

Degradative solvent extraction of rice straw and leucaena by using 1-methylnaphthalene and biodiesel from palm oil at 350°C

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Abstract:

Rice straw and *Leucaena* were subjected to a degradative solvent extraction method that treats biomass in a non-hydrogen donor at around 350°C. The biomasses can be upgraded by removing the oxygen functional group in the form of CO₂ and H₂O. In addition, the low-molecular weight compound can also be extracted. In this study, 1-Methylnaphthalene (1-MN) and Biodiesel from palm oil (B100) were used as a solvent. After treating by this technique, the biomass retained in the reactor was call "Residue" product. The extract dissolved in the solvent was recovered as a solid by evaporation and was called "Soluble". It was found that the carbon-based yields of the Soluble fraction were as large as 57.2 – 58.2 % when using 1-MN as a solvent at 350°C. On the other hand, the carbon-based yields of the Soluble fraction were 43.5 – 46.1% when using B100 as a solvent. The carbon recovered from RS and LC increased to 43.5% and 46.1% (wt%-carbon, d.a.f.) at 380°C. Although, it is difficult to remove the solvent from Soluble fraction when we used B100 as a solvent. It is suggested that B100 has a potential as a solvent for the degradative solvent extraction.

Keywords: Biomass; Degradative Solvent Extraction; Upgrading

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1. Introduction

Biomass is a renewable resource which has received growing attention nowadays. It is the carbon source for energy production and utilization. In an agricultural country as Thailand, very high amount of biomass waste and agricultural residues are generated. Developing the effective methods that convert biomass wastes to energy and/or chemical feedstock is very important. Nowadays the conversion technologies for biomass can be categorized into thermochemical such as pyrolysis, carbonization, gasification, hydrothermal liquefaction and organosolv method, and biochemical conversion such as enzymatic hydrolysis and fermentation. Generally, most of these technologies obtained various products in low yield and low conversion efficiency. Recently, Miura et al. (2013) have proposed the degradative solvent extraction method that converts biomass wastes into high-grade carbonaceous materials and fuel by using 1-Methylnaphthalene as a solvent (Wannapeera et al., 2012). This method is very effective to upgrade and recover solid product in high yield. The method treats raw material in solvent at around 350°C, under pressure, to dewater, remove oxygen functional groups, and to produce low-molecular-weight compounds. The solvent acts as a dispersant for the sample and it does not participate in chemical reaction. 1-Methylnaphthalene (1-MN) was used as a solvent to meet this requirement.

However, to utilize the degradative solvent extraction method more practically, it is suggested to use the cheap and local available solvent. Biodiesel from palm oil (B100), the low cost organic solvent from natural production, was used as the extraction solvent instead of 1-MN. So, this work we examined the degradative solvent extraction of rice straw and leucaena using 1-MN and B100 solvent. The extraction yields as well as the chemical properties of the extracts were examined in detail. Based on these experimental data, the potential of B100 as a solvent for the degradative solvent extraction was discussed.

2. Material and methods

Two biomasses, *Leucaena* (LC) from Saraburi province and Rice straw (RS) from Chiang Mai province

were used as biomass sample. Table 1 summarizes the ultimate and proximate analyses of the samples used. Biodiesel from palm oil (B100) was used as a degrading solvent. 1-methylnaphthalene (1-MN) which is well known as a non hydrogen donor solvent and very effective for degradative solvent extraction was also used for comparison purpose.

The degradative extraction of the sample was performed using a stainless steel tube reactor (12 ml, 12.7 mm I.D.). The reactor was charged with samples (400 mg on dry basis) and 8 ml of solvent. After sufficiently purging the reactor with N₂, the tube reactor was heated up and held for 60 min in sand bath. The extract and the residue (Residue) were separated by PTFE membrane filter (0.5 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 evaporated with 1-MN was call “Liquid”. The yield of Liquid could not be measured directly, but it can be estimated from mass and elemental balances. The extract from B100 solvent was studied in term of “Soluble with Liquid” (Soluble + Liquid).

3. Results and discussion

3.1 Product yield

The effect of the solvent-treatment temperature on the product yield was examined at 300, 350, and 380°C using 1-MN solvent. From the Fig. 1 almost residue yields from extraction at 300, 350 and 380°C were lower than the weight decreasing curves during gas phase pyrolysis (continuous line) from RS and LC. The residue yield decreased when increasing temperature. When comparing with B100, residue yields from 1-MN condition were lower.

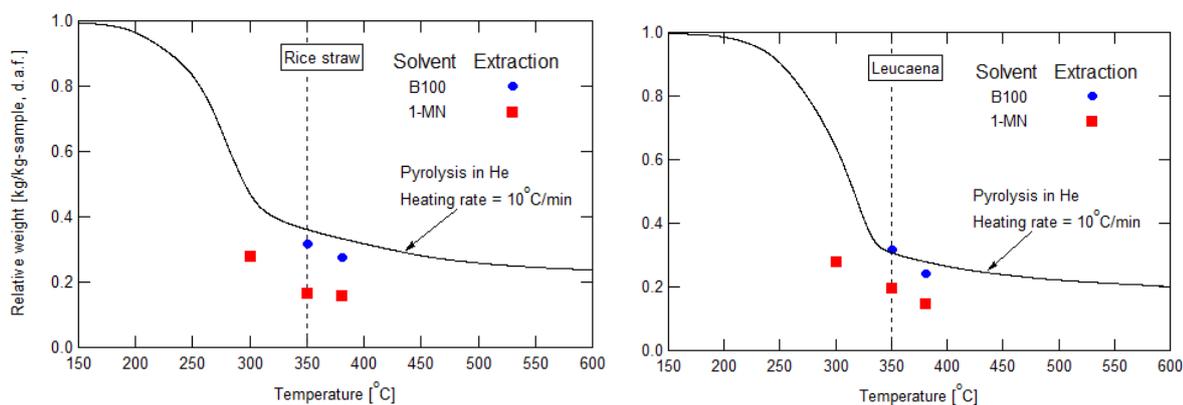


Fig. 1 Change in the residue yield with increasing treatment temperature for RS and LC.

The weight basis yields of the products from RS and LC by using 1-MN and B100 were shown in Table 1. From the result, the oxygen functional group in sample was removed as water and gaseous product (mainly CO₂ and CO) while the sample was heated up to 350°C. The extraction yields, both Soluble and Liquid, increased when increasing the temperature treatment. For 1-MN as a solvent, the soluble yields increased from 25.9% to 33.7% and 29.0% to 34.2% (wt%-d.a.f.) for RS and LC, respectively, when increase the temperature from 300°C to 350°C. However when increasing treatment temperature to 380°C, the soluble yields decreased to 22.3 % and 31.7% (wt%-d.a.f.) for RS and LC, respectively. The potential of using B100 as a solvent for degradative solvent extraction was examined at 350°C and 380°C. It was found that the gaseous products from B100, both from RS and LC, were not significantly different from using 1-MN as a solvent at each temperature. The extraction yields (Soluble + Liquid) when using B100 as a solvent at 350°C were 55.5% and 56% (wt%-d.a.f.) for RS and LC, respectively. At 380°C, the extraction yields (Soluble + Liquid) from LC increased to 61.0% (wt%-d.a.f.) while slightly increased for RS.

3.2 Element distribution of products

Fig. 2 showed the carbon distribution in the products obtained by using 1-MN and B100 as a solvent at 300 – 380°C. The losses of carbon in Gas were 6.9 to 10.6 % for RS and LC at 350°C. It was showed that this method can remove oxygen functional group in biomass as CO₂ and H₂O.

Table 1 Product Yields, ultimate and Proximate Analyses

sample	yield [wt%,d.a.f.]	ultimate analysis [wt%,d.a.f.]				proximate analysis[wt%,d.a.f.]		
		C	H	N	O[diff]	VN	FC	Ash
rice straw		47.0	6.5	0.6	45.9	67.5	15.9	16.6
Treated by 1-MN at 300°C								
Residue	27.8	65.1	4.8	1.1	29.0	38.8	21.6	39.6
Soluble	25.9	78.8	6.3	1.9	13.0	68.4	31.6	0.0
Gas	12.7	31.9	0.0	-	68.0			
Liquid*	33.6							
Treated by 1-MN at 350 °C								
Residue	16.6	68.1	5.4	0.9	25.6	37.6	19.2	43.2
Soluble	33.7	80.0	6.0	1.9	12.1	63.7	36.3	0.0
Gas	15.4	32.5	0.6	-	66.9			
Liquid*	34.3							
Treated by 1-MN at 380°C								
Residue	16.0	68.8	5.4	1.0	24.8	35.7	19.0	45.3
Soluble	22.3	81.3	5.8	1.5	11.4	61.3	38.7	0.0
Gas	18.7	31.8	0.6	-	67.6			
Liquid*	42.9							
Treated by B100 at 350°C								
Residue	31.8	69.9	4.8	0.5	24.8	49.1	19.3	31.6
Gas	12.6	34.0	0.8	-	65.2			
Soluble+Liquid*	55.5	71.8	4.9	0.5	22.7			
Treated by B100 at 380°C								
Residue	27.5	72.3	6.1	0.6	21.0	39.9	26.7	33.4
Gas	16.9	34.5	1.7	-	63.8			
Soluble+Liquid*	55.6							
leucaena		47.7	6.2	0.7	45.4	82.6	16.0	1.4
Treated by 1-MN at 300°C								
Residue	28.1	70.2	5.3	1.6	22.8	66.0	28.4	5.6
Soluble	29.0	76.8	6.0	2.4	14.8	64.1	35.9	0.0
Gas	10.7	30.6	0.1	-	69.4			
Liquid*	32.2							
Treated by 1-MN at 350°C								
Residue	19.5	66.3	4.4	1.8	27.5	55.2	38.1	6.7
Soluble	34.2	81.1	6.1	2.0	10.8	64.0	36.0	0.0
Gas	12.7	32.7	0.6	-	66.7			
Liquid*	33.6							
Treated by 1-MN at 380°C								
Residue	14.6	74.0	4.6	0.9	20.5	42.8	48.9	8.3
Soluble	31.7	82.5	5.6	1.8	10.2	63.6	36.4	0.0
Gas	13.7	34.2	1.2	-	64.6			
Liquid*	39.9							
Treated by B100 at 350°C								
Residue	31.6	68.9	3.9	0.9	26.3	59.7	37.4	2.9
Gas	12.2	31.9	0.6	-	67.5			
Soluble+Liquid*	56.1							
Treated by B100 at 380°C								
Residue	24.3	74.0	5.0	0.8	20.2	54.5	41.1	4.4
Gas	14.7	34.5	1.8	-	63.7			
Soluble+Liquid*	61.0							

* Calculated by different

Using 1-MN as a solvent, the carbon loss in the Liquid at 350°C was very small about 7.9% and 3.3% (wt%-carbon, d.a.f.) for RS and LC, respectively. The carbon which recovered in the soluble was very high up to 57.4% and 58.2% (wt%-carbon, d.a.f.) for RS and LC, respectively. Similar trend with product yield, the carbon recovered in the soluble decreased when increasing the treatment temperature to 380°C.

For using B100 as a solvent, the carbon in gas fraction was not significant different from using 1-MN. The carbon which can be recovered from RS and LC at 350°C were 43.5% and 46.1% (wt%-carbon, d.a.f.) in the Soluble + Liquid fraction. At 380°C, the carbon recovered from RS and LC increased to 45.3% and 51.7% (wt%-carbon, d.a.f.), respectively. The carbon contained in residue product was higher than the residue obtained using 1-MN as a solvent. These results show that B100 can be used for the purpose of solvent treatment.

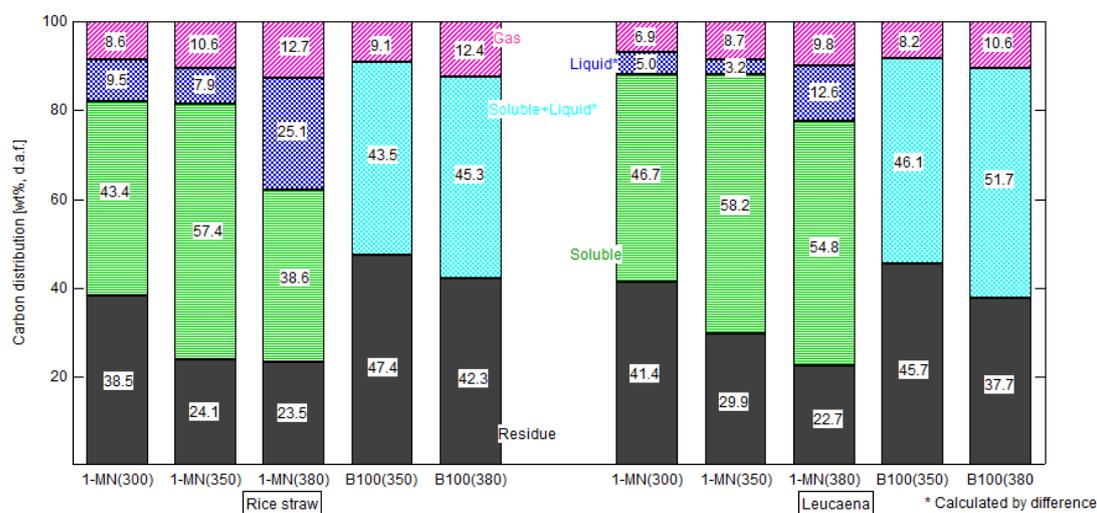


Fig. 2 Carbon distribution from degradative solvent extraction of RS and LC using 1-MN and B100 solvent.

4. Conclusion

Biodiesel from palm oil can be applied for solvent treatment. The carbon which can be recovered from RS and LC were 43.5% and 46.1% (wt%-carbon, d.a.f.), respectively, in the Soluble + Liquid fraction at 350°C. At 380°C, the carbon recovered from both RS and LC increased to 45.3% and 51.7% (wt%-carbon, d.a.f.), respectively. These results show that B100 can be used as a solvent for the degradative solvent extraction method.

5. References

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