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ORIGINAL

Influence of solvent type on microwave-assisted liquefaction of bamboo

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Abstract Microwave-assisted liquefaction of bamboo in glycerol, polyethylene glycerol (PEG), methanol, ethanol, and water were comparatively investigated by evaluating the temperature-dependence for conversion and liquefied residue characteristics. The conversion for the liquefaction in methanol, ethanol, and water increased with an increase in reaction temperature, while that for liquefaction in glycerol and PEG was converse. The results of Fourier transform-infrared spectra for the liquefied residues revealed that cellulose was the main resistance to bamboo liquefaction in methanol, ethanol, and water. Glycerol could be selected as a commendable liquefacient for the solvolysis of bamboo components at low temperature using microwave energy. Moreover, liquefaction behaviors in glycerol and methanol under different temperatures were also distinguished by scanning electron microscopy images.

1 Introduction

Bamboo has become one of the most important non-timber forest products in China and other Asian countries. This is primarily due to its rapid growth rate, availability, renewable nature, high productivity, short maturity cycle, and multiple uses. Currently, bamboo has been used in the preparation of high-value added products, such as panel, parquets, furniture, and structural composites. However, in the manufacturing of bamboo-based materials, the epidermis and wax layer of bamboo are usually split off. This is because of the poor wettability or penetration of these portions for subsequent treatments, for example, coating and preservative treatments, etc. Thus, large quantities of bamboo processing residues, such as epidermis, are cast aside as waste.

Recent achievements in techniques for converting woody materials into value-added liquid products under mild conditions using organic solvent and an acid catalyst have stimulated certain studies focused on evaluating bamboo as a raw material for manufacturing bio-products. Several studies have been conducted to formulate liquefied bamboo for bio-polyols and polyurethane foams (Yip et al. 2009; Zhang et al. 2013; Liu et al. 2008; Gao et al. 2010). Although pilot-scale evaluation of liquefied bamboo as chemical feedstocks for the preparation of polyurethane foams have shown encouraging results, an economically viable bamboo waste conversion technology is yet to be realized because of the high cost of the liquefaction process. Alcohols have been proven to be effective solvents for liquefaction of lignocellulosic biomass (Xu et al. 2013; Toor et al. 2013). The benefit from using alcohols in liquefaction is that they can be easily recovered after liquefaction.

Microwave energy has recently been applied in the liquefaction of lignocellulosic biomass (Pan et al. 2012; Li et al. 2013; Xiao et al. 2013). In a microwave heating system, microwave energy penetrates and produces a volumetrically distributed heat source; heat is generated throughout the material and leads to faster heating rate

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and improved kinetics as compared to conventional heating. However, microwave dielectric heating is based on the ability of a specific reagent or substance to absorb such radiation and convert it into heat at a given frequency (Cinta et al. 2014). Thus, solvents with different specificities that will be applied in a microwave-assisted liquefaction system may have an influence on the liquefaction behavior of biomass. In this study, liquefaction of bamboo with five different solvents (glycerol, PEG, methanol, alcohol, and water) using microwave energy was systematically investigated. The chemical structure and the surface morphology of the liquefied residues from different reaction conditions were comparatively analyzed. The specific objective of the study is to provide a primary understanding of the influence of solvents on the extent of liquefaction with microwave as heating energy.

2 Experimental

2.1 Materials and chemicals

Bamboo (*Phyllostachys pubescens*) wastes were obtained from the Kisatchie National Forest near Pineville, LA, USA. The particles were screened to collect particles that passed through a 40-mesh sieve and retained on a 100-mesh sieve and then dried to a constant weight in an oven at 80 °C. The dried particles were stored in polyethylene bags and used without further treatment. The holocellulose, α-cellulose, lignin, extractives, and ash content for the raw material were 63.08, 41.72, 20.91, 7.24, and 1.76 %, respectively (Qi et al. 2013). Sulfuric acid, PEG 400#, glycerol, methanol, and ethanol used were of reagent grade and obtained from commercial sources.

2.2 Liquefaction reaction

Liquefaction of bamboo was carried out in a Milestone (Shelton, CT) MEGA laboratory microwave oven. Figure 1 presents a schematic diagram for the experiment setup. Solvent (PEG 400#, glycerol, methanol, ethanol, water) was used at a solvent to bamboo ratio of 4/1 (w/w). Sulfuric acid content of 1.75 % of solvent weight was used as the catalyst. A typical reaction mixture consisting of 2 g of bamboo particles, 8 g of solvent, and 0.14 g of sulfuric acid was loaded in the Teflon vessels with a magnetic stirring bar. The Teflon vessels were then placed on the rotor tray inside the microwave cavity. The temperature was monitored using an ATC-400FO automatic fiber optic temperature control system. Based on monitored temperature, the output power was auto-adjusted during liquefaction, and the maximum power used in this experiment was 550 W. In this study, the temperature was increased from room temperature to 150 °C at a heating rate of 37.5 °C min^{-1} and then kept constant for 3 min unless otherwise noted. After a cooling period of 30 min, at the end of the reaction, the material was dissolved in 150 mL of methanol under constant stirring for 4 h. The liquefied solutions were then vacuum-filtered through Whatman No. 4 filter paper. The solid bamboo residue retained on the filter paper was oven-dried to a constant weight at 105 °C and the conversion was calculated as follows:

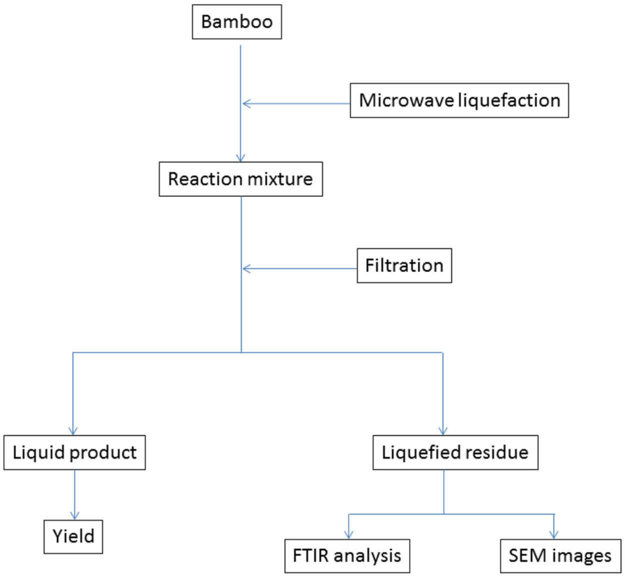

Fig. 1 Schematic diagram for the experiment setup

$$\text{Conversion}\ (\%) = \left(1 - \frac{\text{weight of residue}}{\text{weight of raw material}}\right) \times 100$$

2.3 Fourier transform-infrared (FT-IR)

The FT-IR analysis of the liquefied bamboo residues was performed by a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. A small amount of residue was applied directly on the diamond crystal. Data collection was performed with a 4 cm^{-1} spectral resolution and 32 scans were taken per sample.

2.4 Scanning electron microscopy (SEM)

The structure and the surface morphology of the liquefied bamboo residues were observed using scanning electron microscopy (SEM, JSM-6610). Test samples were coated with gold using a vacuum sputter coater before subjected to the SEM analysis.

3 Results and discussions

3.1 Liquefaction process

Liquefaction of bamboo wastes with PEG, glycerol, ethanol, methanol, and water were conducted under the same conditions. Conversion was used as the index to evaluate the liquefaction extent. Table 1 shows the temperature-dependence of the liquefaction curves for conversion in the five different solvents. As shown in Table 1, when the liquefaction was carried out in methanol, ethanol, and water, the conversion increased with an increase in temperature. For comparison, liquefaction conducted in methanol had higher conversion than in ethanol and water. The conversion dramatically decreased as the liquefaction temperature increased from 120 to 180 °C when glycerol and PEG were selected as the reagent, and conversion for liquefaction in glycerol was higher than that for PEG 400#.

The feedstock was almost decomposed in glycerol within 7 min at 120 °C with a maximum conversion of 96.7 %. The different conversion in liquefaction process may be due to the characteristics of the solvents. Accordingly, in lignocellulosic biomass liquefaction process, ionic reactions and radical reactions took place in the closed reaction system including nucleophilic, electrophilic, elimination reaction. These reactions are related to the polarity of the reaction system (Kabyemela et al. 1997; Antal et al. 1991; Liu and Zhang 2008). Thus, in this present study, the highest conversion achieved under rather low reaction temperature in glycerol (i.e., 120 °C) may be attributed to the fact that glycerol has higher dipole moment, i.e., dipole moment for glycerol is 2.68 (Rizk and Elanwar 1968). Furthermore, the higher polarity glycerol resulted in faster heating rates with the irradiation of microwave, which further enhanced microwave to create a heating system which is very probable for complete decomposition/degradation of bamboo at low temperature.

It is generally recognized that liquefaction of lignocellulosic biomass in an organic solvent with an acid catalyst at high temperature is a complex solvolysis process involving simultaneous reactions of chemical degradation/decomposition, de-polymerization, and re-condensation depending on the process parameters. Thus, in the liquefaction with methanol, ethanol, and water, the increasing conversion is mainly due to that degradation/decomposition outweighs repolymerization. Then, in the liquefaction with glycerol and PEG, repolymerization plays the main role in liquefaction, which is attributed to the decreasing conversion (Zhuang et al. 2012). To further explain the difference, liquefied residues from liquefaction in glycerol and methanol were characterized by FT-IR and SEM.

3.2 FT-IR analysis

The transmittance spectra of the residues from liquefactions using glycerol and methanol are shown in Fig. 2. Accordingly (Popescu et al. 2009), a broad peak at around 3320 cm^{-1} was assigned to –OH groups and the peak at around 2880 cm^{-1} was related to methyl and methylene stretching. The absorbance peak at 1735 cm^{-1} was assigned to C=O stretching vibration of the carboxyl and acetyl groups in hemicelluloses. The absorbance at 1596 and 1506 cm^{-1} arising from the aromatic skeletal vibration, the absorbance at 1456 cm^{-1} assigned to C–H deformation combined with aromatic ring vibration, and the band at 1230 cm^{-1} corresponding to methoxyl groups were contributed to the groups of lignin. The methylene groups at 1420 and 1365 cm^{-1}; CH_2 rocking vibration at 1320 cm^{-1}, and C–O band 1108 cm^{-1} and CH deformation at 899 cm^{-1} represented different functional groups of cellulose.

As shown in Fig. 2A, significant differences for the spectra were found between the original bamboo (spectra a) and liquefied residues (spectra b, c, d). Absorption bands of hemicelluloses and lignin (bands at 1735, 1596, 1506, 1456, and 1230 cm^{-1}) were weakened in the spectra of residue at 120 °C; and the peaks at 1735 and 1506 cm^{-1} in the spectrum for liquefied residue at 150 °C became small shoulders and the peaks at 1596 and 1456 cm^{-1} disappeared, indicating the cleaving of the functional groups in lignin/hemicelluloses, such as syringyl and guaiacyl units, with the microwave liquefaction process in methanol. However, the peaks at 1596 and 1506 cm^{-1} intensified again in the spectra of residue at 180 °C, which indicated that the decomposed compounds such as aromatic ketone groups interact with the aromatic hydroxyl group to form an aromatic network. Thus, it can be concluded that hemicelluloses and lignin were decomposed at the

Table 1 Conversion for liquefactions in different solvents. Liquefaction conditions: reaction time, 7 min; microwave power, 550 W; sulfuric acid, 1.75 %; solvent/bamboo, 4/1

Temperature (°C)	Glycerol (%)	PEG400# (%)	Methanol (%)	Ethanol (%)	Water (%)
120	96.71	74.10	36.47	24.97	17.74
150	83.35	57.72	54.89	47.19	38.32
180	61.87	47.36	82.85	70.65	56.41

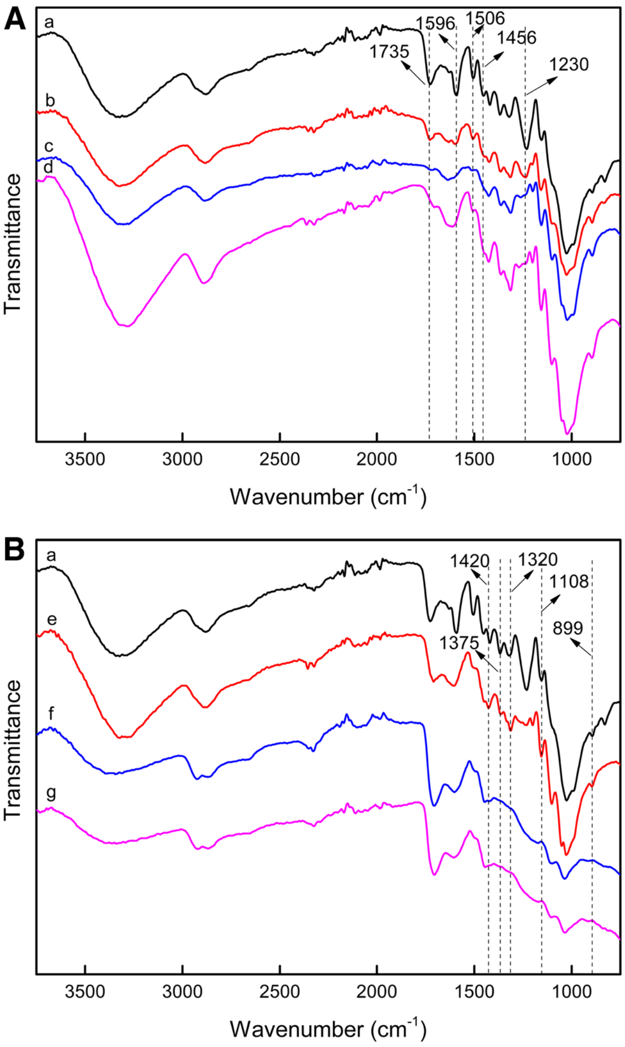

Fig. 2 FT-IR transmittances of *a* original bamboo and residues: *b* 120 °C, methanol, *c* 150 °C, methanol, *d* 180 °C, methanol, *e* 120 °C, glycerol, *f* 150 °C, glycerol, *g* 180 °C, glycerol. Other conditions: microwave power, 550 W; sulfuric acid, 1.75 %; solvent/bamboo, 4/1

temperature below 150 °C and then undergo repolymerization at higher temperature. No significant difference was found in the absorption bands of cellulose between the original bamboo and the liquefied residues. This result revealed that cellulose was still retained in the residues even with the liquefaction process at 180 °C.

As shown in Fig. 2B, it was obvious that absorbance bands that characterized functional groups of hemicelluloses, lignin, and cellulose have become weakened in the spectrum for residue at 120 °C. This was in good agreement with the conversion result which showed more than 95 % of the solid bamboo was converted into the liquid phase. The disappearing bands assigned to the functional groups of cellulose (1420, 1365, 1320, 1108, and 899 cm^{-1}) and the existing bands for those of the hemicelluloses (1735 cm^{-1}) and lignin (1596 and 1506 cm^{-1}) in the FT-IR spectra (spectra e, f) of the residues at 150 and 180 °C suggested that liquefaction in glycerol using microwave heating was a complex reaction involving the cellulose decomposition reactions and the lignin/hemicelluloses repolymerization.

For comparison, the difference in reaction behaviors between glycerol and methanol liquefactions could be clearly distinguished from the FT-IR spectra. In the methanol solvolysis process, the hemicelluloses and lignin almost completely decomposed and the cellulose was the main resistance to the liquefaction of bamboo. While all the components including hemicelluloses, lignin, and cellulose could be liquefied by glycerol with an appropriate conversion at lower temperature. Though, the cellulose could be completely decomposed in glycerol at 150/180 °C, this also enhanced the recondensation reactions induced by the decomposed hemicelluloses and lignin compounds obtained in the initial stage. The recondensation reactions outweighed the decomposition rate of cellulose as evidenced by the decreasing conversion.

3.3 SEM analysis

The SEM images of original bamboo and liquefied residues are shown in Fig. 3. The original bamboo (Fig. 3a) showed uneven-sized bundles with many small fragments on the rough surfaces. As can be seen in the images of the methanol liquefied residue at 120 °C (Fig. 3b), small fiber bundles with smooth surfaces were observed, indicating that the small fragments attached on the surface of the original bamboo were removed during the liquefaction reaction. Moreover, broken single fibers were observed from the SEM image (Fig. 3c) of the methanol liquefied residue at 150 °C. It was apparent that the lignin component, which works as binding and supporting materials in the middle lamella, were removed, leaving the retained tissue cells in an untidy order. This was in accordance with the disappeared or weakened absorption bands of lignin in the FT-IR spectra of the residues at 150 °C. The image (Fig. 3d) of the methanol liquefied residue at 180 °C showed a relatively homogeneous texture with many small granules on the surface (app. 0.2–0.3 µm in diameter). These observations were similar to findings in the case of aqueous ethanol autocatalytic organosolv pulping, for which Zhang noticed some spherical sediment on the fiber surface, and she argued that the spherical granule was a lignin scrap fraction (Zhang 2003). According to the difference in absorption bands of hemicelluloses/lignin in the FT-IR spectra between the residue at 150 °C and that at 180 °C (i.e., peaks disappeared/weakened at 150 °C, while peaks intensified again at 180 °C), the granules observed in

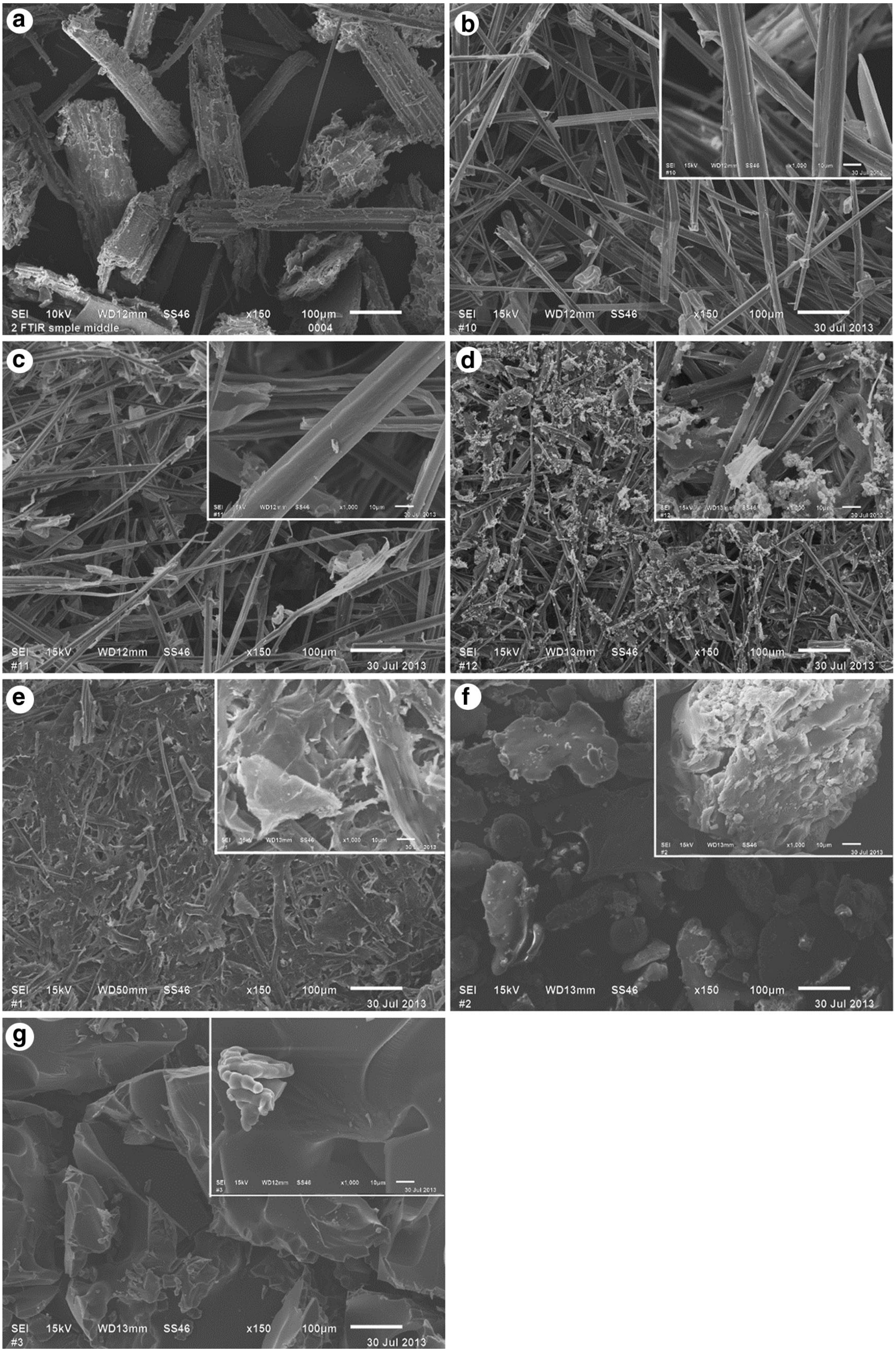

Fig. 3 SEM images of **a** original bamboo and residues: **b** 120 °C, methanol, **c** 150 °C, methanol, **d** 180 °C, methanol, **e** 120 °C, glycerol, **f** 150 °C, glycerol, **g** 180 °C, glycerol. Other conditions: microwave power, 550 W; sulfuric acid, 1.75 %; solvent/bamboo, 4/1

this study may be ascribed to the recondensed hemicelluloses/lignin derivatives.

The significant temperature effect on liquefaction was most evident with liquefaction in glycerol. In the SEM image at 120 °C, bamboo cells were broken, looking like a multilayer sheet and resulting in a large surface area (Fig. 3e). This may be caused by the destroying of cellulose framework. As liquefaction temperature increased to 150 °C, the liquefied residues showed no tissue fragments at all and were made commonly of spherical granules (Fig. 3f); and finally, the granules fused into a conglomerate mass as the temperature increased to 180 °C (Fig. 3g). It was proposed that a somewhat carbonization reaction occurred under such high temperature in glycerol.

4 Conclusion

Significant difference was found in the liquefaction of bamboo using glycerol and methanol. Solid bamboo was almost completely liquefied (conversion, 96.7 %) by glycerol at 120 °C; while the conversion (17.7 %) was the minimum for the liquefaction in water. The decreased efficiency in conversion with respect to reaction temperature indicated that recondensation took place in the liquefaction reactions using glycerol and PEG; while the increased efficiency in conversion with increase in temperature revealed that decomposition outweighed recondensation in the liquefaction using methanol, ethanol, and water.

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