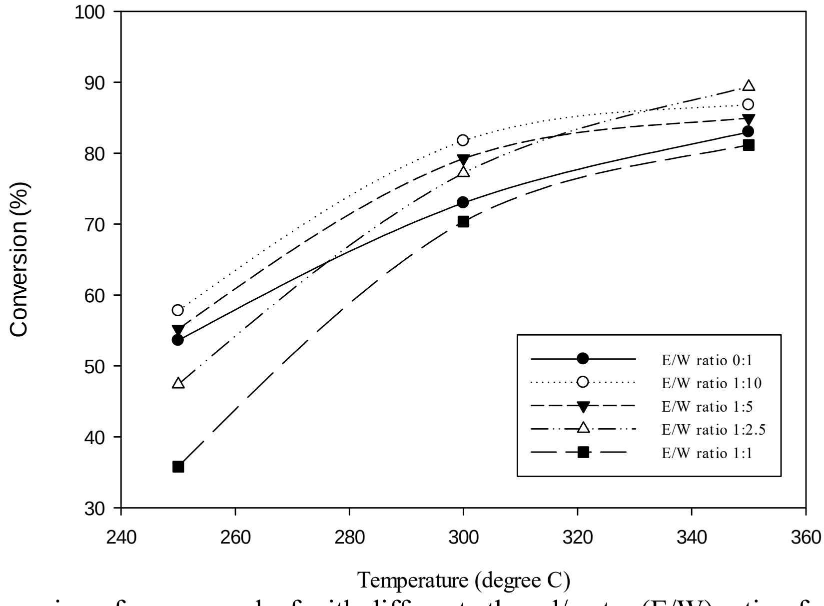

Figure 4 Conversion of sugarcane leaf with different ethanol/water (E/W) ratio of various reaction temperature.

3.2 Effect of ethanol/water ratio

Figure 5 – Figure 7 illustrates bio-oil yield and conversion relate to various E/W ratio at reaction temperature 250 °C, 300 °C, and 350 °C respectively.

Figure 5 shows the relation of bio-oil yield with different E/W ratio at the reaction temperature 250 °C. It can observe that bio-oil yield increased significantly when increasing E/W ratio from 0:1 to 1:5, then the bio-oil yield fell slightly. Also, the maximum bio-oil yield at temperature 250 °C is 17.4 % acquired from E/W ratio 1:5.

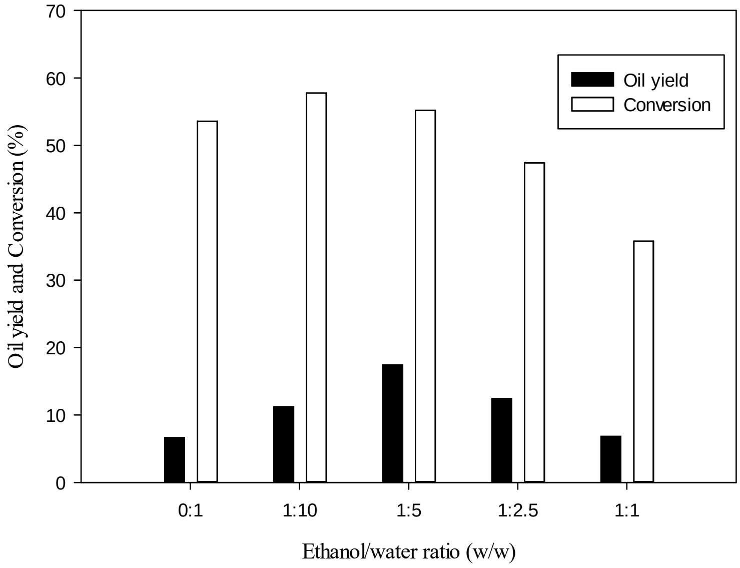

Figure 5 Effect of ethanol /water ratio *(*w/w*)* to oil yield and conversion at temperature 250 °C

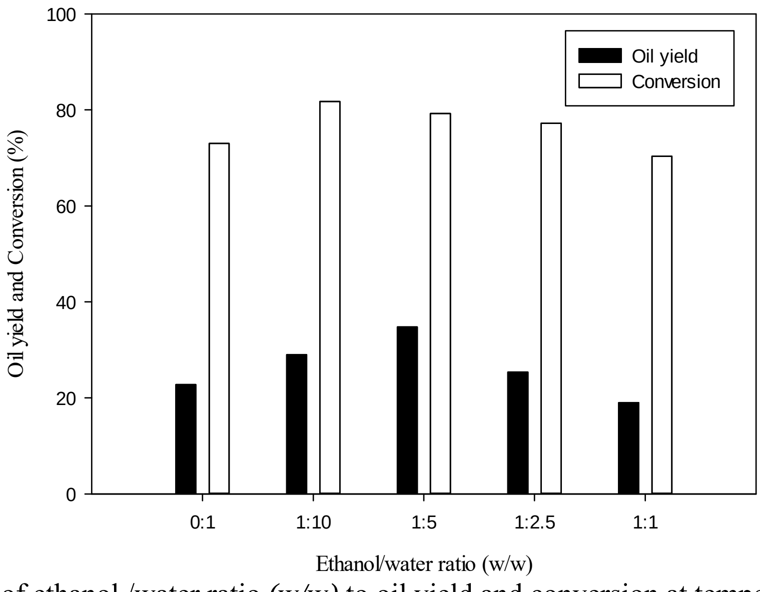

Figure 6 Effect of ethanol /water ratio *(*w/w*)* to oil yield and conversion at temperature 300 °C

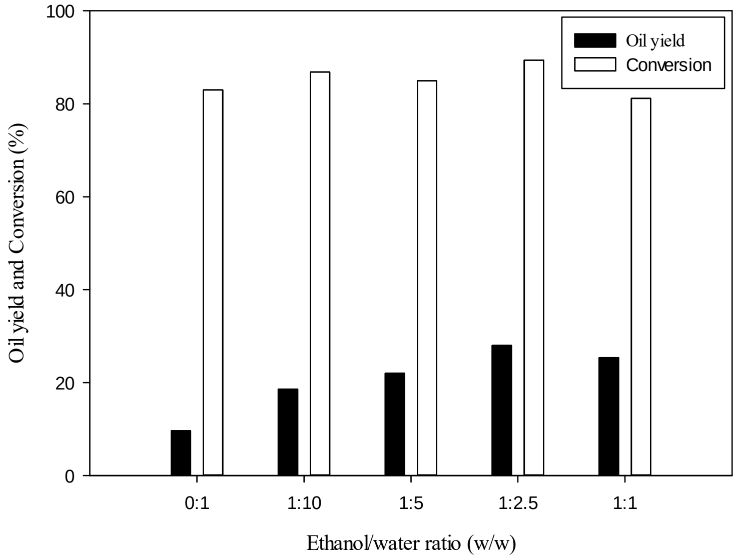

Figure 7 Effect of ethanol /water ratio *(*w/w*)* to oil yield and conversion at temperature 350 °C

Figure 6 depicts the relation of bio-oil yield and conversion relate to different E/W ratio at the reaction temperature 300 °C. We can see from the data that bio-oil yield rise slightly from 22.8% to 34.8%, when E/W increase from 0:1 to 1:5. In contrast, the conversion increase steadily then dropped continuously to 70.36%. Moreover, Figure 7 depicts the result of bio-oil yield and conversion at the reaction temperature 350°C. The result shows that bio-oil increase steadily over E/W ratio 0:1 to 1:2.5 then decrease to 25.4% with E/W ratio 1:1. Moreover, the conversion trend downward and upward, the maximum conversion is 89.36% gained from E/W 1:1.25. From overall these results indicated that quantity of ethanol affected with conversion decreasing. In contrast, bio yield significantly increases when rising E/W ratio from 0:1 to 1:5 and then slightly reduce in case of reaction temperature 250°C and °C. Furthermore, in case of reaction temperature 350°C similar trend is founded, but the maximum bio-oil yield is obtained from E/W ratio 1:2.5.

4. Concluding Remarks

The present study was designed to investigate the effect of E/W ratio, and reaction temperature on conversion and bio-oil yield from the HTL of sugarcane leaf with the Na_2CO_3 catalyst. This is the first study that sugar cane leaf has been the used as feedstock in HTL. The result of this investigation shows that co-solvent (Ethanol + Di water) can enhance bio-oil yield at the same operating conditions compare with Di water.However, the low conversion occurred with increasing E/W ratio, especially at a temperature of 250°C. It should be concluded that the sugar leave is feasible to use as raw material for HTL process to produce renewable bio-oil. However, some important parameters should be considered in the further study. Firstly, the effect of the reaction time should be varied while it was fixed at only 60 minutes in this study. Second, the effect of types of catalysts should be investigated as well.

Acknowledgment

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