

Co-Liquefaction of Shengli Lignite and *Salix psammophila* in a Sub/Super-Critical Water-Ethanol System

Yuling Liu, Keping Wang,* Yuan Zhong, and Xue Wang

The co-liquefaction of *Shengli lignite* and *Salix psammophila* was used to produce the bio-oil with sub/super-critical water-ethanol as the reaction medium in a WHF-0.1 stainless steel autoclave. The effects of experimental conditions including reaction temperature, holding time, the ratio of *S. lignite* to *S. psammophila*, and addition of catalyst were investigated. NaOH is most beneficial to co-liquefaction of *S. lignite* and *S. psammophila*. The characteristics of bio-oil and solid residue under the best conditions were determined, and the chemical compositional analysis of bio-oil was done using Fourier transform infrared (FTIR) spectroscopy. Scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) were used to characterize the solid residue after the liquefaction. The melting degree of *S. lignite* in co-liquefaction residue was deeper than that in L-residue, which showed there is a synergic effect between *S. lignite* and *S. psammophila* in co-liquefaction.

Keywords: Water-ethanol system; Sub/super-critical; Co-liquefaction

Contact information: College of Science, Inner Mongolia Agricultural University, Huhhot 010018, China;

* *Corresponding author:* wkb0803@163.com

INTRODUCTION

Energy is a prerequisite for human survival and development. The progress of human civilization and social development are closely related to the development and utilization of energy. Humans are dependent on fossil energy, and the excessive consumption of fossil energy leads to serious environmental problems, such as the greenhouse effect caused by large carbon dioxide emissions, acid rain caused by sulfur dioxide, *etc.* Because of the gradual shortage of fossil energy, the energy problem will become the potential crisis in the future society. With the increase of global energy consumption and the gradual shortage of petroleum resources, it is urgent to find an environmentally friendly way to convert other natural resources into chemical fuels. The exploitation and utilization of renewable biomass and coal resources have received great attention in various countries. The development and utilization of biomass and coal energy is of great significance to the development of the future society.

China is rich in coal resources, which plays an important role in improving the national economy. With a massive extent of coal mining, China's high-quality coal resources are become gradually reduced, and lignite resources are rich but inadequately used. From the perspective of industrial energy prices and national security, it is of great social and economic significance to use the rich reserves of lignite resource in an efficient way. The clean and effective conversion process of coal has gained increasing interest all over the world (Yang *et al.* 2013).

The biomass is the 4th most frequently used energy source in the world, following oil,

coal, and natural gas (Durak and Genel 2018). Biomass is a potential alternative to fossil fuels due to its high productivity, renewability, environmental friendliness, and carbon-neutrality (Du *et al.* 2018). In general, biomass sources can be classified as agricultural, forestry, household wastes, and organic wastewater. First, biomass has a moderately high energy density; therefore, it can be stored and transported easily (Durak 2019). The bio-oil can be used directly in engines, turbines, and combustion units as fuel oil, and it can be converted into products of higher quality and density by catalytic cracking, hydrodeoxygenation, emulsification, and steam reforming (Durak 2015). The lignocellulosic biomass, which is comprised of cellulose, hemicellulose, and lignin as its main components, can be used for the production of bio-oil by means of the biomass liquefaction method (Durak 2017).

Salix psammophila is a flowering plant of the willow family. Owing to its propensity for even stubble rejuvenation, a large number of *S. psammophila* timbers can be obtained each year. Although *S. psammophila* has been liquefied or pyrolyzed by many researchers to produce adhesives and injection molding materials, the resource of *S. psammophila* has still been mostly wasted; therefore, co-liquefaction of lignite and *S. psammophila* is a promising method.

Direct liquefaction is a way to obtain chemical fuels. The critical temperature (374 °C) and critical pressure (22.13 MPa) of water are higher than those of ethanol (243 °C and 6.38 MPa, respectively). Compared with liquid water in the environment, sub/super-critical water has lower dielectric constant, fewer and weaker hydrogen bonds, a higher isothermal compressibility, and higher solubility (Cheng *et al.* 2010). Moreover, sub/critical water promotes the reaction of ions and free radicals very effectively. The addition of ethanol to the subcritical water system makes the reaction conditions much milder. Xue *et al.* (2016) proposed that ethanol acting as a hydrogen donor provides active hydrogen during liquefaction. Therefore, the co-solvent of water and ethanol is a promising reaction medium in the sub/super-critical system with broad application prospects.

There is a synergistic effect in co-liquefaction of coal and biomass. Co-liquefaction of white pine sawdust and Shenmu sub-bituminous coal in sub/super-critical ethanol was investigated by Duet *et al.* (2018). The results showed that the synergistic effect of white pine sawdust and Shenmu sub-bituminous coal has little effect on the conversion rate, but the yield of bio-oil is increased. In addition, FTIR and GC/MS analysis of bio-oil showed that the bio-oil of co-liquefaction of white pine sawdust and Shenmu sub-bituminous coal were similar to those of Shenmu sub-bituminous coal liquefaction, mainly phenols and ketones. Therefore, the main liquid products of Shenmu sub-bituminous coal liquefaction are aromatics, aliphatic hydrocarbons and phenol. Lalvani *et al.* (1991) indicated that lignin improves the stability of depolymerization and increases conversion of coal. Shuna *et al.* (2010) proposed that there is a synergistic effect between alcohol and water in direct liquefaction. When the ratio of ethanol (or methanol)/water is 1:1, the liquefaction effect of the wood dust is preferable. The coal conversion into chemical fuel by this approach has attracted much attention.

This research investigated co-liquefaction of *Salix psammophila* and Shengli lignite in subcritical/supercritical system when the ratio of water/ethanol volume was 1:1. The effects of reaction temperature, the ratio of lignite/*S. psammophila*, reaction time, and the addition of different catalysts on the co-liquefaction were examined. The liquid products were characterized by Fourier transform infrared spectroscopy (FTIR). X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) was used to verify the morphology of lignite, *S. psammophila*, and residue after liquefaction.

EXPERIMENTAL

Materials

Salix psammophila was collected from Inner Mongolia Aotonomus Region (Ordos, China), and Shengli lignite was collected from Inner Mongolia Aotonomus Region (Xilinguole, China). *S. psammophila* and the lignite were bought pulverized, sieved, and dried for 4 h at 105 °C before use. The particle sizes of the material were in the range of 125 µm to 150 µm. The proximate and ultimate analyses of the *S. psammophila* and Shengli lignite are summarized in Table 1. Ethanol(analytical pure), *n*-hexane(analytical pure), butylene oxide(analytical pure), caustic soda(analytical pure), and ferric oxide(analytical pure) were purchased from Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd. (Tianjin, China). Ferrous sulfide (analytical pure) and potassium tert-butoxide (analytical pure) were bought from Shanghai McLilin Biochemical Technology Co., Ltd.

Table. 1. Proximate and Ultimate Analysis of *Salix psammophila* and Shengli lignite

Sample	Proximate Analysis (wt%, ad)				Ultimate Analysis (wt%, ad)				
	Moisture	Ash	Volatile matter	Fixed Carbon	C	H	O	N	S
Salix	5.10	4.69	83.07	7.14	55.84	6.82	36.89	0.31	0.14
Shengli lignite	10.54	12.05	49.21	28.29	67.71	4.89	25.22	0.91	1.27

Experimental apparatus

WHF-0.1 high pressure reactor: The maximum reaction pressure and temperature of this reactor are 30 MPa and 400 °C, and the maximum volume is 0.1 L. Figure 2 shows the extraction plant.

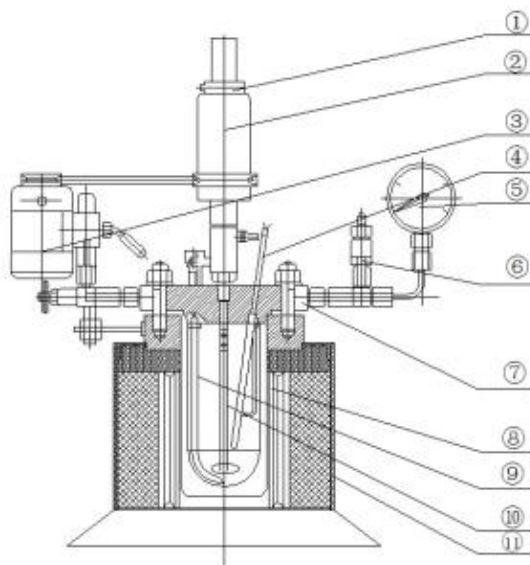


Fig. 1. WHF-0.1 high pressure reactor: 1. Speed measuring device; 2. Magnetic stirring apparatus; 3. Power-driven machine; 4. Platinum resistance; 5. Pressure gage; 6. Explosion protection device; 7. Needle valve; 8. Autoclave; 9. Sampling tube; 10. Under the blender; 11.

Heating equipment

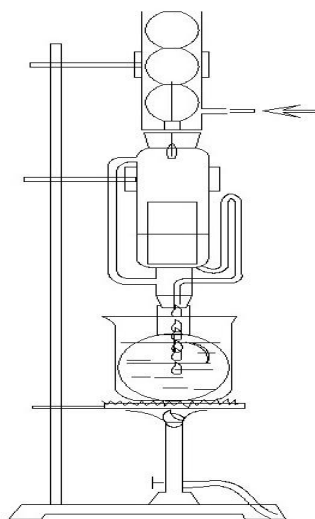


Fig. 2. Extraction plant

Liquefaction Methods

The liquefaction experiment was performed in a 0.1 L stainless steel batch autoclave reactor. The maximum reaction pressure and temperature of this reactor are 30 MPa and 400 °C, respectively. In each test, the reactor was first loaded with *S. psammophila*, *S. lignite*, ethanol, water ($V_{\text{water}}: V_{\text{ethanol}}=5:5$), and catalyst when desired. The amount of the catalyst (NaOH, Na₂CO₃, But-K, FeS, and Fe₂O₃) in each experiment was fixed at 12.5 wt.% of raw material on a dry basis. After being loaded, the reactor was sealed and heated from ambient temperature to the required temperature (°C), where it was maintained for a designed reaction time (15 to 120 min). After the desired reaction time, the reactor was cooled to room temperature with a built-in water cooling system.

Separation Methods

Figure 3 depicts the detailed steps of the procedure for the separation of liquefaction products. The liquefied product in the reactor was transferred to the extraction device. After refluxing with n-hexane, rotary evaporation was conducted to obtain bio-oil. Then, refluxing with butylene oxide was followed by rotary evaporation to obtain bio-oil. The final remaining solid products were dried in an oven at 105 °C overnight.

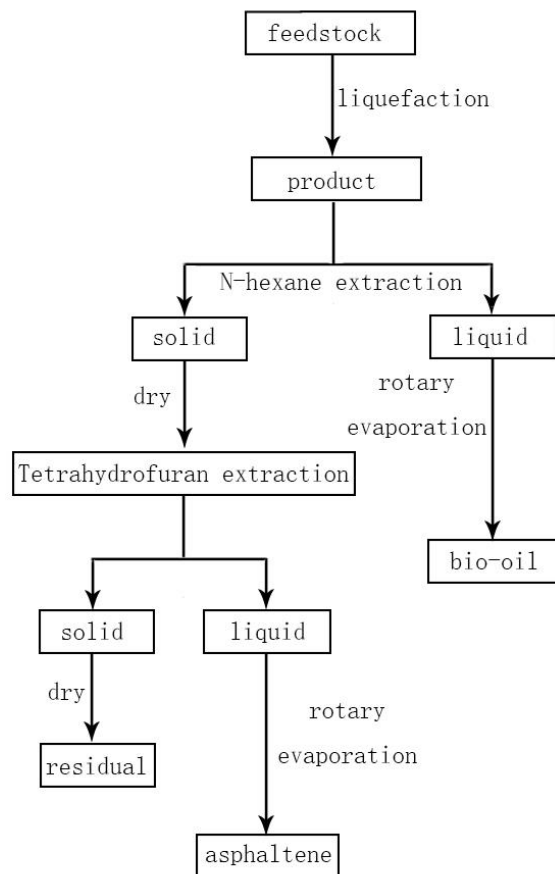


Fig. 3. The steps for the separation of liquefied products

The yield of liquefaction products (bio-oil and PAA) and conversion rate were all expressed in wt.% and calculated using the equations below.

$$\text{Yield of bio-oil} = (\text{mass of bio-oil})/(\text{mass of feedstock}) \times 100 \quad (1)$$

$$\text{Yield of PAA} = (\text{mass of PAA})/(\text{mass of feedstock}) \times 100 \quad (2)$$

$$\text{Conversion} = 100\% - (\text{mass of residue})/(\text{mass of feedstock}) \times 100 \quad (3)$$

Note: The lignite, *S. psammophila*, and residue were dried.

RESULTS AND DISCUSSION

The Effect of Reaction Temperature on Co-Liquefaction

The direct liquefaction of biomass or coal can be summarized as weak chemical bond fracture in biomass or coal, where C—O—C and C—C bonds are converted into H—O, or gas (Shui *et al.* 2013; Liang *et al.* 2016). Thus, temperature is an important factor in liquefaction (Paysepar *et al.* 2018). Figure 4 depicts the effect of reaction temperature (270 to 350 °C) on the co-liquefaction behaviors in isometric ethanol-water mixed solvent with a fixed *S. lignite*/*S. psammophila* ratio (2:2) and time (90 min) (Lai *et al.* 2018).

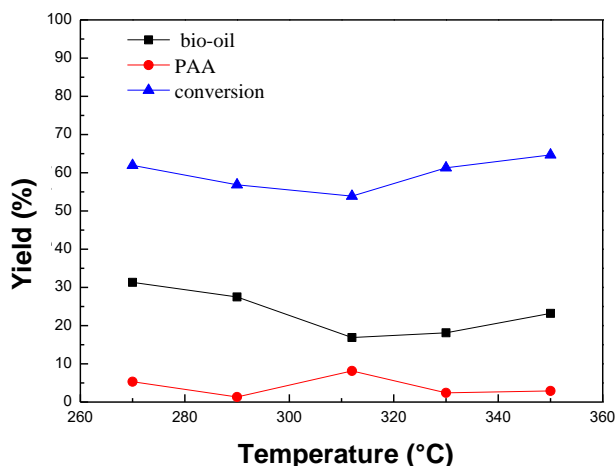


Fig. 4. Effect of reaction temperature on co-liquefaction

In previous tests, it was concluded that the optimum liquefaction temperature of *S. psammophila* and Shengli lignite are 260 °C and 350 °C, respectively. *S. psammophila* is easier to liquefy than the lignite. Therefore, the liquefaction rate is the highest at 270 °C. A higher reaction temperature results in a more active defragmentation of macro-molecule components into bio-oil products. During the process of direct liquefaction, a series of competitive reactions might be involved, *i.e.*, (1) the formation of solid by re-polymerization and cyclization of the liquid products (Lai *et al.* 2018); (2) the formation of gases from degradation of the liquid products; and (3) the formation of liquid products by decomposition of the solid and the aggregation of the gases (Liu and Zhang 2008; Huang *et al.* 2011). With increasing reaction temperature, the macromolecules are more easily broken, which results in sufficient liquefaction of *S. lignite* and *S. psammophila* and decrease in biochar.

Effect of the Ratio of *S. lignite*/*S. psammophila* on Co-liquefaction

Figure 5 shows that the higher the content of *S. psammophila*, the higher was the liquefaction rate, which indicates that the ratio of raw materials has a great influence on the effect of co-liquefaction. *S. psammophila* is composed of hemicellulose, cellulose, and lignin, which contain a high percent of hydrogen. Large amounts of hydrogen radicals promote *S. lignite* liquefaction into stable liquid products (Shao 2018).

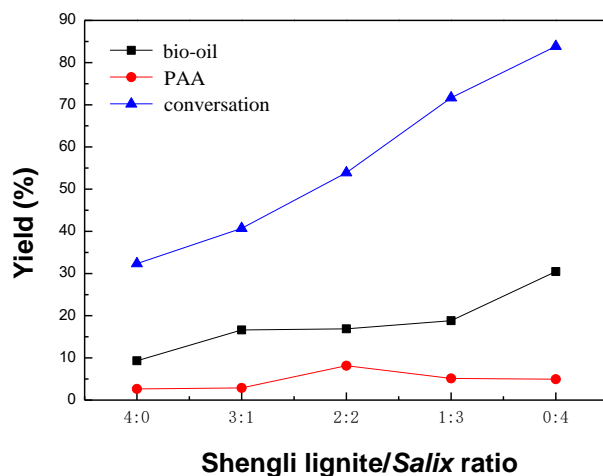


Fig. 5. Effect of the ratio of Shengli lignite to *S. psammophila* on co-liquefaction

The Effect of Reaction Time on Co-liquefaction

The co-liquefaction of Shengli lignite and *S. psammophila* was investigated in sub-/supercritical water-ethanol at different reaction times, varying from 15 min to 120 min at 350 °C with the water/ethanol volume ratio of 5:5, and the lignite/*S. psammophila* quality ratio of 2:2. The bio-oil, PAA, and the conversion were plotted against the reaction time, as shown in Fig. 6.

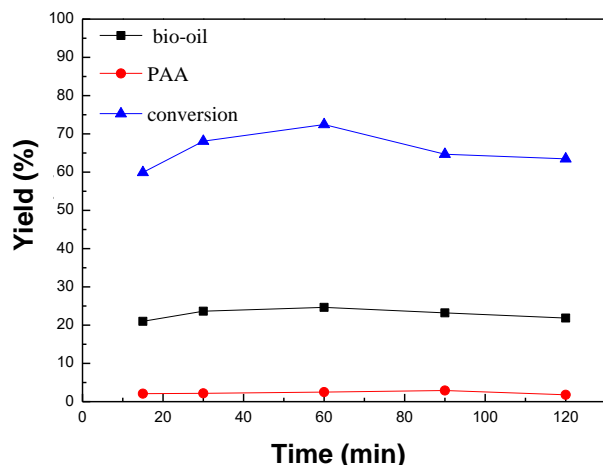


Fig. 6. Effect of reaction time on co-liquefaction

With increased reaction time, the bio-oil yields and conversion increased at 15 min to 60 min, then the bio-oil yields and conversion decreased. When the reaction time was 60 min, the maximum value was reached, which was 24.6% and 72.4%, respectively. However, the upward and downward trends were not very obvious, and the PAA yield was basically unchanged, which indicates that the time had a little influence on the effect of co-liquefaction. The results indicated that reaction time had little effect on the co-liquefaction of *S. psammophila* and the lignite. In the initial stage of reaction, the weak chemical bond in *S. psammophila* molecules and lignite molecules break to form small molecules or free

radical fragments. With the increase of reaction time, the free radical fragments break further and combine with H^+ in the system to form bio-oil. When the reaction time is long enough, the H^+ is insufficient in the system, so that the free radical fragments in the system are polymerized again (Li *et al.* 2015). Thus, the macro-molecular products are generated, and the bio-oil yield and the liquefaction rate are reduced.

Effect of Catalyst on Co-liquefaction

The catalyst influenced the co-liquefaction of the Shenli lignite and *S. psammophila*. The co-liquefaction of the lignite and *S. psammophila* was carried out with different catalysts at 350 °C, the lignite/*S. psammophila* ratio of 2:2, water/ethanol volume ratio of 5:5, and holding time 90 min (Fig. 7). Adding FeS, Fe₂O₃, NaOH, t-BuOK, and K₂CO₃ promoted the co-liquefaction of *S. psammophila* and lignite. The conversion and bio-oil yield were improved, but the yield of the asphalt was reduced. The effects of different catalysts were in the following order: NaOH > K₂CO₃ > t-BuOK > Fe₂O₃ > FeS. FeS and Fe₂O₃ inhibited the liquefaction of *S. psammophila*, but promoted the co-liquefaction of *S. psammophila* and the *S. lignite*. The results indicated that the positive effect of FeS and Fe₂O₃ on the liquefaction of *S. lignite* was much greater than that on the liquefaction of *S. psammophila*. NaOH and t-BuOK promoted co-liquefaction, which indicated that alkaline catalyst was beneficial to the degradation of lignite and *S. psammophila*. These catalysts inhibited the formation of macro-molecules, thus increasing the liquefaction rate and oil yield (Liang *et al.* 2015).

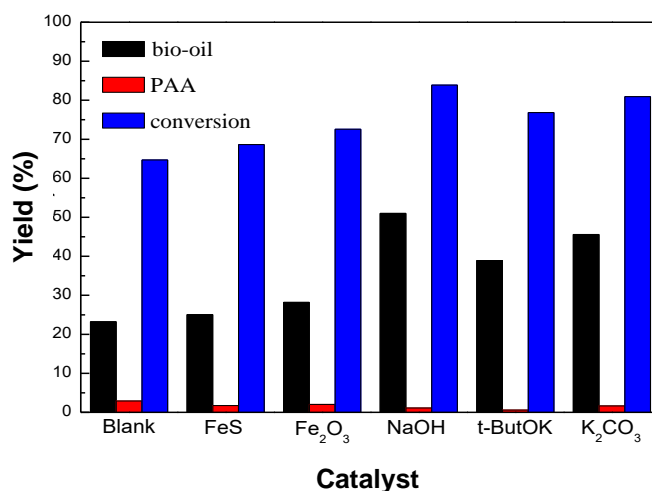


Fig. 7. Effect of catalyst on co-liquefaction

Characterizations of Liquefaction Production

FTIR analysis of bio-oil at different reaction temperatures

The FTIR spectra for the bio-oil from the liquefaction at different reaction temperatures are illustrated in Fig. 8. All bio-oil displayed similar IR spectra adsorption profiles, indicating similar chemical structures. With increasing temperature, the -OH stretching vibration band at 3200 cm^{-1} to 3500 cm^{-1} became weaker, suggesting that the content of hydroxyl group in liquefaction product decreased gradually and that the increased temperature facilitated the removal of hydroxyl groups. A new absorption peak gradually appeared near 3000 cm^{-1} with increasing temperature, which indicates that the increase of temperature is beneficial to the hydrogenation and cracking of aromatic ring. The peaks at 1450 cm^{-1} , 1560 cm^{-1} , and 1680 cm^{-1} were assigned to the aromatic C=C units. The peaks of 1200 cm^{-1} and 1050 cm^{-1} represent C—O absorption, indicating that liquefied oils contain phenols and ethers. Liu *et al.* (2013) analyzed the liquefied oil of rice husk by GC-MS, and it was also concluded that the liquefaction product contained these substances.

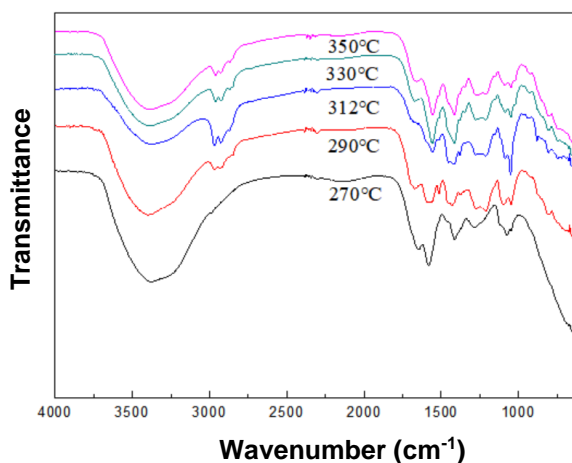


Fig. 8. FTIR spectra of bio-oil at different reaction temperatures

FTIR analysis of bio-oil with different feedstock

The FTIR spectra of bio-oil obtain from liquefaction of Shenli lignite, *Salix*, and lignite + *Salix* are presented in Fig. 9. The range of 1000 cm^{-1} to 1300 cm^{-1} was attributed to the C—O bands, implying the presence of alcohols and esters (Wu *et al.* 2018). The band intensity near 3400 cm^{-1} of the FTIR spectra for bio-oil_{shengli}, was obviously higher than that of bio-oil_{salix} and bio-oil_{mix}, suggesting the *Salix* is helpful for hydroxyl removal. The absorption peak at the range of 2800 cm^{-1} to 3000 cm^{-1} represented symmetrical and as symmetrical C—H stretching vibration, implying that aliphatic hydrocarbons may appear (Song *et al.* 2017). Compared with the bio-oil_{shengli} and bio-oil_{salix}, bio-oil_{mix} is higher (2800 cm^{-1} to 3000 cm^{-1}). The IR adsorption profiles of bio-oil_{mix} changed intensely (Yang *et al.* 2013). Thus, *Salix* promoted the reaction of coal and increased the quality of bio-oil. The synergetic effect between *S. lignite* and *S. psammophila* should be taken into account. Paysepar *et al.* (2018) obtained similar conclusions on the co-liquefaction of lignin and lignite in an ethanol-water system.

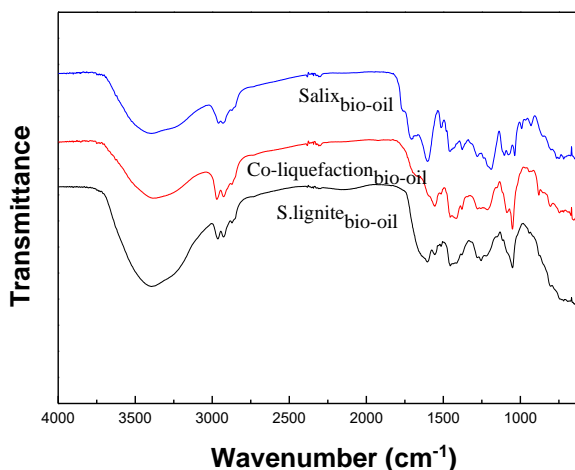


Fig. 9. FTIR spectra of bio-oil with different feedstock

FTIR analysis of bio-oil with different reaction time

The FTIR spectra for the bio-oil from the co-liquefaction with different reaction times are shown in Fig. 10. The absorption in the range of 3200 cm⁻¹ to 3500 cm⁻¹ was assigned to O-H stretching vibration. The peaks at 1450 cm⁻¹, 1560 cm⁻¹, and 1680 cm⁻¹ are the stretching vibration of aromatic ring, indicating that the liquefied oil contained aromatic compounds and their derivatives. The bands observed at 1050 cm⁻¹ were typical for the C—O stretching vibration. The reaction time was 15 min produced the lowest absorption, indicating that the content of ether is low. Using a liquefaction reaction that is too long or too short is not conducive to the liquefaction of Shengli lignite and *S. psammophila* (Zhai 2017).

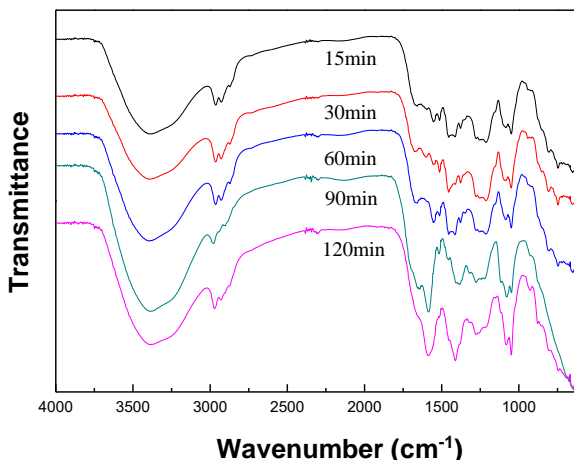


Fig. 10. FTIR spectra of bio-oil at different reaction time

FTIR analysis of bio-oil with different catalysts

A comparison of the FTIR spectra for the bio-oil in the co-liquefaction with different catalysts is given in Fig. 11. The absorption peak at 3200 cm⁻¹ to 3500 cm⁻¹

represented the OH group, and the absorption peak at 1050 cm^{-1} represented C-O stretching vibration. The intensity of absorption peak was reduced by adding different catalysts (NaOH, K_2CO_3 , t-BuOK, Fe_2O_3 , FeS), indicating the catalysts promote the deprivation of OH and C-O. Absorption between 2800 cm^{-1} and 3000 cm^{-1} was attributed to symmetrical and asymmetrical C-H stretching vibrations of methyl and methylene groups (Cheng *et al.* 2010), suggesting the presence of aliphatic hydrocarbons. The intensity of absorption became higher with the addition of catalyst, which indicate the catalyst promote the co-liquefaction of Shengli lignite and *S. psammophila*.

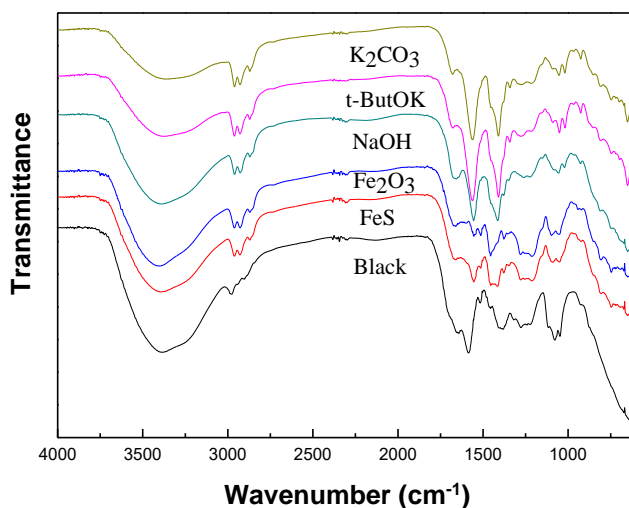


Fig. 11. FTIR spectra of bio-oil with different catalysts

FT-IR of feedstock and co-liquefaction residue

The FTIR of the raw *S. psammophila*, Shengli lignite, and solid residue from the co-liquefaction (at 350 °C for 90 min) is shown in Fig. 12. The FT-IR spectra of the solid residues changed notably compared with the raw material. There was an absorption peak from 3000 cm^{-1} to 2800 cm^{-1} , which can be attributed to C-H stretching vibrations. The region of 1000 cm^{-1} to 1100 cm^{-1} was assigned to C-O stretching vibrations, which became stronger than that of the raw material. The result suggests that the co-liquefaction of *S. lignite* and *S. psammophila* promoted the reaction of *S. lignite* and increased the quality of bio-oil compared to that obtain from pure *S. lignite* liquefaction.

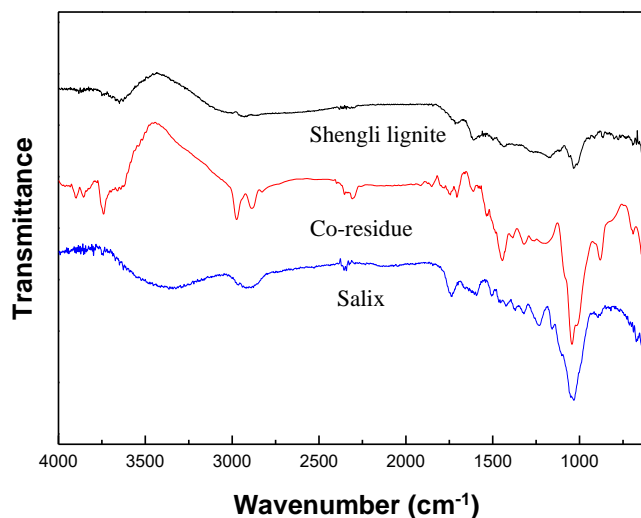


Fig. 12. FT-IR spectra of feedstock and co-liquefaction residue

Thermogravimetric analysis (TGA)

Results of thermogravimetric (TGA) analysis of feedstock and residue are shown in Fig. 13. The maximum rate of weight loss for *S. psammophila* appeared at 350 °C, while that of *S. lignite* and co-liquefaction residue appeared at 400 °C. In this temperature range, feedstock and residue were pyrolysed to form small molecular gases and macromolecules. In the DTG diagram, *Salix* has a strong peak with a shoulder peak. First, the rate of weight loss is slow, and then pyrolysis occurs rapidly at a narrow temperature range (350 °C to 400 °C). The hemicellulose structure has a branched chain, which is easier to decompose than cellulose, so *Salix* has a shoulder peak. The pyrolysis of lignin is relatively slow, and the pyrolysis cycle is long. The pyrolysis temperature range of *S. psammophila* and Shengli lignite are 250 °C to 500 °C, while the pyrolysis temperature of co-liquefaction residue is between 400 °C to 1000 °C. *Salix* is the easiest to decompose, and the residue needs a higher temperature to decompose. This is due to the degradation of feedstock into small molecular substances during liquefaction, which leads to the decrease of active groups in co-liquefaction residue and makes it more difficult for the residue to decompose (Zhang *et al.* 2017). This shows that the degradation reaction of feedstock had taken place during the liquefaction process.

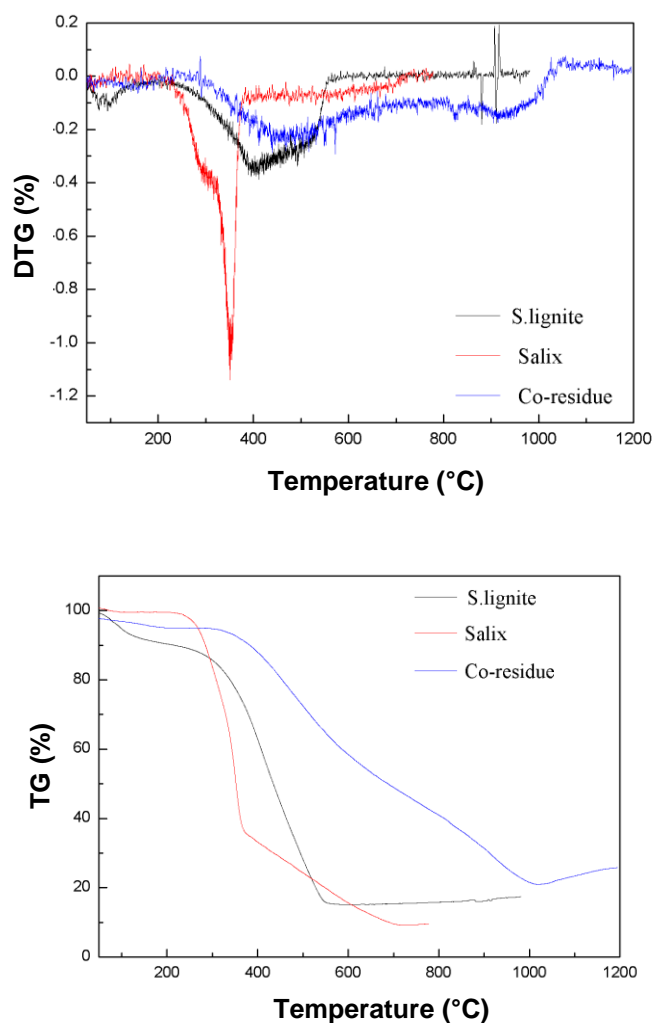


Fig. 13. Thermogravimetric analysis of feedstock and residue

Scanning electron microscopy

Figure 14 shows the micro-fabric features of the feedstock and liquefaction residue. Compared with (a₂), the particles in (b₂) are smaller. In the process of Shengli lignite liquefaction, small molecular gas adsorbed on the lignite surface escaped, the gas existing internal the lignite were released, resulting in many fissures appearing in the lignite. With the deepening of the degree of the liquefaction reaction, more fissures appeared until a hole was shaped (b₁). Compared with (c), the structure of the *Salix* is broken and is stacked in an irregular shape. Compared with (b₂) and (d), the fiber structure in residue of co-liquefaction (e) disappeared, and the residue of co-liquefaction (e) particles were smaller. The melting degree of Shengli lignite in co-liquefaction residue was deeper than that in L-residue, which indicated that there was a synergistic effect between Shengli lignite and *S. psammophila*.

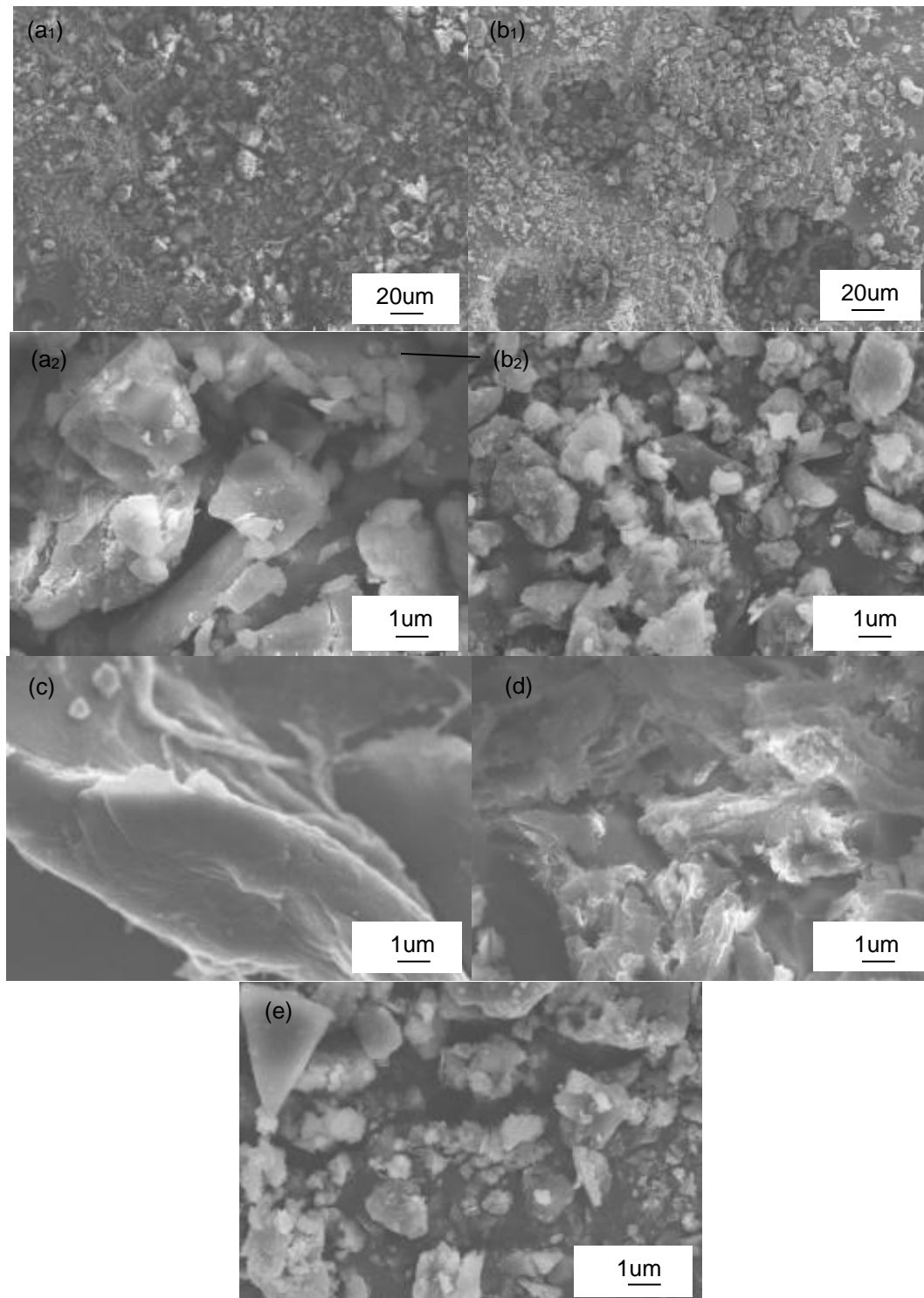


Fig. 14. SEM images of *S. lignite*, *Salix*, residue:(a₁) lignite, (b₁) L-residue, (a₂) Lignite, (b₂) L-residue, (c) *Salix*, (d) S-residue, (e) Co-residue

GC-MS analysis results of bio-oils

Table 2. GC-MS Analysis Results of Bio-oils

No.	RT (min)	Compound name	molecular formula
1	3.39	Ethyl Acetate	C ₄ H ₈ O ₂
2	4.35	Ethanol	C ₂ H ₆ O
3	13.54	2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O
4	14.685	2-Cyclopenten-1-one,2,3-dimethyl-	C ₇ H ₁₀ O
5	15.355	Cyclopentanecarboxaldehyde, 2-methyl-3-methylene	C ₈ H ₁₂ O
6	15.966	2-Cyclopenten-1-one,2,3-dimethyl-	C ₇ H ₁₀ O
7	16.311	Cyclohexanol, 5-methyl-2-(1-methylethyl)-, [1S-(1.alpha.,2.alpha.,5.beta.)]-	C ₁₀ H ₂₀ O
8	16.376	Cyclopentane, 1-methyl-1-(2-methyl-2-propenyl)-	C ₁₀ H ₁₈
9	19.758	Phenol, 2-methoxy-	C ₇ H ₈ O ₂
10	20.773	Creosol	C ₈ H ₁₀ O ₂
11	21.27	Phenol	C ₆ H ₆ O
12	21.524	Phenol, 4-ethyl-2-methoxy-	C ₉ H ₁₂ O ₂
13	21.865	Phenol, 2-ethyl-	C ₈ H ₁₀ O
14	22.297	Phenol, 2-methoxy-4-propyl-	C ₁₀ H ₁₄ O ₂
15	22.913	Phenol, 3-ethyl-	C ₈ H ₁₀ O

Gas chromatography-mass spectrometry (7890 B-5977B) was conducted for the co-liquefaction bio-oil. The experimental conditions were as follows: The co-liquefaction bio-oil components were identified by a gas chromatograph-mass spectrometer (GC-MS, 7890B-5977B) with a AB-Inowax column (30m × 320 μm × 0.5 μm) and a temperature program of 40°C (hold for 5 min), and 220°C (10°C/min, hold for 30 min).

According to the results of the GC-MS analysis of bio-oil, the compounds they contain are classified as aliphatics, aromatics, esters, phenols, and oxygen compounds. The ratios are presented in Table 2. C₄H₈O₂ is ethyl acetate, indicating that the bio-oil contained esters, which consistent with the conclusion in Fig. 9. C₆H₆O is phenol. No. 9 to No. 15 contain aromatics rings, which is consistent with what is shown in Figs. 8 and 10. C₁₀H₁₈ is aliphatic hydrocarbons, which is consistent with the conclusion in Fig. 11.

CONCLUSIONS

1. NaOH is most beneficial to co-liquefaction of Shengli lignite and *S. psammophila*.
2. Alkaline catalyst was beneficial to the degradation of the lignite and *S. psammophila*. It inhibited the formation of macromolecules, thus increasing the liquefaction rate and oil yield.
3. *S. psammophila* was the easiest to decompose, and the residue needs a higher temperature to decompose. The degradation reaction of feedstock occurred during the liquefaction process.
4. Bio-oil contains phenols and ethers. The results showed that there is synergic effect between Shengli lignite and *S. psammophila* with respect to co-liquefaction. *S. psammophila* promoted the reaction of liquefaction and increased the quality of bio-oil.

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REFERENCES CITED

- Cheng, S., D'cruz, I., Wang, M., Leitch, M., and Xu, C. (2010). "Highly efficient liquefaction of woody biomass in hot-compressed alcohol-water co-solvents," *Energy & Fuels* 24(9), 4659-4667. DOI:10.1021/ef901218w
- Du, J.J., Zhao, Y.p., and Tian, Y. J. (2018). "Co-alcoholysis of white pine sawdust and Shenmu sub-bituminous coal in sub- and supercritical ethanol," *Journal of the Energy Institute* 91(6), 1085-1090. DOI: 10.1016/j.joei.2017.07.001
- Durak, H., and Genel, Y. (2018). "Hydrothermal conversion of biomass (*Xanthium strumarium*) to energetic materials and comparison with other thermochemical methods," *The Journal of Supercritical Fluids* 140, 290-301. DOI: 10.1016/j.supflu.2018.07.005
- Durak, H. (2019). "Hydrothermal liquefaction of *Glycyrrhiza glabra* L. (Licorice): Effects of catalyst on variety compounds and chromatographic characterization," *Energy Sources Part A: Recovery, Utilization, and Environmental Effects* DOI:10.1080/15567036.2019.1607947
- Durak, H. (2015). "Thermochemical conversion of *Phellinus pomaceus* via supercritical fluid extraction and pyrolysis processes," *Energy Conversion and Management* 99, 282-298. DOI: 10.1016/j.enconman.2015.04.050
- Durak, H. (2017). "*Trametes versicolor* (L.) mushrooms liquefaction in supercritical solvents: Effects of operating conditions on product yields and chromatographic characterization," *The Journal of Supercritical Fluids* 1-33. DOI: <http://dx.doi.org/10.1016/j.supflu.2017.09.013>
- Huang, H. J., Yuan, X. Z., and Zeng, G.M. (2011). Thermochemical liquefaction characteristics of microalgae in sub- and supercritical ethanol," *Fuel Processing Technology* 92(1), 147-153. DOI:10.1016/j.fuproc.2010.09.018
- Lai, F.Y., Chang, Y.C., Huang, H. J., Wu, G. Q., Xiong, J. B., Pan, Z. Q., and Zhou, C. F. (2018). "Liquefaction of sewage sludge in ethanol-water mixed solvents for bio-oil and biochar products," *Energy* 148, 629-641. DOI:10.1016/j.energy.2018.01.186
- Lalvani, S. B., Muchmore, C. B., and Koropchak, J. (1991). "Lignin-augmented coal depolymerization under mild reaction conditions," *Energy Fuels* 5(2), 347-352. DOI:10.1021/ef00026a021
- Li, Q. Y., Peng, P., Liu, D., Li, M., Song, L. H., Li, M. F., Yan, Z. F., and Geng, Y. R. (2015). "Hydro-liquefaction of woody biomass for bio-oil in supercritical solvent with [BMIM]Cl/NiCl₂ catalyst," *Applied Petrochemical Research* 5(4), 363-369. DOI:10.1007/s13203-015-0111-4
- Li, L. (2015). *Study on Direct Liquefaction performance of Shengli lignite and its Co-Liquefaction Performance with Other Materials*, MS Thesis, East China University of Science.
- Li, L., You, Q., and Wu, S. Y. (2016). "Co-liquefaction behavior of corn straw and Shengli lignite," *Journal of the Energy Institute* 89(3), 335-345. DOI: 10.1016/j.joei.2015.03.006

- Liu, Y., Yuan, X. Z., Huang, H. J., Wang, X. L., Wang, H., and Zeng, G. M. (2013). "Thermochemical liquefaction of rice husk for bio-oil production in mixed solvent (ethanol–water)," *Fuel Processing Technology* 112, 93-99. DOI: 10.1016/j.fuproc.2013.03.005
- Liu, Z. G., and Zhang, F. S. (2008). "Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstock," *Energy Conversion & Management* 49(12), 3498-3504. DOI:10.1016/j.enconman.2008.08.009
- Paysepar, H., Ren, S. B., Kang, S. G., Shui, H.F., and Xu, C.B. (2018). "Catalytic co-liquefaction of lignin and lignite coal for aromatic liquid fuels and chemicals in mixed solvent of ethanol-water in the presence of a hematite ore," *Journal of Analytical and Applied Pyrolysis* 134, 301-308. DOI: 10.1016/j.jaap.2018.06.020
- Shao, T. (2018). *Studies on the Co-liquefaction Technology of Shengli Brown Coal and S. psammophila in Sub-super Critical Ethanol*, Inner Mongolia Agricultural University.
- Shui, H. F., Jiang, Q. Q., and Cai, Z. Y.(2013). "Co-liquefaction of rice straw and coal using different catalysts," *Fuel* 109(7), 9-13. DOI: 10.1016/j.fuel.2012.06.032
- Song, W.H., Wang, S. Z., and Guo, Y. (2017). "Bio-oil production from hydrothermal liquefaction of waste Cyanophyta biomass: Influence of process variables and their interactions on the product distributions," *International Journal of Hydrogen Energy* 42(31), 20361-20374. DOI:10.1016/j.ijhydene.2017.06.010.
- Wu, X. F., Zhou, Q., Li, M. F., Li, X. H., Bian, J., and Peng, F. (2018). "Conversion of poplar into bio-oil via subcritical hydrothermal liquefaction: Structure and antioxidant capacity," *Bioresource Technology* 270, 216-222. DOI:10.1016/j.biortech.2018.09.032
- Xue, Y., Chen, H. Y., and Zhao, W. N. (2016). "A review on the operating conditions of producing bio-oil from hydrothermal liquefaction of biomass," *International Journal of Energy Research* 40(7), 865-877. DOI:10.1002/er.3473
- Yang, R., Chen, Y., Wu, Y., Hua, D., Yang, M., Li, C., Chen, Z., and Liu, J. (2013). "Production of liquid fuel via coliquefaction of coal and *Dunaliella tertiolecta* in a sub-/supercritical water-ethanol system," *Energy & Fuels* 27(5), 2619-2627. DOI:10.1021/ef4001242
- Zhai, S. (2017). *Study on Liquefaction of Shengli Lignite and Its Co-liquefaction with Biomass*, Anhui University of Technology.
- Zhang, J. Xu, W., Zhang, Y., Li, R., and Meng, F.(2017). "Chitin liquefaction and kinetics," *Chemical Industry and Engineering Progress* 36(8), 3085-3092.

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