

Upgrading of Woody Biomass by Solvent Treatment at Temperature Below 350°C

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Abstract: We have recently presented “Degradative solvent extraction” to upgrade as well as to dewater low rank coal and biomass wastes at 350°C using 1-methylnaphthalene (1-MN). In this work we examined the possibility to use kerosene as a practical solvent to upgrade biomass in reference to 1-MN. It was found that the thermal degradation behavior of Leucaena in kerosene and 1-MN was rather similar. The yields of the solvent treated biomass (STB) using kerosene and 1-MN were close to each other. At 350°C as large as 71.1%, and 73.3% of carbon were recovered in the STBs prepared from using kerosene and 1-MN, respectively. The higher heating values (HHV) of the STBs were as high as 29.9 MJ/kg, and 30.9 MJ/kg for the STBs prepared from using kerosene and 1-MN, respectively. These results showed that kerosene was very effective to upgrade biomass by solvent treatment method.

Keywords: Biomass, Upgrading, Degradative solvent extraction.

1. Introduction

Biomass is a renewable resource which has received growing attention nowadays. This is because biomass is considered as a carbon neutral fuel and it also emit less sulfur compared to fossil fuel when it is combusted. However, biomass is classified as a low-grade fuel which naturally contains undesired properties, such as high moisture content, high ash content and low energy density. Considering the biomass as feedstock for power generation, particularly in a direct comparison with coal, biomass often reveals undesirable properties. Moreover, some biomass has high ash content especially alkaline, which will lead to the agglomeration of the bed material inside the reactor as well as the fouling problem found at the surface of water tube in combustion chamber [1-2]. Thus, direct utilization of biomass seems to face great barrier overcoming the above drawback. Development of efficient biomass conversion technologies is essential to utilize the biomass more efficiently [3-5]. Various technologies have been proposed for upgrading biomass and/or producing valuable chemicals from biomass including torrefaction [6-9], gasification [10], hydrothermal liquefaction [11-12], organosolv [13], etc. Each technology has been developed for specific purposes and has some merits and demerits.

The authors have recently proposed a degradative solvent extraction method to separate low rank coal and biomasses into three solid fractions under mild condition [14-16]. The method treats biomass in a non-hydrogen donor at around 350°C, under pressure, using a batch autoclave to dewater without phase change, to remove oxygen functional groups, and to produce low-molecular-weight compounds. The core concept underlying this method involves exposing the entire sample to thermal reaction in a non-polar solvent at around 350°C. The upgraded product was fractionated into three solid fractions: Soluble, Deposit, and Residue. The carbon based yield of Soluble reached as high as 70% for some biomass. Soluble were free from water and mineral matters, and their physical and chemical properties were almost independent of raw materials. Elemental compositions of Soluble, for example, were C = 81.8 – 84.8 wt%, H = 7.5 – 8.1 wt%, and O = 6.5 – 10.2 wt% [14]. In this study, the possibility to use kerosene as a practical solvent to upgrade biomass was examined in reference to 1-MN. We prepared “solvent treated biomass” (STB) without separating the upgraded biomass into three fraction, and the STBs prepared were also characterized in detail.

2. Experimental

2.1. Raw material

Leucaena wood (LC) was used as a raw material in this work. The properties of leucaena are shown in Table 1. Kerosene was used as solvent in this study. The boiling point of Kerosene is 169.2–219.0°C. Kerosene is composed of saturated long chain hydrocarbons and some of aromatic compounds.

2.2 Solvent treatment experiment

The solvent treatment was performed at 300–350°C using a small tube reactor (12.7 mm O.D. and 12 mL in volume). The schematic diagram of the apparatus is shown in Figure 1. On each run, around 400 mg of sample on a dry basis (d.b.) and 8 mL of solvent were charged into the small tube reactor. After sufficiently purging the reactor with N₂, the reactor was heated to 300°C or 350°C at a rate of ca. 10°C/min and held for 60 min at the final temperature. After cooling down the reactor to room temperature, the gaseous products were collected in gas bag and they were analyzed for CO₂, CO, and hydrocarbon gases by using a micro gas-chromatograph (Varian, CP4900). The volume of gaseous product was measured by using gas syringe glass. The treated biomass obtained as solid

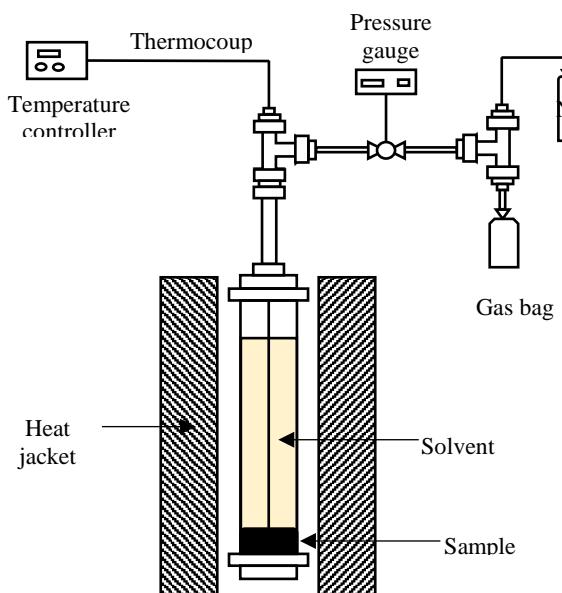


Figure 1. The schematic diagram of solvent treatment experiment.

product was called solvent treated biomass (STB). The STB in the tube reactor was collected by removing the solvent using a rotary evaporator and drying in vacuum oven for 24 h to remove the remaining solvent. The yield of STB are determined through measuring their weight. Some small molecular weight compounds were recovered together with solvent when separating STB and solvent. They are water and small molecular-weight hydrocarbons dissolved in the solvent, this fraction called liquid in this paper. The yields of liquid products were calculated from the difference between the yield of gaseous products and the yield of solid products. For comparison, torrefied leucaena in nitrogen atmosphere and under pressure were also prepared under the same temperature and holding time as that of the solvent treated biomass.

2.3 Torrefaction under nitrogen atmosphere experiment

Figure 2 shows a schematic diagram of the apparatus used for the torrefaction under nitrogen atmosphere in horizontal quartz tube reactor. About 400 mg of sample was placed in alumina boat located at the center of quartz reactor. N₂ was then purged through the reactor at the flow rate of 50 ml/min for several time. Then the reactor was heated to 300°C or 350°C by using furnace at a rate of ca. 10°C/min and held for 60 min at final temperature. The gaseous product occurred during process was collected in the gas bag continuously from start to the end of process. After cooling down quartz tube reactor to room temperature, the yield of solid product was determine by measured their weight. The solid product obtained by this method is abbreviated to “N₂ atmosphere”.

2.4 Torrefaction in nitrogen under pressure experiment

To prepare the biomass torrefied in nitrogen under pressure, the same apparatus shown in Figure 1 for solvent treatment was used. The experiment was performed by following the same experiment procedure as the solvent treatment, but the solvent does not applied in this section. Around 400 mg of sample on a dry basis (d.b.) was charged into the small tube reactor. After sufficiently purging the reactor with N₂, the reactor was heated to 300°C or 350°C at a rate of ca. 10°C/min and held for 60 min at the final temperature. The treated biomass in the tube reactor was carefully collected using propan-2-ol (IPA) by filtration. After that the treated biomass was dried in vacuum oven, the treated biomass was recovered as solid product. The solid product obtained by this method is abbreviated to “N₂ under pressure”.

2.5 Analyses of solvent treated biomass

The STBs were characterized by various analyses. Proximate analysis and thermal decomposition behaviors were conducted by using a thermogravimetric analyzer (Shimadzu, TGA 50). On each run, 8 mg of sample in platinum pan was heated up to 900°C in nitrogen atmosphere at heating rate 10°C/min. The elemental analysis was performed by a CHN corder (J-Science, JM10 CHN). The higher heating values of the

STBs on the dry and ash-free (d.a.f.) basis were calculated by using the Dulong equation as show in equation (1):

$$\text{HHV (MJ/kg, d.a.f.)} = \frac{(338.1C + 1441.8H - 180.2O)/1000}{(1)}$$

where C, H, and O represent the weight percentages of carbon, hydrogen, and oxygen, respectively.

3. Results and Discussion

3.1 Product yields of STBs

Table 1 lists the yields of solid product, gaseous products, and liquid from the treatment in nitrogen atmosphere, nitrogen under pressure, and solvent treatment using both kerosene and 1-MN of LC at 300°C and 350°C. The table also lists the proximate analyses, elemental compositions, atomic ratios, the higher heating values (HHVs), and energy yield of solid products. Figure 3 compared the product yield distributions for LC prepared at various conditions at 300°C and 350°C. First, the effect of solvent treatment on the product yields was examined by comparing with the product yields from the treatment by 1-MN and the torrefaction under nitrogen atmosphere. The solid yields of LC torrefied under nitrogen atmosphere were 46.7 wt%, and 32.6 wt% at 300°C, and 350°C, respectively. On the other hand, the solid yields of STBs treated by 1-MN were 49.0 wt%, and 44.0 wt% at 300°C, and 350°C, respectively. The liquid yield of the torrefaction under nitrogen atmosphere at 350°C was 53.4 wt%, whereas the liquid yield of the solvent treatment by 1-MN at 350°C was 42.5 wt%. These results showed that the solvent treatment gave higher solid yield while the liquid yield was lower when compare with the torrefaction at the same temperature. Next, we will examine the effect of solvent treatment on the product yields by comparing with the product yields from the treatment by 1-MN and the torrefaction in nitrogen under pressure. The solid yields of LC treated in nitrogen under pressure were respectively 49.3 wt%, and 42.0 wt% at 300°C, and 350°C. These results indicated that the solvent treatment by 1-MN gave higher solid yields than the treatment in nitrogen under pressure. The effect of solvent on the thermal degradative reaction of biomass and product distributions can be examined by focusing on the yield of gaseous products and solid products of solvent treatment using 1-MN and kerosene. The gaseous products were collected in the gas bag were solely CO₂, CO, and a very small amount of hydrocarbon gas for both 1-MN and kerosene. The yields of gaseous products were formed in comparable amount for both solvents as shown in Figure 3. The yields of STBs prepared by both solvents were rather close to each other at either 300°C or 350°C. These results suggested that the mechanism and the degree of the thermal decomposition reaction at both 300°C and 350°C in the two solvents were similar for LC [16]. These results showed that the solvent did not significantly affect the product yields during the solvent treatment.

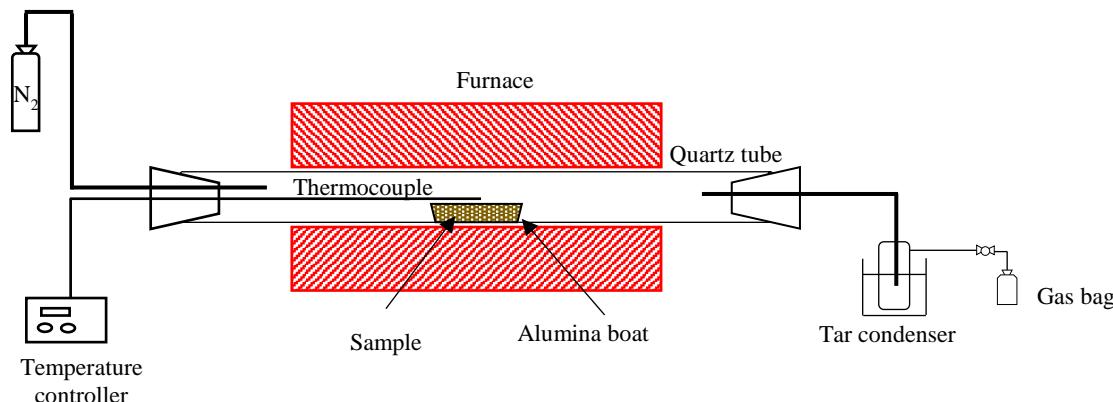
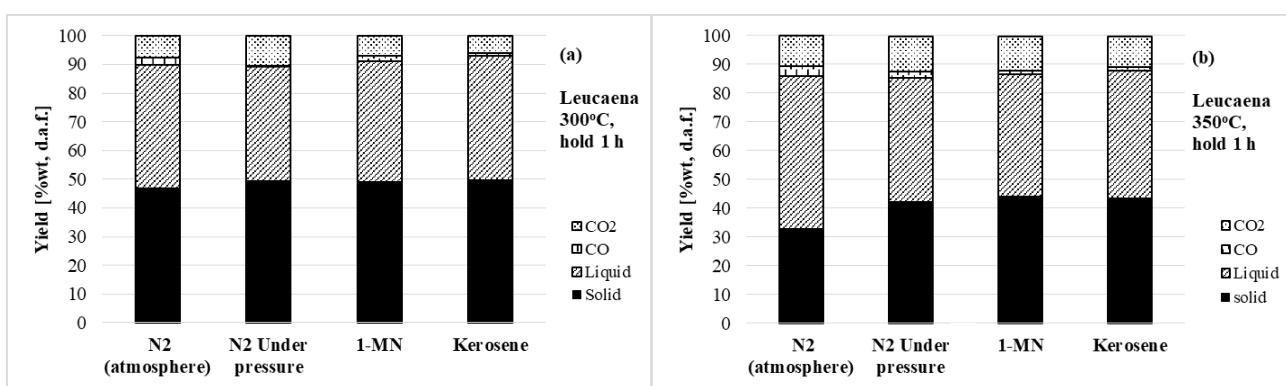


Figure 2. The schematic diagram of torrefaction under nitrogen atmosphere experiment.

**Figure 3.** Products distribution through the solvent treatment at 300°C and 350°C.**Table 1** Yields, proximate, ultimate analysis, atomic ratio, and HHV of STBs.

Sample	Yield (% wt, d.a.f)	Proximate Analysis (% wt, db)				Ultimate Analysis (% wt, d.a.f.)			Atomic ratio		HHV (MJ/kg, d.a.f.)	Energy yield
		VM	FC	Ash	H	C	N	O (diff.)	O/C	H/C		
Raw LC	81.3	17.5	1.2	6.5	47.0	0.6	45.9	0.73	1.66	17.0	100	
Treated at 300°C												
N ₂ atmosphere												
Solid	46.7	54.5	42.9	2.6	5.2	59.0	0.8	35.0	0.44	1.06	21.1	58.1
Liquid		10.1										
Gas		43.2										
N ₂ under pressure												
Solid	49.3	41.1	56.5	2.4	5.4	72.6	0.8	21.2	0.22	0.89	28.5	82.7
Liquid		10.9										
Gas		39.8										
1-MN												
Solid	49.0	48.6	48.6	2.8	5.5	73.5	1.1	19.9	0.20	0.90	29.2	84.2
Liquid		8.8										
Gas		42.2										
Kerosene												
Solid	49.6	42.3	55.1	2.6	5.0	72.5	0.8	21.7	0.22	0.83	27.8	81.2
Liquid		6.8										
Gas		43.6										
Treated at 350°C												
N ₂ atmosphere												
Solid	32.6	33.9	62.4	3.7	4.4	67.8	0.8	27.0	0.30	0.78	24.4	46.8
Liquid		14.0										
Gas		53.4										
N ₂ under pressure												
Solid	42.0	31.3	65.8	2.9	4.7	75.7	1.1	18.5	0.18	0.75	29.0	71.8
Liquid		14.6										
Gas		43.4										
1-MN												
Solid	44.0	45.4	51.9	2.7	5.1	78.3	0.4	16.2	0.16	0.78	30.9	80.0
Liquid		13.5										
Gas		42.5										
Kerosene												
Solid	43.4	37.3	59.9	2.8	4.9	76.8	0.8	17.5	0.17	0.77	29.9	76.5
Liquid		12.2										
Gas		44.4										

3.2 Elemental analyses of STBs

Next, we will examine the elemental composition of the solid products. It was found that the carbon content of the solid products of LC torrefied under nitrogen atmosphere were 59.0 wt%, and 67.8 wt% at 300°C, and 350°C, respectively. On the other hand, the carbon contents of the STBs treated by 1-MN were 73.5 wt%, and 78.3 wt% at 300°C, and 350°C, respectively. Moreover, the oxygen content of the solid product of LC torrefied under nitrogen atmosphere at 350°C was 27.0 wt%, whereas the oxygen content of STB treated by 1-MN at 350°C was only 16.2 wt%. These results showed that the deoxygenation reaction proceeded during the solvent treatment and resulted in high HHV of STB. The HHV of STB treated by 1-MN at 350°C was as high as 30.9 MJ/kg. STBs prepared in this work can be regarded as high quality solid fuels. This result indicated the effectiveness of the solvent treatment method to upgrade biomass. The carbon contents of STBs prepared at 350°C were respectively 78.3 wt%, and 76.8 wt% for 1-MN, and kerosene. The oxygen contents of STBs prepared at 350°C were respectively 16.2 wt%, and 17.5 wt% for 1-MN, and kerosene. These results again showed that the elemental compositions of the STBs prepared by kerosene and 1-MN at the same temperature were not significantly different. These results shown above suggested that kerosene can well be used to prepare STBs as high quality solid fuels.

In order to examine the fuel properties of STBs, the elemental composition of LC treated at various conditions and STBs prepared by 1-MN, and kerosene were also plotted on H/C vs. O/C diagram as shown in Figure 4. Raw leucaena was plotted at H/C = 1.66 and O/C = 0.73, while the LC torrefied in N₂ atmosphere and N₂ under pressure and STBs prepared by 1-MN, and kerosene were plotted at lower values, lying along the dehydration reaction line (-H₂O). The H/C and O/C values of STBs prepared by kerosene, for example, move from H/C = 1.66 and O/C = 0.73 to H/C = 0.77 and O/C = 0.17 when treated at 350°C. This result indicated that the solvent treatment of LC proceed through the coalification process resulted in the values of H/C and O/C very close to lignite [6]. The position of H/C and O/C values also showed that the STBs prepared from LC gave better fuel properties than that of LC prepared from torrefaction under nitrogen atmosphere.

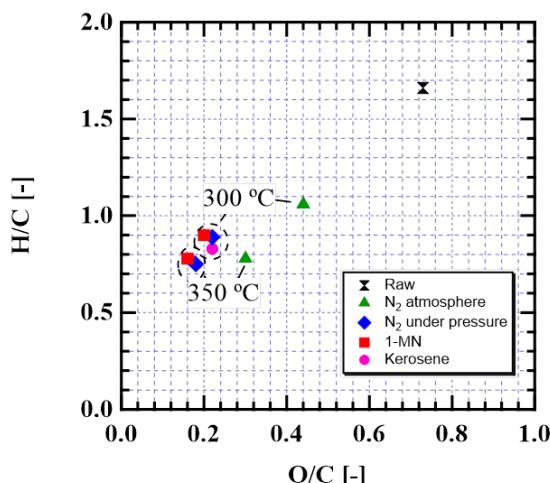


Figure 4. O/C and H/C diagram of raw and treated leucaena.

Table 1 also shows the energy yields of the solid products of LC treated in nitrogen atmosphere, nitrogen under pressure, and solvent treatment using both kerosene and 1-MN at 300°C and 350°C. The energy yield is defined as follows:

$$\text{Energy yield} = \frac{\text{mass yield} \times \text{HHV}_{\text{solid product}}}{\text{HHV}_{\text{raw sample}}} \quad (2)$$

It was found that the energy yields of STBs prepared by 1-MN were respectively 84.2%, and 80.0% at 300°C, and 350°C. On the other hand, the energy yields of LC torrefied in nitrogen atmosphere were respectively 58.1%, and 46.8% at 300°C, and 350°C. Moreover, the energy yields of STBs prepared by kerosene were not significantly different from those of prepared by 1-MN.

Table 2 shows the mass energy density of the solid products of LC treated in nitrogen atmosphere, nitrogen under pressure, and solvent treatment using both kerosene and 1-MN at 300°C and 350°C. The mass energy density is defined as follows:

$$\text{Mass energy density} = \frac{\text{energy yield}}{\text{mass yield}} \quad (3)$$

It was found that the mass energy densities of LC torrefied in nitrogen atmosphere were respectively 1.24, and 1.44 at 300°C, and 350°C. On the other hand, the mass energy densities of STBs prepared by 1-MN were respectively 1.72, and 1.82 at 300°C, and 350°C. The mass energy densities of STBs prepared by kerosene were respectively 1.64, and 1.76 at 300°C, and 350°C. These results clearly showed that the mass energy density of LC was increased significantly by the solvent treatment method.

Table 2. Mass energy density of STBs.

Sample	Mass energy density
Raw LC	1.00
Treated at 300°C,	
N ₂ atmosphere	1.24
N ₂ under pressure	1.68
1-MN	1.72
Kerosene	1.64
Treated at 350°C,	
N ₂ atmosphere	1.44
N ₂ under pressure	1.71
1-MN	1.82
Kerosene	1.76

3.3 Thermal analyses of STBs

Figure 5 shows the weight changes during the pyrolysis of raw and the LC treated in nitrogen atmosphere, nitrogen under pressure, and solvent treatment using both kerosene and 1-MN at 300°C and 350°C. In order to compare with the raw leucaena, the weights of the treated LC were normalized by multiplying the weights with the values corresponding to the solid yields. The weight change behaviors of the STBs were significantly different from the raw leucaena. The weight of raw leucaena started to decrease at above 200°C, while the weight of STBs started to decrease at temperature higher than the treatment temperature. For example, the weight of STB prepared by kerosene at 350°C started to decrease at temperature higher than 350°C. The weight of raw leucaena decreased rapidly at 250 – 350°C. After that, the weight decreased gradually when increasing the temperature further from 350 – 900°C. The weight of STB decreased more gradually than the raw leucaena at 350 – 400°C. Moreover, it was found that the char yield at 900°C for the STBs prepared at 350°C by 1-MN, and kerosene, were respectively 23.4 wt%, and 26.7 wt%, while the char yield at 900°C for raw leucaena was only 18.1 wt%. The char yield at 900°C for the LC torrefied in nitrogen atmosphere at 350°C was 21.2 wt%. These results indicated that the solvent treatment could increase the char yield during the pyrolysis at 900°C. It was suggested that the structure of LC was changed by the solvent treatment at 350°C and the cross-linking reactions occurred during the pyrolysis resulting in increase in char yields [6].

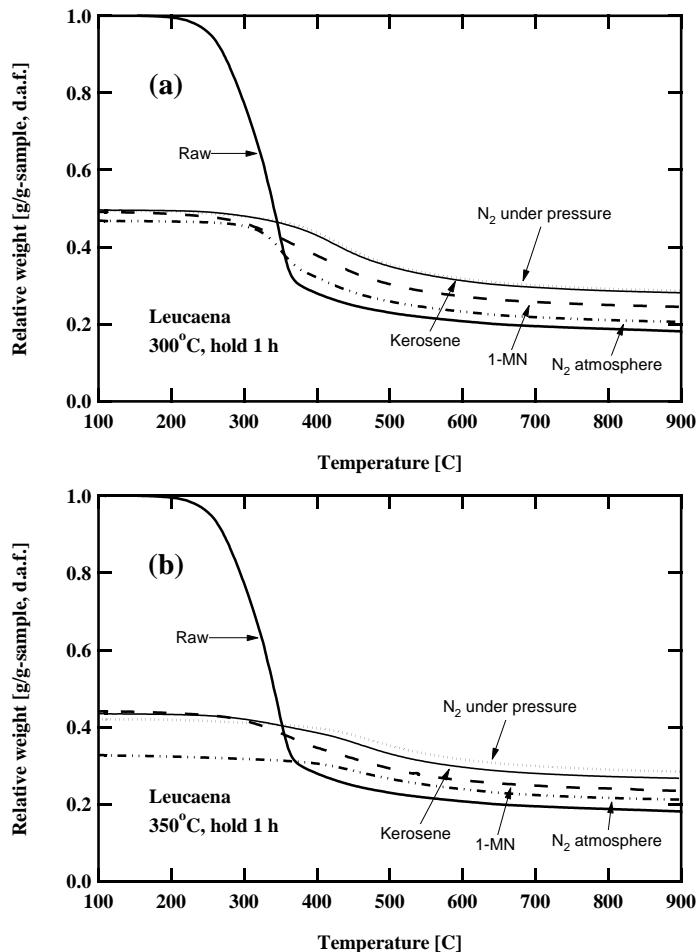


Figure 5. TG curve of STBs compared with torrefied leucaena.

4. Conclusions

The possibility to use kerosene as a practical solvent to upgrade biomass by degradative solvent extraction method was examined in reference to 1-MN. It was found that the thermal degradation behavior of Leucaena in kerosene and 1-MN was rather similar. The yields of the solvent treated biomass (STB) using kerosene and 1-MN were close to each other. It was found that at 350°C as large as 71.1%, and 73.3% of carbon were recovered in the STBs prepared from using kerosene and 1-MN, respectively. On the other hand, the oxygen yields were only 16.5%, and 15.5% for the STBs prepared from using kerosene and 1-MN, respectively. The higher heating values (HHV) of the STBs prepared at 350°C were as high as 29.9 MJ/kg, and 30.9 MJ/kg for the STBs prepared from using kerosene and 1-MN, respectively. The mass energy densities of STBs prepared by kerosene and 1-MN at 350°C were respectively 1.76, and 1.82. From the results of TGA analyses, it was concluded that the structure of leucaena was changed by the solvent treatment at 350°C and the cross-linking reactions occurred during the pyrolysis resulting in increased in char yields. These results showed that kerosene was very effective to upgrade biomass by solvent treatment method.

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