

Production of liquid bio-fuel from biomass by degradative solvent extraction at 350°C

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Abstract:

Rice straw was subjected to a degradative solvent extraction method that treats biomass in a non-hydrogen donor below 350°C. In this study, we used 1-Methylnaphthalene (1-MN) and Biodiesel from palm oil (B-100) as a solvent. Rice straw is extracted in the solvent at 350°C, under pressure, using a batch autoclave. Then, after the extraction, the residue will be separated from the solvent by filtration. The Soluble fraction, which is solubilized in the solvent, will be upgraded by catalytic hydrogenation. It was found that the amount of C-21 in the soluble fraction decreased significantly, while the amount of C-12, C-14, C-16, C-18, and C-20 increased after the hydrogenation at desired condition. It is suggested that B-100 has potential as a solvent in order to produce liquid bio fuel.

Keywords: Biomass; Degradative Solvent Extraction; Upgrading

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1. Introduction

Fossil fuel has been consumed for a long time and most of industrial fuels are fossil fuel such as natural gas, petroleum and coal. Recently, renewable energy has become more important as the fossil fuel reserve gradually been depleted and also because of the concerns over global climate change. Biomass is one of the most plentiful and well-utilized sources of renewable energy in the world. At the present, biomass has received more attention for using as an alternative fuel resource. But the direct uses of the biomass wastes is not effectively, so the effective methods that convert biomass wastes to energy and/or chemical feedstock is very important. Recently, Wannapeera et al. (2012) have presented a degradative solvent extraction method which convert biomass into high quality carbonaceous extract having similar chemical and physical by using 1-methylnaphthalene as a solvent (Wannapeera et al., 2012). The method treats raw material in solvent below 350°C, under pressure without phase change, to dewater, remove oxygen functional groups, and to produce low-molecular-weight compounds. However, the main drawback of the degradative solvent extraction is to recover the soluble fraction by removing the solvent. So, if we could utilize the soluble fraction without removing the solvent, it will make the utilization of biomass more effective and practical. Thus, we propose the production of liquid bio-fuels from biomass by the degradative solvent extraction. Biomass is extracted in the solvent at 350°C, under pressure, using a batch autoclave. Then, the soluble fraction, which is solubilized in the solvent, will be upgraded by catalytic hydrogenation. The liquid bio-fuels produced from the soluble fraction will be analyzed in details.

2. Experiment

Table 1 summarized the ultimate analyses, proximate and structural compositions of rice straw (RS). Rice straw from Chiang Mai was used as a sample in this study. The size of the sample is less than 5 mm in length. Biodiesel from palm oil (B100) and 1-methylnaphthalene (1-MN) was used as a solvent.

The degradative solvent extraction was performed using an autoclave batch reactor (5 L). The reactor was charged with samples (100 g on dry basis) and 2 L of solvent. Then the reactor was purged with N₂ several times, the reactor was heated up to 350°C and held for 60 min. After cooling the reactor to room temperature, the gaseous products were collected in a gas bag.

Table 1 Analyses of the samples used

Biomass (Abbreviation)	Ultimate analysis (wt%, d.a.f.)				Proximate analysis (wt%, d.b.)			Structural compositions (wt %, d.a.f.)			
	C	H	N	O*	VM	FC	ash	cellulose	hemi- cellulose	lignin	extractive
Rice straw (RS)	47.0	6.5	0.6	45.9	67.5	15.9	16.6	35.1	40.2	20.3	4.3

The extract and the residue (Residue) were separated by PTFE membrane filter (0.45 μm opening). The extract from 1-MN was treated by a rotary evaporator at around 140°C under reduced pressure to remove 1-MN. The extract recovered as solid was called “Soluble” and the extract from B100 solvent was studied in term of “Soluble + Liquid” because B-100 solvent cannot be removed from the soluble fraction after the extraction method was conducted.

The Soluble fraction obtained as a liquid will be upgraded by using a micro hydro treat unit (HTU) through the hydrogenation process under the condition: temperature 275-300°C, pressure 34 bar, LHSV 0.1-0.25 h^{-1} , hydrogen to feed ratio 1,000. The catalyst used through this process is hydrogenation catalyst (Ni/Mo catalyst) and the amount of catalyst used in this reactor is 67.5 g.

3. Results and discussion

3.1 Degradative solvent extraction

This part consists of two main results from degradative solvent extraction procedure which used 1-MN and B-100 as a solvent. The degradative solvent extraction method is essential for convert the biomass (rice straw), which is in form of solid, into the liquid like biofuel and then upgrade it by using hydrogenation process in order to utilize it as a biofuel. Fig. 1 shows the yields of product obtained from extraction of RS at 350°C by using 1-MN and B-100 as a solvent.

The results for using 1-MN as a solvent shows that the amount of hydrogen which contain in raw biomass going to Liquid in form of water. The main gaseous product consists of carbon and oxygen in form of CO_2 and CO , the amount of hydrogen in gaseous product was very small. The largest yields among the solid product was Soluble which is 28.3%.

So the authors applied B-100 as a solvent but after extraction the authors cannot remove the B-100 out of the Soluble which mean that the Soluble and B-100 are in the liquid from. Since the Soluble fraction and the solvent cannot be separated yet so called “Soluble+Liquid” the author need to find the actual amount of Soluble by difference as shown in Fig. 1. The largest yields among the product was Soluble+Liquid which is 55.4%

3.2 Hydrogenation treatment

The upgrading of the Soluble+Liquid fraction obtained from the degradative solvent extraction method by using the catalytic hydrogenation process.

First, we will examine the catalytic hydrogenation of the soluble fraction. The Soluble+Liquid fraction before and after the catalytic hydrogenation were analyzed by GC. Fig. 2 shows the chromatogram of Soluble+Liquid fraction (RS+B100) before the hydrogenation. Fig. 3 shows the chromatogram of the upgraded product at the condition of 275°C, 34 bar and LHSV 0.1 h^{-1} . It was found that the amount of C-17 and C-18 in the soluble fraction decreased significantly, While the amount of C-7 to C-16 increased after the hydrogenation at 275°C and 34 bar.

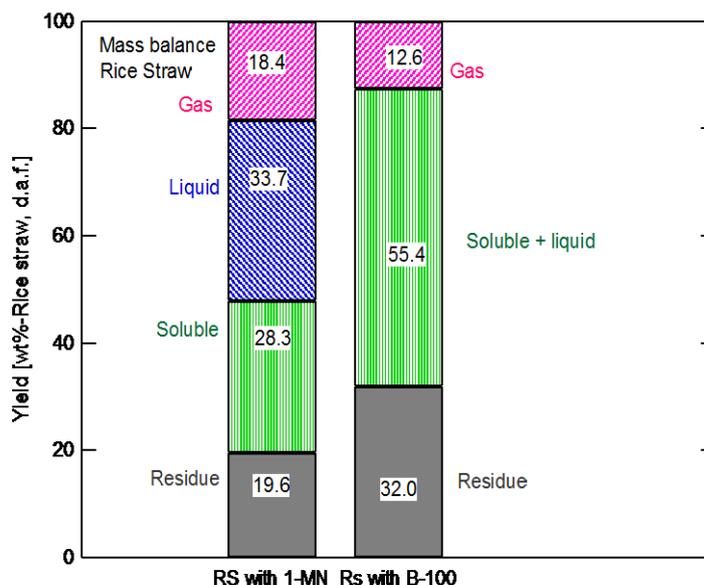


Fig. 1 Yields of product obtained from extraction of RS at 350°C by using 1-MN and B-100 as a solvent.

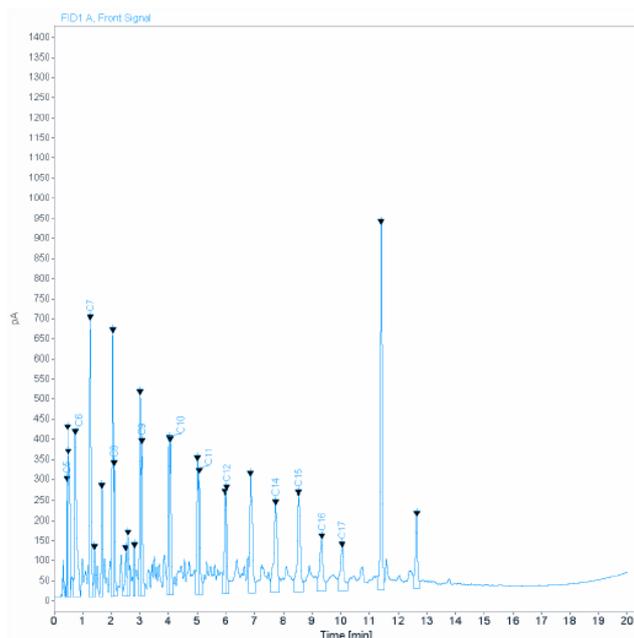


Fig. 2 GC results of RS+B100 feed.

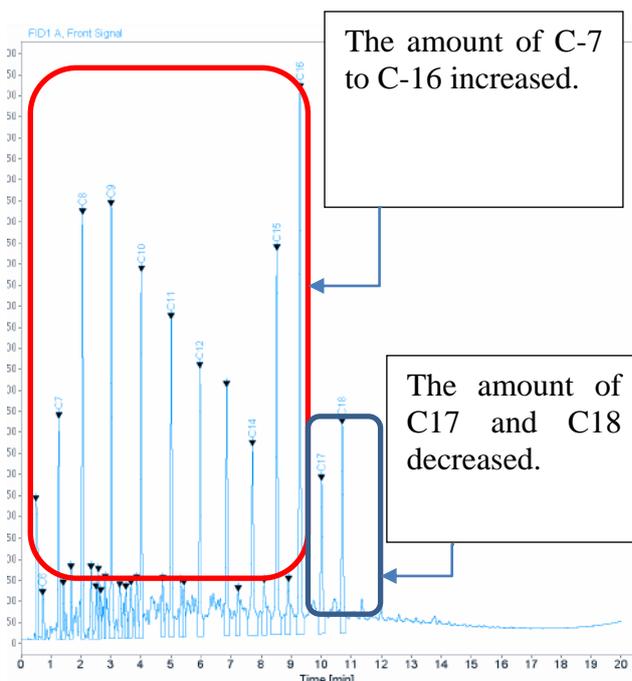


Fig. 3 GC results of RS+B100 after hydrogenated at 275°C, 34 bar and LHSV 0.1 h⁻¹.

Next, we will examine the effect of liquid hourly space velocity (LHSV) on the hydrogenation process of the soluble fraction. Fig. 4 shows the chromatogram of the upgraded product at the condition of 275°C, 34 bar and LHSV 0.25 h⁻¹. Fig. 5 shows the chromatogram of the upgraded product at the condition of 275°C, 34 bar and LHSV 0.1 h⁻¹. It was found that the amount of C-15 to C-18 decreased, while the amount of C-7 to C-14 increased with the decrease LHSV from 0.25°C to 0.1°C. It means that the soluble fraction could be upgraded to be lower carbon number fraction at LHSV 0.1 h⁻¹. It is suggested that B-100 has potential as a solvent in order to produce liquid bio fuel.

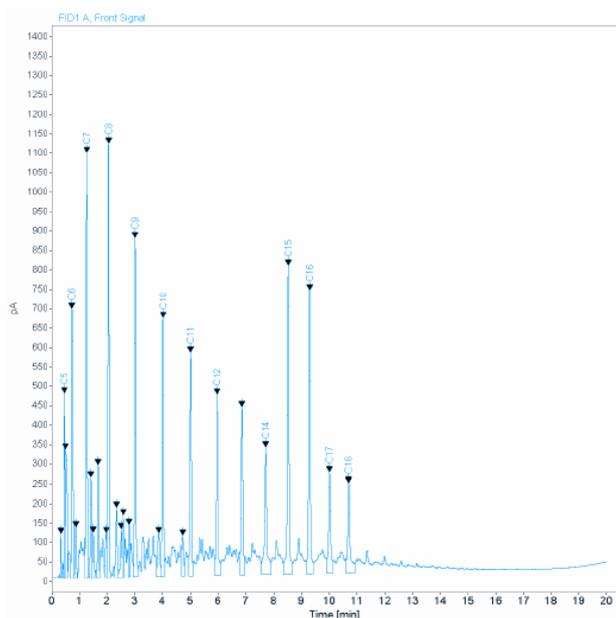


Fig. 4 GC results of RS+B100 after hydrogenated at 300°C, 34 bar and LHSV 0.25 h⁻¹.

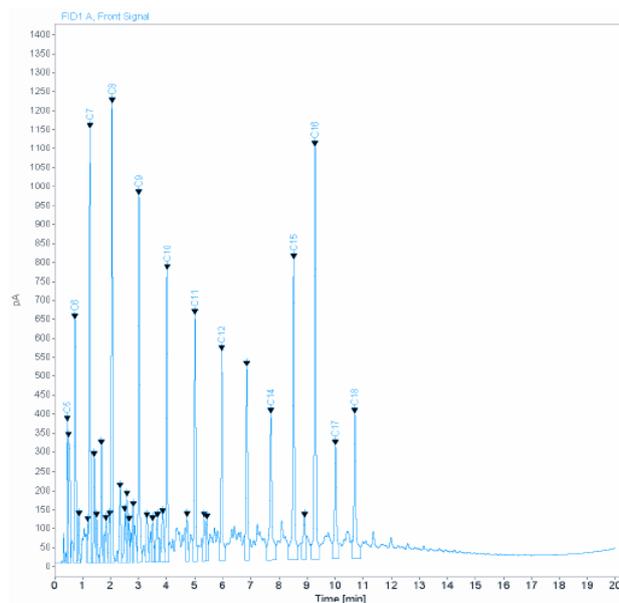


Fig. 5 GC results of RS+B100 after hydrogenated at 300°C, 34 bar and LHSV 0.1 h⁻¹.

4. Conclusion

Rice straw was subjected to a degradative solvent extraction method by using 1-Methylnaphthalene (1-MN) and Biodiesel from palm oil (B-100) as a solvent. The Soluble fraction, which is solubilized in the solvent, was upgraded by the catalytic hydrogenation. It was found that the amount of C-18 in the Soluble fraction decreased significantly, while the amount of C-7 to C-14 increased after the hydrogenation at 275°C and 300°C. It is suggested that B-100 has potential as a solvent in order to produce liquid bio-fuel.

5. Reference

Wannapeera, J., Xian, L., Worasuwanarak, N., Ashida, R., and Miura, K. 2012. Production of High-Grade Carbonaceous Materials and Fuel Having Similar Chemical and Physical Properties from Various Types of Biomass by Degradative Solvent Extraction. *Energy&Fuels* 26: 4521–4531.