



Production of bio-fuel from alcohothermal liquefaction of rice straw over sulfated-graphene oxide

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Abstract

The objective of this research is to investigate the parameters for supercritical ethanol liquefaction of rice straw over sulfated graphene oxide. Graphene oxide was synthesized from thermal treatment of humic acid and then treated with different concentration of sulfuric acid using the wet impregnation technique. Results from liquefaction demonstrated that reaction temperature helped support the production of biofuel, but increase the formation of gas due to cracking reaction. An increase in sulfuric acid helped increase the amount of biofuel produced at first. However, as the sulfuric acid concentration increased higher than 6M, biofuel started to decrease because it is turned into gas and char products. Cracking and isomerization reactions are responsible for these products. The amount of catalyst also have an impact on the liquefaction reaction when it was increased from 5% to 10%. However, as the amount of catalyst increased further the liquefaction did not have a significant change in the ability to produce biofuel. The liquefaction reaction was optimized at 320 °C, 6M sulfuric acid concentration and 10wt% catalyst producing 33.4% biofuel.

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Keywords: Sulfated-graphene oxide; Alcohothermal liquefaction; Rice straw; Biofuel; Humic acid

1. Introduction

Due to petroleum shortage it is important for the research communities to seek for alternative sources of energy. Liquefaction is a process in which biomass can be disintegrate in the molecular level to yield bio-oil, which can directly use as transportation fuel or gasified to produce hydrogen gas. The main benefit of liquefaction is that it can help get rid of waste organic material with high lignin content and at the same time generate bio-oil. One of the difficulty of the reaction is that it is hard to break down the molecule of the carbohydrate in the organic

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Nomenclature

X	Conversion (%)
M_f	Mass of feedstock (rice straw)
M_R	Mass of residual rice straw after reaction
M_B	Mass of biofuel produced
M_C	Mass of char produced

material. For this reason, liquefaction need to be conduct under solvent which help dilute solid material. Current, liquefaction technique involved performing the reaction under high pressure and temperature in order to transform liquid solvent into its supercritical state which have been found to enhance the reaction even further. Many researches used supercritical ethanol as a solvent system for the liquefaction of various high lignin materials. The temperature and pressure required to reach the threshold of supercritical state for ethanol is 243 °C and 6.3 MPa.

Catalytic supercritical alcohol reaction have been employed widely for both liquefaction and gasification of biomass to produce bio-fuel and synthetic gas. There are two main categories of catalyst including heterogeneous and homogeneous catalyst. Acid heterogeneous catalyst help promote the disintegration of cellulose and hemicellulose structure inside the biomass. Zeolite catalyst was among the acid heterogeneous catalyst that have been used to convert saw dust into biofuel. The acidic sites available inside the catalyst were either bronsted or lewic acid type which are responsible for the enhancement of hydrocarbon production instead of ketone and ester molecule that can be produced via alkali heterogeneous catalyst [1]. Geng et al. demonstrated the usage of three different type of zeolite catalysts (ZSM-5, mordenite and HY) for liquefaction of wet algae. The liquefaction was optimized at 280 °C, reaction time of 15 min and 15 wt% ZSM-5 catalyst producing bio-oil yield as high as 29% [2]. Bifunctional type catalyst was also proposed for the liquefaction reaction (sulfated and ammonia on SBA support). Acid sites on the catalyst were responsible for the hydrolysis of cellulosic material and deamination of amino acid into glucose and fatty acid. The alkaline sites then turn these intermediates (fatty acids) into hydrocarbon which increases the hydrogen content which help improved the thermal properties of biofuel [3]. Another bifunctional catalyst employed carbon nanotubes as catalyst support with sulfuric acid and ammonium hydroxide as acid and alkali precursor. Research showed that carbon nanotube demonstrated high thermal stability under severe operating condition [4]. Another interesting support that can be used for the liquefaction reaction is the graphene oxide. However, to the best of researcher knowledge no research have ever conduct liquefaction on graphene oxide catalyst.

The discovery of graphene in 2004 had promoted many other researches in the field of energy [5–7], material strength [8], adhesive [9,10], hydrogen storage [11,12], and electrochemical [13]. Similar to carbon nanotubes, graphene consist of carbon atom however graphene contained only one layer of carbon atom [8,14]. For this reason, graphene have very large specific area, high thermal stability and excellence electric conductivity. Graphene is synthesized via the top-down method which is extremely difficult and cost a lot of money to accomplish. For this reason, a bottom-up method was employed, but it is not possible to synthesize a one-layer carbon atom structure. The bottom-up method can only produce few layer graphene or graphene oxide. Example of the bottom-up method included physical exfoliation [15], hummer method [16], and thermal treatment [17,18]. Since graphene oxide have never been used for liquefaction before, using it as catalyst support is considered as a novelty of this research.

This research aimed to evaluate the acidic graphene oxide for supercritical ethanol liquefaction of rice straw. The observed operating parameters included reaction temperature, concentration of sulfuric acid used to treat graphene oxide, and the amount of catalyst. Graphene oxide was synthesized through the thermal treatment of humic acid. The properties of bio-oil are also tested in term of heat value, viscosity and density in order to evaluate the synthesized bio-oil as a replacement for petroleum-based transportation fuel. The results from this research can paved way for the application of graphene oxide for the synthesis of bio-oil as transformation fuel.

Highlights

1. Graphene oxide can be synthesized from humic acid and can be modified by sulfuric acid solution.
2. High yield of bio-oil (33.4%) can be obtained via alcohothermal liquefaction of rice straw at 320 °C and graphene oxide modified using 6M concentrated sulfuric acid.
3. Bio-oil synthesized from alcohothermal liquefaction over sulphated-graphene oxide have heating value close to that of gasoline.

2. Methodology

2.1. Biomass preparation

Rice straw was harvested from Chainat province and kept refrigerated until used. A motor blender was used to reduce the size of rice straw for liquefaction reaction. The obtained powdered form biomass (500 mesh) was dried at 100 °C in an oven for 12 h. The heat treated powder were kept inside a desiccator until used. The materials were refrigerated at −4 °C

2.2. Catalyst preparation

Humic acid (high purity) was used as a precursor for the synthesis of graphene oxide. This method was chosen because it does not require hazardous chemicals compared with the hummer method or difficult synthesis system compared with the bottom-up method. Approximately 10 grams of humic acid was transferred to an acid digester, sealed properly by tighten the nut, then placed inside the oven. Temperature was set at 190 °C and the acid digester was left inside the oven for 10 h. After thermal treatment, the brown graphene oxide material was obtained, poured inside the glass vial and placed inside a desiccator.

Treatment of graphene oxide in sulfuric acid solution was conducted using the wet impregnation method. For each treatment, 1 gram of graphene oxide was put inside a one-neck round bottom flask with a magnetic stirrer. The flask was placed inside a heating mantle and connected to a reflux which is fed with cool water from the water circulator. The flask was filled with 100 mL of different concentration sulfuric solution and stirred vigorously for 4 h at 50 °C. The treated graphene oxide was then passed through the vacuum filtration which separated it from the sulfuric solution. After separation the solid was heated in an oven at 110 °C for 12 h. The catalyst was denoted as SO₄²⁻/GO-xM, where x is the concentration of sulfuric acid solution used to treat the catalyst.

2.3. Supercritical liquefaction

Conversion of rice straw to biofuel through the alcohothermal or supercritical ethanol liquefaction method was conducted in a stainless steel autoclave reactor at different operating parameters (Reaction temperature, sulfuric acid concentration and the amount of catalyst). This synthesis method is novel and interesting because it can effectively transform wet type biomass into bio-oil and syngas. The designed maximum usage condition of the autoclave was 25 MPa at 450 °C. The reactor was purged with 1 MPa of nitrogen gas three times before setting temperature to set point. The powdered rice straw (10 g) was added to the reactor along with the weighted amount of catalyst. Ethanol solvent was added into the reactor using compressed gas cylinder. The temperature was adjusted to the set point and agitated at 200 rpm. After 1 h of liquefaction reaction, the reactor was cooled down to room temperature. The solid and liquid product and residual was collected at separated using a vacuum filtration technique. Liquid portion of the product was then centrifuged at 6,000 rpm for 15 min to separate micro particle from aqueous solution.

2.4. Calculation of liquefaction reaction

Biofuel, residual biomass, char and gas produced from the liquefaction can be calculated after the product was collected separated and weighted. Calculation to find each results are shown below.

$$X = \left(\frac{M_f - M_R}{M_f} \right) \times 100 \quad (1)$$

$$\text{Biofuel amount} = \frac{M_B}{M_f} \times 100 \quad (2)$$

$$\text{Char amount} = \frac{M_C}{M_f} \times 100 \quad (3)$$

$$\text{Gas amount} = \frac{M_f - M_B - M_C - M_R}{M_f} \times 100 \quad (4)$$

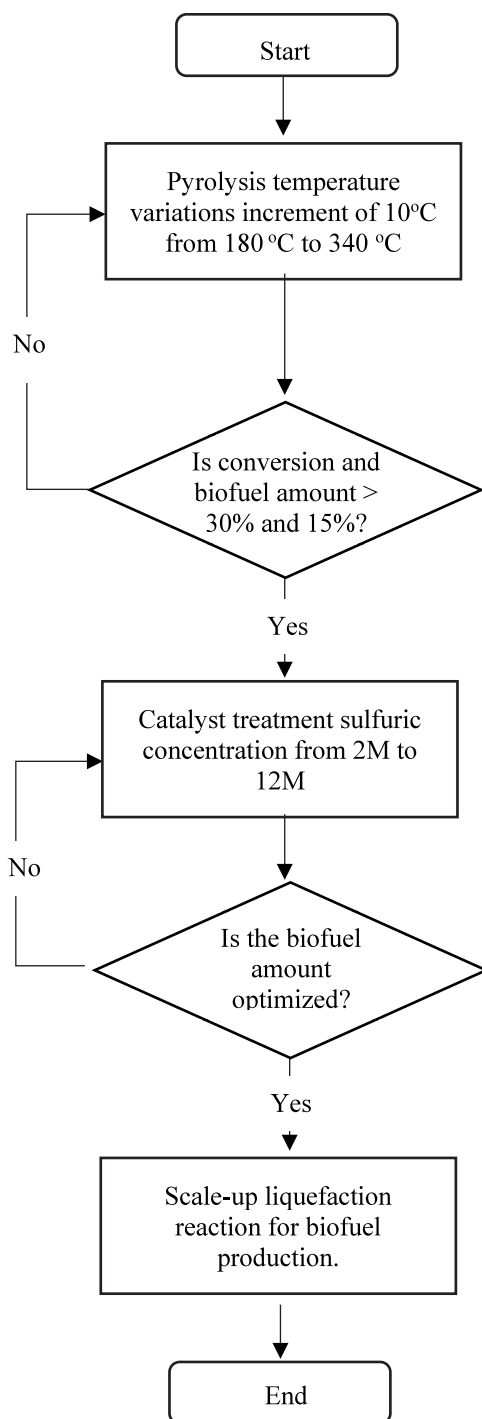


Fig. 1. Flow chart of the experimental optimization for scale-up of the biofuel production process.

where X is the percentage conversion of rice straw biomass, M_f is the weight of feedstock rice straw used for the liquefaction reaction, M_R is the weight of rice straw remaining after the reaction, M_B is the weight of biofuel product during the reaction, and M_C is the weight of char produced during the reaction. The amount of biofuel, char, and gas produced during the liquefaction reaction were demonstrated as percentage. Gas and char produced during the experiment are the product of cracking and isomerization reaction on strong acidic sites in the catalyst (see Fig. 1).

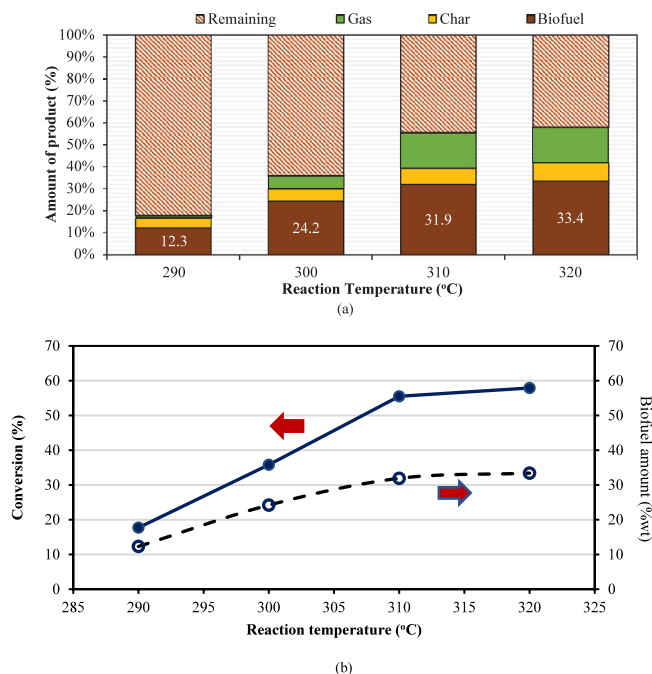


Fig. 2. Effect of reaction temperature on (a) the products of supercritical ethanol liquefaction of rice straw and (b) on conversion of rice straw (Reaction conditions: 10%wt catalyst, 6M sulfuric acid concentration, and 200 rpm agitation speed).

3. Results and discussions

Liquefaction reaction was performed inside a stainless steel autoclave using ethanol as solvent. The operating conditions investigated included reaction temperature in the range of 290 °C to 320 °C, sulfuric solution concentration in the range of 4M to 10M and amount of catalyst from 5 wt% to 20 wt%.

3.1. Effect of reaction temperature on production of biofuel

The temperature of this reaction was controlled accurately with percentage error of only ± 1 °C. According to Fig. 2a, an increase in temperature have a drastic effect on the activity of liquefaction reaction. The amount of biofuel produced increased from 12.3% to 33.4% as temperature increased from 290 °C to 320 °C using 10%wt catalyst and treatment of graphene oxide with 6M sulfuric acid. Reaction temperature enhanced the decomposition of cellulose and hemicellulose and also supported high solubility of intermediate in ethanol solvent. Under supercritical condition rice straw was found to dissolve well in ethanol after the reaction temperature is higher than 290 °C. The supercritical condition of ethanol also helps penetrate the lignin barriers inside the biomass which promote catalyst activities. However, as reaction temperature increased from 290 °C to 320 °C, conversion of biomass into gas product increased from 1.0% to 16.2%. This inclined in transformation of biomass into gaseous state product is due to the cracking reaction which caused the intermediate molecule to break down even further. Additionally, the presence of acidic sites on graphene oxide also help promote the cracking reaction [19,20]. Formation of char raises slightly as reaction temperature increases. Fig. 2b demonstrated an increase in conversion from 17.7% to 57.9% as reaction temperature increases from 290 °C to 320 °C.

3.2. Effect of sulfuric acid concentration on production of biofuel

The prepared graphene oxide was treated in different concentration of sulfuric acid solution from 4M to 10M Fig. 3a demonstrated the influence that sulfuric acid concentration have on products of the supercritical ethanol liquefaction of rice straw using 10%wt catalyst and reaction temperature of 300 °C. The production of biofuel peaked

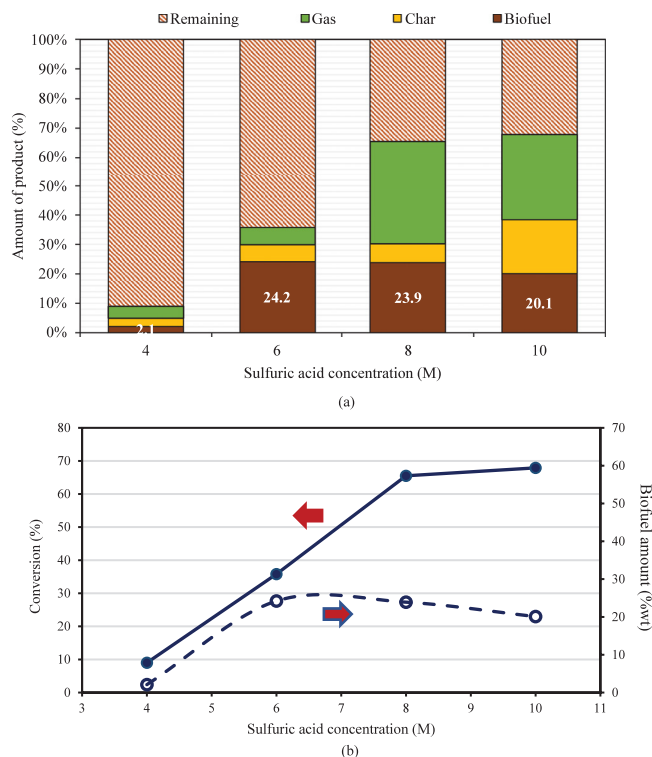


Fig. 3. Effect of sulfuric acid concentration on (a) the products of supercritical ethanol liquefaction of rice straw and (b) on conversion of rice straw (Reaction conditions: 10%wt catalyst, 300 °C, and 200 rpm agitation speed).

at 24.2% when the sulfuric concentration used was 6M. The reduction in biofuel as sulfuric acid concentration increased beyond 6M due to the increase in cracking activity which promote formation of gas product. These gas products included CO₂, CO and H₂ which can also be used as syngas for the production of electricity. Additionally, char formation increased as well when sulfuric acid concentration increases indicating there are stronger acid sites on the treated catalyst which promote isomerization reaction. Isomerization reaction caused the straight molecule to transform into branched molecule which have a higher tendency to be turned to char [21–23]. Catalyst deactivation can occurred at high temperature due to formation of coke which plugged the catalyst pores. Fig. 3b illustrated the conversion of biomass during liquefaction of different sulfuric acid concentration treatment of graphene oxide. Conversion was found to increase from 9% to 67% as sulfuric acid concentration increased from 4M to 10M.

3.3. Effect of the amount of catalyst on production of biofuel

The amount of catalyst used was varied from 5%wt to 20%wt while the reaction temperature was constant at 300 °C, 6M sulfuric acid and 200 rpm. According to Fig. 4a, the amount of biofuel produced dramatically from 3.9% to 24.2% as the amount of catalyst increased from 5%wt to 10%wt. This is due to the increase the number of active sites available for the liquefaction reaction. The breakdown of lignocellulosic material required acidic active sites located inside the catalytic support. Further increase in the amount of catalyst have very little effect on the amount of biofuel produced. Only formation of char was increased gradually as the amount of catalyst used increased. Fig. 4b demonstrated that conversion of biomass increased only when the amount of catalyst changed from 5%wt to 10%wt. These data correlated well with other researches [24,25]

After optimization of the operating conditions (reaction temperature 320 °C, sulfuric concentration 6M, amount of catalyst 10%), a scale-up production unit was designed and used to produced larger amount of bio-oil, which was used for testing different properties as shown in Table 1. The lower and higher heating value were tested using protocol D4809 (Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter

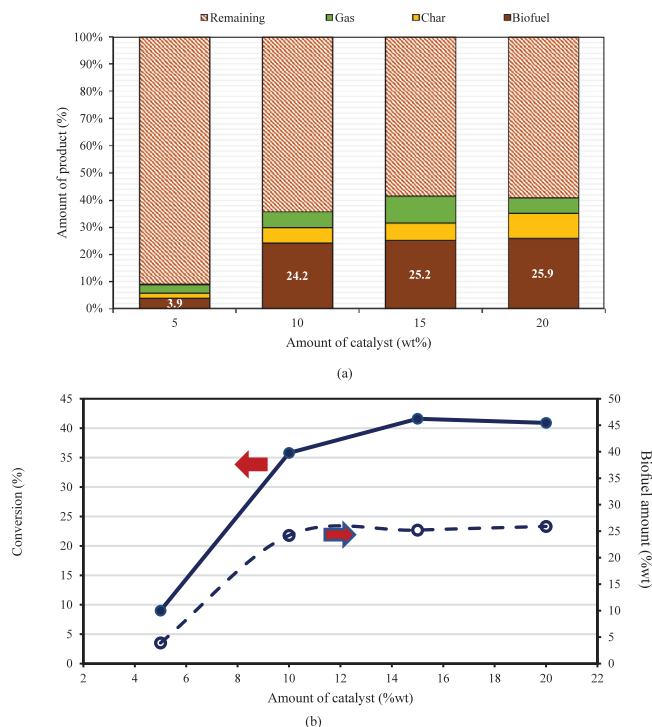


Fig. 4. Effect of amount of catalyst on (a) the products of supercritical ethanol liquefaction of rice straw and (b) on conversion of rice straw (Reaction conditions: 6M sulfuric acid concentration, 300 °C, and 200 rpm agitation speed).

Table 1. Properties of bio-oil produced in the research and reference gasoline.

	Bio-oil synthesized from the research	Reference gasoline
Lower heating value (MJ/kg)	38.952	39.532
Higher heating value (MJ/kg)	40.193	41.581
Relative density @ 20 °C	0.745	0.739
Kinematic viscosity @ 40 °C (cST)	0.421	0.447
Vapor pressure @ 40 °C (kPa)	49.253	50.323

hydrocarbons). According to [Table 1](#), bio-oil produced from this research had lower LHV and HHV compared with the reference gasoline. This is due to the presence of lighter weight molecule generated during the liquefaction reaction. Additionally, liquefaction reaction may also produce phenol and cresol at high reaction temperature which cause a reduction in the viscosity of the fuel.

4. Conclusion

Graphene oxide was successfully synthesized and treated with sulfuric acid solution via the wet impregnation method. The obtained acidic heterogeneous catalyst was used for the supercritical ethanol liquefaction reaction. The reaction was performed in an autoclave reactor with a build-in agitation blade and motor. Results demonstrated reaction temperature to have a positive effect on the production of biofuel. However, it was also found that cracking activities also increase causing the large formation of gaseous product as temperature increases to 320 °C. Sulfuric acid concentration have a significant effect on both decomposition and cracking reaction. Large amount of biomass is converted to gaseous product when the sulfuric acid concentration was higher than 6M. The amount of char also increased significantly as sulfuric acid concentration increased beyond 6M. This is due to the stronger acid sites being formed at higher sulfuric acid concentration causing intermediate to undergo branching producing branch molecules that are more susceptible to turn into char. Important thermal characteristic of the bio-oil was found to

be similar to gasoline. This indicated that the bio-oil produce from this experiment can be blend with gasoline and used as transportation fuel.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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