The Atmospheric Catalytic Liquefaction of Corn Stalk by Phosphoric Acid and Polyethylene Glycol For the Production of Biofuels

Zhiqiang Zhao  
Tianjin University of Science and Technology

Haitang Liu (liuhaitang@tust.edu.cn)  
Tianjin University of Science and Technology  https://orcid.org/0000-0001-7910-1637

Yan Xu  
Tianjin University of Science and Technology

Lin Chen  
Tianjin University of Science and Technology

Xin Jin  
Tianjin University of Science and Technology

Jie Li  
Tianjin University of Science and Technology

Jing Liu  
Tianjin University of Science and Technology

Yongzhen An  
Tianjin University of Science and Technology

Zhong Liu  
Tianjin University of Science and Technology

Research Article

Keywords: Agricultural wastes, Liquefaction, Biofuels, GC-MS, FT-IR

DOI: https://doi.org/10.21203/rs.3.rs-421809/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Abstract

The liquefaction and reuse of plant biomass have attracted the attention of researchers because the fossil energy is running out gradually, corn stalk waste is rich and can be converted into high quality biofuels through the liquefaction process. The effects of polyethylene glycol on the atmospheric liquefaction yield of corn stalk and the properties of biofuel products were investigated. It was found that the optimal temperature was 170 °C, reaction time was 60 min, liquid solid ratio was 5:1, catalyst concentrated phosphoric acid dosage was 10%, the maximum liquefaction rate reached 97.19%. GC-MS analysis showed that the composition of biofuels is complex, which mainly including alcohols, organic acids, esters, ketones, sugars and other compounds. Results of FT-IR demonstrated that the characteristic functional groups of cellulose, hemicellulose and lignin in liquefied corn stalk were almost completely disappeared, SEM analysis showed that the surface morphology of liquefaction residue and original corn stalk was completely different, the fiber structure could not be seen in the residue, all these phenomenons indicating that corn stalk was completely liquefied.

Statement Of Novelty

This paper provided new insight for liquefaction of corn straw biomass as raw material using polyethylene glycolwell-performing products can be obtained and used in a variety of industries.

Introduction

Limited natural resources and the advancing climate change in light of an increasing world population, urges society to deal smarter with available resources and environment problems. In a circular economy perspective, efforts at looking for efficient reuse or recovery of resources from any valuable waste stream originated by the production cycles need to be boosted. To this respect, ambitious valorisation options aiming at producing either biofuels or biochemicals from organic waste streams are fully included in the definition of biorefinery given by the International Energy Agency Bioenergy Task 42 [1]. Biofuels, in conjunction to their positive carbon balance with regards to fossil fuels, also represent a significant potential for sustainability and economic growth. Biofuels are usually classified as follows: First-generation biofuels are directly related to a biomass (agricultural crops) that is generally edible; Second-generation biofuels are defined as fuels produced from a wide array of different feedstock, ranging from lignocellulosic feedstocks (agricultural crop residues, forest residues and perennial grasses) to municipal solid wastes; Third-generation biofuels are, at this point, related to algal biomass but could to a certain extent be linked to utilization of CO2 as feedstock. The biofuels production methods encompass anaerobic digestion, pyrolysis, fermentation, and liquefaction technologies [2, 3]. Biofuels, are considered very promising in the future energy portfolio [4, 5], increasing studies have been conducted about biofuels formation from different resources. Yun et al. studied the effect of NaCl on biofuel production potential of freshwater microalgae Chlorella vulgaris YH703, it shows biomass productivity of freshwater microalgae
Chlorella vulgaris YH703 was increased by 1.3 times with the addition of 30 mM of NaCl to BG-11 medium [6]. Kaushal et al. demonstrated a cost-effective process for liquid biofuel production (butanol and ethanol) from non-acetone forming strain C. sporogenes NCIM 2918 using low-cost dual substrate combination of sugar hydrolysate and crude glycerol. It is a major step towards the development of sustainable bioprocess for production of liquid biofuels.

How to use biomass conversion technology rationally is the focus in the world [7]. The valorisation processes encompassed by the biorefinery concept could be biochemical (e.g. fermentation, enzymatic conversion), thermochemical (e.g. gasification, pyrolysis, liquefaction), chemical (e.g. acid hydrolysis, synthesis, esterification), mechanical (e.g. fractionation, pressing, size reduction) or an adequate combination of these [8].

Biomass conversion technology is one of the bioeconomy solutions which could pave a pathway towards increasing economic and environmental sustainability [9]. An increasing number of countries have deployed strategic plans to promote the growth of a bioeconomy by encouraging private investment in biotechnology development and the production of biobased products, like biofuels [10]. Investment in research and development by the private industrial sector leads to innovations in renewable energy technologies and new biomaterials, further supporting the expansion and sustainability of the bioeconomy [11]. Bioeconomy is seen as a key strategic innovation pillar in the European Union, and this involves, among other things, mobilizing biomass resources [12–14], the production of advanced biofuels have been explicitly supported by the EU since 2015 [15]. The United States Department of Agriculture (USDA) projected that biobased chemical production could grow from its current share of 2–22% of the total market share for chemicals by 2025 [16]. The annual economic impact of the biobased products industry reached $ 369 billion in the US in 2013, with the biobased chemical sector contributing $ 5032 million to the total direct economic value added [17].

All countries or area, including USA, China, and EU, are facing economic and technological challenges [10, 18] to establish an operational industrial-scale production capacity, and hence a mature bioeconomy market [19]. China has abundant biomass resources, but their utilization is still in a low level [20–21], corn stalk can be used by farmers as feed, bedding followed by soil amendment, and field burning to destroy residue after the harvest, resulting in a serious waste of crop resources and crop residues burning have caused pollution to the atmospheric environment [22]. Nowadays, these practices are no longer considered sustainable due to concerns about the potential adverse effects on the environment and animals health conditions [23].

Agricultural crop residues are the main feedstock of lignocellulosic biomass and are expected to provide a major contribution to the production of advanced biofuels [24], they are likely to play a major role as raw materials for various industries that do not compromise food or feedstuff production [25]. Especially agricultural harvesting residues like corn stalk, wheat straw, barley straw and rapeseed straw show large sustainably-available potentials [26]. The valorisation of lignocellulose feedstock into intermediates, products and biofuels will take place in biorefineries with different conversion routes. The variety of
possible products from biorefineries is large and could be placed on the traditional petrochemical market, biofuel market as well as on a future bio-based market [19, 27, 28], bring more economic benefits to our society.

The biomass conversion technology of agricultural straw is mainly liquefaction technology, including liquefaction of biomass and atmospheric catalytic liquefaction:

Liquefaction of biomass mainly including bio-chemical preparation of fuel ethanol and chemical preparation of biofuels, the former generally refers to the use of hydrolysis and fermentation of straw and other biomass into fuel ethanol, the latter is through fast pyrolysis liquefaction, catalytic liquefaction of transformation. Fundamentally, pyrolysis is usually carried out at high temperatures, for examples, involves the heating of organic materials to temperatures greater than 400 °C in the absence of oxygen. At these temperatures, organic materials thermally decompose releasing a vapor phase and a residual solid phase (biochar). Flash pyrolysis, the oxygen causes partial combustion of the biomass, which generates the heat needed to sustain the reaction. The reaction temperature is generally quite high (800–1200 °C). Operated at sufficiently high temperatures, a gasifier produces very little char or biofuels [29].

Atmospheric catalytic liquefaction technology has been used in high efficiency and utilization of biomass comprehensively and it is considered to be one of the most promising methods of liquefaction [30, 31]. It is a thermochemical process in which biomass is converted to a liquid mixture with a wide range of molecular mass under the action of atmospheric pressure and temperature (150°C to 180°C), as well as under the action of the agent and catalyst [32]. Li Mingyang studied the behavior of corn stover liquefaction in the ethanol-water co-solvent and results showed that, the yield and heating value of bio-oil obtained from corn stover liquefaction with NiMoS /Al₂O₃ as catalyst increased. [33] However, the direct study and analysis of biofuels from atmospheric catalytic liquefaction on agricultural residues are few.

In this study, the common agricultural waste-corn stalk was liquefied by multi hydroxy alcohol. With concentrated phosphoric acid as catalyst and polyethylene glycol as the liquefaction agent, the optimum condition of stalk liquefaction was preliminarily determined, and the GC-MS, FTIR and SEM analysis were carried out for the liquefaction products.

Materials And Methods

Materials

Corn stalk used in this study was obtained from Tanggu District (Tianjin City), particle size was defined at 20 mesh to 80 mesh using crushing and sieving two steps, stored in a sealed plastic bag to balance moisture content. Concentrated phosphoric acid, polyethylene glycol 400 (PEG-400), 1,4-dioxane, ethanol, dichloromethane and pyridine were analytical purity. The silane reagent (BSTFA 90%, TMCS 10%) and potassium bromide were all Chromatographic purity.
CJF-1 type high pressure reactor; Ultra GCMS-QP2010; FTIR-650 type Fourier transform infrared spectrometer; JSM-IT300LV scanning electron microscope.

**Corn stalk liquefaction**

In this study, 10 g corn stalk powder was placed in a high temperature and high-pressure reaction kettle liner, then a certain amount of catalyst concentrated phosphoric acid and polyethylene glycol liquefying agent were added in to the system, stirring with a glass rod. The liner containing uniform solids and liquor was put into the high-pressure reaction kettle for liquefaction, and the reaction temperature was set to 170 °C, and the rotation speed was 380 r / min. When the temperature raised to 170 °C, the reaction was maintained 60 min, and the temperature rising curve and the reaction curve of the reaction process were recorded. After reaction, opening the cooling water so that the temperature of the reaction kettle was reduced to room temperature.

**Determination of liquefaction yield**

The liquefaction products were cleaned by water and 1,4-dioxane mixed liquid (1:4/V:V), and poured into the beaker with 30 min magnetic stirring. The upper solution was taken out after the mixed solution was centrifuged. The organic solvent of the upper solution was removed by rotary evaporation at 50 °C. Remaining concentrated liquid was the biofuel oil that we want. The residue was washed repeatedly with the recovered solvent and the hot distilled water until the filtrate was colorless. At the end, the residue and filter paper were put in a 105 °C oven and baked to a constant weight. After cooling, the quality of the residue was weighed to calculate the rate of liquefaction. The residue rate = residue quality / stalk quality * 100%; liquefaction rate = 1 - residue rate.

**Characterization of liquefaction products**

**GC-MS analysis of liquefied biofuel oil**

Silanization: 2 mg biofuel oil was put into the sample bottle, solvent was dried under the protection of nitrogen carefully, and put into a vacuum drying oven at 40 °C for 30min, then 80 µL pyridine and 150 µL silylating agents were added and shaken gently, put into an oven with 70 °C, silanization for 45min.

Gas Condition: RTX-5MS (30 m × 0.32 mm × 0.25 µm), carrier gas for high pure helium, flow rate 3mL / min; split ratio of 10: 1; injection volume 0.2 µL; inlet temperature of 300 °C, solvent delay 3min, temperature program: initial temperature of 80 °C, holding 3 min, to 5 °C / min raised to 150 °C holding 0 min, to 10 °C / min raised to 300 °C to maintain 5min, a total analysis time of 37min.

MS conditions: interface temperature 220 °C, ion source temperature 200 °C, mass scanning range 40 to 1000, ionization mode for EI (electron bombardment).

**Fourier transform infrared spectroscopy (FT-IR) analysis of liquefaction residue**
The FTIR analysis of the liquefied residues was performed by using KBr salt tablet method, with scanning range of 4000 ~ 370 cm$^{-1}$, resolution 4 cm$^{-1}$, scan 16 times in ambient air.

**Scanning electron microscope (SEM) analysis of liquefaction residue**

Scanning electron microscopy was used to observe the microstructure of the surface of stalk and liquefied residue. Samples were dried to constant weight fixed on the tape, and then spraying under vacuum, the photos of 250 times was taken.

**Results And Discussion**

**Influencing factors of liquefaction reaction**

**Effect of reaction time on liquefaction experiment**

The liquid solid ratio was 5: 1, the catalyst mass fraction was 10%, the reaction temperature was 170 ℃. Fig. 1 shows, with the extension of the reaction time, the liquefaction rate of corn stalk increased gradually, it reached the maximum of 97.19% at 60 min. The main reason was that the corn stalk and the liquefaction agent were fully mixed in the reaction system with the increase of reaction time, so that the liquefaction rate was accelerated, which was conducive to the liquefaction of corn stalk. The liquefaction rate showed a slow downward trend when the reaction time lasted longer. It will produce a series of complex side effects as the reaction time was prolonged, such as polymerization, which resulted in the reduction of liquefaction rate. The reaction varied as time added up, there was a highest liquefaction rate at a certain time point, because side reactions took place when the degradation products were exposed too long to high temperatures [34].

**Effect of reaction temperature on liquefaction experiment**

The catalyst mass fraction was 10%, the liquid solid ratio was 5: 1, the reaction time was selected according to above optimum temperature of 60 min. As can be seen from Fig. 2, at 150℃ to 170℃, with the increase of temperature, the liquefaction rate increased significantly. This was mainly because the reaction temperature helped the acidic groups of concentrated phosphoric acid access to the fiber structure of the corn stalk and destroyed the crystal structure of cellulose, which made the corn stalk liquefaction rate speed up [35]. When the reaction temperature was more than 170 ℃, the liquefaction rate showed a downward trend. Until the temperature was further raised to 190 ℃, the liquefaction rate significantly reduced. Due to the high temperature resulting in condensation reaction between the liquefaction products, high temperature carbonization and partial product wall sticking phenomenon [36]. The reaction temperature plays a significant role in the control of the thermochemical conversion of biomass, and working at the appropriate temperature is a key factor in the improvement of the conversion and prevention of most side reactions, necessary to obtain high-purity and high liquefaction rate products [37].
Effect of catalyst content on liquefaction experiment

At the condition of the liquid to solid ratio was 5:1, the reaction time was 60 min, and the reaction temperature was 170 °C. From Fig. 3, it could be seen that when the dosage of catalyst in the reaction system was relatively low, liquefaction reaction was relatively slow, and the liquefaction rate of corn stalk was relatively lower. With the increase of the amount of the catalyst, the liquefaction rate increased gradually. When the amount of the catalyst was 10%, the liquefaction rate of corn stalk was the highest, but the liquefaction rate decreased slightly when the amount of catalyst was over 10%. This was due to the degradation of lignin in acidic conditions into a free radical intermediate product, which can easily generate condensed residue, and the higher the concentration of acid, the more obvious of the condensation effect [38,39], in other words, lignin fragments are more apt to recondense in acid medium [40,41]. Therefore, the concentration of phosphoric acid did not only play a lytic role in the degradation reaction, but also played a catalytic role in the condensation reaction. To sum up, the liquefaction effect showed the optimum result when the catalyst dosage was 10%.

Effect of liquid solid ratio on liquefaction experiment

Liquid to solid ratio: it is the mass ratio of polyethylene glycol 400 and corn stalk powder in the liquefaction reaction. When the reaction temperature was 170 °C, the reaction time was 60 min, and the catalyst dosage was 10%. As shown in Fig. 4, when the liquid to solid ratio was 1:1, the liquefaction rate was really low, when the liquid to solid ratio increased to 5:1, the liquefaction rate of corn stalk significantly increased and the liquefaction rate reached to the maximum. It can be seen that the liquid to solid mass ratio has a direct effect on the residue content and biofuel oil formation. The main reason was that, the liquid agent can fully make the raw material of corn stalk soaked with the increase of the ratio of liquid to solid, so that the raw material was in full contact with the agent, which was beneficial to the normal liquefaction reaction. Another reason is, with the increasing of liquid to solid mass ratio, degraded corn stalk components in the liquefied product’s fragments decreased, the recondensation of degradation products was impeded drastically. Hence the dosage of corn stalk should not be too high compared to liquid addition. As the liquid to solid ratio continued to increase on the basis of 5:1, the liquefaction rate didn't raise obviously. Some side reactions might happen between lignin and liquefaction agent during the liquefaction process when the liquid to solid ratio is too high [42]. Considering the economic feasibility of liquefaction reaction, the liquid solid ratio 5:1 was chosen as the most suitable condition.

GC-MS analysis of liquefied biofuel oil

As shown in Fig. 5, in this study, GC-MS method was used to analyze the total ion flow diagram (TIC) of the biofuel oil prepared with polyethylene glycol 400 (PEG-400) as the agent. As shown in Table 1, the main components of biofuel oil and the relative peak area of biofuel oil were obtained by the spectral library retrieval and integration of the total ion flow chart.

| Table 1 | Analysis of main components of liquefied biofuel oil |
| Serial number | molecular formula | compound name                                           | relative peak area % |
|---------------|-------------------|---------------------------------------------------------|----------------------|
| 1             | C₂H₆O            | ethanol                                                 | 1.027                |
| 2             | C₂H₆O₂           | Glycol                                                  | 28.879               |
| 3             | C₃H₆O₃           | lactic acid                                             | 0.473                |
| 4             | C₅H₈O₃           | Acetyl propionate                                       | 0.429                |
| 5             | C₄H₁₀O₃          | Diethylene glycol                                        | 26.572               |
| 6             | C₁₂H₂₂O₈         | Polyethylene glycol succinate                           | 0.310                |
| 7             | C₃H₈O₃           | Glycerol                                                | 1.52                 |
| 8             | C₆H₆O₄           | 2-methyl-5-oxo-tetrahydrofuran-2-carboxylic acid        | 3.984                |
| 9             | C₆H₁₄O₄          | Triethylene glycol                                       | 12.0135              |
| 10            | C₄H₆O₂           | 3-hydroxyl-3-butene-2-ketone                             | 1.091                |
| 11            | C₈H₁₈O₅          | Tetraethylene glycol                                     | 6.206                |
| 12            | C₁₆H₃₂O₂         | Palmitic acid                                            | 2.552                |
| 13            | C₁₈H₃₆O₂         | stearic acid                                             | 1.202                |
| 14            | C₁₂H₂₆O₇         | hexaethylene glycol                                      | 0.459                |
| 15            | C₂₂H₄₆O₁₂        | Eleven glycol                                            | 4.579                |
| 16            | C₁₈H₃₈O₁₀        | Nine glycol                                              | 1.818                |
| 17            | C₂₉H₅₀O           | beta-sitosterol                                          | 0.452                |
| 18            | C₂₄H₅₀O₁₃        | Twelve glycol                                            | 4.030                |

Note: Table 1 only shows the peak area of the compound group, which is more than 0.3%

The biofuel oil obtained in a dark brown organic liquid form, similar morphology to many researches' [43-45], results from GC-MS analysis showed that the composition of corn stalk liquefaction was quite complex. Prepared with polyethylene glycol as liquid agent of biofuel oil were detected, there were 31 kinds of organic compounds. The main ingredients included alcohols, organic acids, esters, ketones and sugars compounds. The biofuel oil components were close to those from deoxy-liquefaction and fast pyrolysis, which contain organic compounds that belong to alkanes, aromatic hydrocarbons, phenol derivatives and little amounts of ketones, esters, ethers, sugars, amines and alcohols [46, 47].
Table 1 lists the 18 major compounds (peak area of compound group was greater than 0.3% of total peak area). As can be seen from Table 1, a large number of oxygens containing functional groups existed in biofuel oil, they made the biofuel oil with a high oxygen content. This did not only reduce the calorific value of biofuel oil, but also affect the stability of biofuel oil [48, 49]. Also, can be seen from Table 1, the biofuel oil alcohols accounted for a large proportion, consisted of 11 species, of which the most abundant were ethylene glycol and diethylene glycol, 28.879% and 26.572%, respectively. The biofuel oil contained a large number of hydroxyls, which could be used for the preparation of polyurethane foam and polyurethane adhesive materials etc. [50]. There were 5 kinds of organic acids, the 2-methyl-5-oxo-tetrahydrofuran-2-carboxylic acid was the toppest, 3.984%. In addition, the biofuel oil also contained a small number of esters and ketones, respectively, polyethylene glycol single amber esters and 3-hydroxyl-3-buten-2-ketone.

**Infrared spectrum analysis of liquefaction residue and biofuel oil**

By comparing the infrared spectra of the raw materials and the liquid products, the changes of the composition and functional groups of the corn stalk were investigated before and after the experiment. The composition of corn stalk mainly consisted of 3 main components, namely, cellulose, hemicellulose and lignin. The structure and properties of corn stalk in the process of liquefaction have been changed. As shown in Fig. 6, raw material (curve B): 3398cm-1 absorption peak was O-H stretching vibration; 2918cm-1 absorption peak was C-H stretching vibration; 1731 cm-1 absorption peak was C=O stretching vibration, which was the characteristic absorption peak of hemicellulose. 1601 cm-1 and 1512 cm-1 absorption peak was lignin benzene skeleton stretching vibration; C-O stretching vibration (methoxy benzene) was 1251cm-1 absorption peaks; beta glycosidic bond stretching vibration was 894 cm-1 absorption peaks, which was the characteristic absorption peak of cellulose. Liquefaction residue (curve A): 3398 cm-1, 2918 cm-1, 894cm-1 absorption peak was narrow and the intensity was weakened, which was caused by the liquefaction of cellulose in the raw material [51,52]. The disappearance of 1731 cm-1 absorption peak showed that the raw material in the hemicellulose has been basically liqueed. The liquefaction residue had absorption peak at 1601cm-1, which proved the presence of lignin, and there was no absorption peak at 1251 cm-1 and 1512 cm-1, which proved that the C-O of aromatic cyclic lignin was degraded [53]. Liquefied biofuel oil (curve C): there was a strong absorption peak at 3398cm-1 and 2918 cm-1, which showed the reaction generated a large number of hydroxyl groups, that was, biofuel oil contained more alcohol. These signs were consistent with the results of GC-MS analysis. The absorption peak of 1635 cm-1 was the stretching vibration of C = O bond, which indicated that the reaction produced ester compounds.

**SEM analysis of raw material and liquefaction residue**

The main components of corn stalk powder were cellulose, hemicellulose and lignin. As can be seen from the Fig. 7 (a), the structure of the internal structure of stalk was layered structure, it was arranged in order, and the gap between two layers was large, and the combination was not tight [54]. Seen from Fig. 7 (b),
fber structure could not be observed from the liquefaction residue, and the residue was basically loose bulk and granular, which indicated that the corn stalk fber was almost totally liquefied and had been destroyed in the process of liquefaction. It has reached a consensus for researchers that the key challenges in the material and biofuel utilisation of lignocellulose include: its resistance to breaking down into its components cellulose, hemicellulose and lignin [55]. Here, the atmospheric catalytic liquefaction showed great breakdown ability is of considerable economic importance for biofuel oil production.

Conclusions

The system which used phosphoric acid as catalyst and PEG-400 as the liquid agent has been developed and used for corn stalk liquefaction. And the best process of liquefaction is reaction temperature 170°C, reaction time 60 min, liquid solid ratio 5:1, catalyst dosage of 10%, then the liquefaction rate can reach 97.19%.

Concentrated phosphoric acid used as catalyst and PEG-400 as liquefer of corn stalk liquefaction, the characteristic functional groups of stalk cellulose, hemicellulose and lignin almost disappeared in infra-red spectrogram, indicating that the a sound liquefaction method was obtained. The biofuel oil contained a large number of hydroxyls, which can be used for preparing polyurethane foam and polyurethane adhesive materials. The main components of the liquefaction biofuel oil contain 18 kinds of compounds, including alcohols, organic acids, esters, ketones and sugar, most of which were alcohols and organic acids. The fiber structure could not be observed in the liquefaction residue, and the residue was granular, which indicated that the corn stalk was drastically liquefied and corn stalk fber had been destroyed in the process of liquefaction.

Declarations

Acknowledgements

The Project is Supported by National Natural Science Foundation of China (No. 31700516), Special Project No.2017YFB0307901 in the National Key Research and Development Program of China and the Foundation of Tianjin Key Laboratory of Pulp & Paper (No. 202005), the Project program of Key Laboratory of Food Nutrition and Safety, Ministry of Education & Tianjin Key Laboratory of Food Nutrition and Safety, China (No. TJS202001)

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References
1. de Jong, E., Higson, A., Walsh, P., Wellisch, M.. Bio-based chemicals value added products from biorefineries, IEA Bioenergy, Task42 Biorefinery. (2012) 34

2. He-Lambert, L., Shylo, O., English, B.C., Eash, N.S., Zahn, J.A.: D. M. Lambert. Supply chain and logistic optimization of industrial Spent Microbial Biomass distribution as a soil amendment for field crop production. Resour. conserv. recy. 146, 218–231 (2019)

3. Lee, R.A.: J.-M. Lavoie. From first- to third-generation biofuels: Challenges of producing a commodity from a biomass of increasing complexity. Anim. Front. 3(2), 6–11 (2013)

4. Roman, S., Nabais, J.M.V., Laginhas, C., Ledesma, B.: J. F. Gonzalez. Hydrothermal carbonization as an effective way of densifying the energy content of biomass. Fuel Process. Technol. 103, 78–83 (2012)

5. Agblevor, F.A., Besler, S.: A. E. Wiselogel. Fast Pyrolysis Of Stored Biomass Feedstocks. Energ. Fuel 9(4), 635–640 (1995)

6. Yun, C.-J., Hwang, K.-O., Han, S.-S., Ri, H.-G.: The effect of salinity stress on the biofuel production potential of freshwater microalgalae Chlorella vulgaris YH703. Biomass Bioenergy 127, 105277 (2019)

7. Garcia, R., Pizarro, C., Lavin, A.G.: J. L. Bueno. Biomass sources for thermal conversion. Techno-economical overview, Fuel 195, 182–189 (2017)

8. Asunis, F., De Gioanniss, G., Isipato, M., Muntoni, A., Polettini, A., Pomi, R., et al.: Control of fermentation duration and pH to orient biochemicals and biofuels production from cheese whey. Bioresour. Technol. 289, 121722 (2019)

9. Dubois, O., M. Gomez San Juan. How sustainability is addressed in official bioeconomy strategies at international, national and regional levels: An overview, Environment and Natural Resources Management. Working Paper (FAO) eng no. 63: (2016)

10. G. B. Council. Bioeconomy Policy (Part III)—Update Report of National Strategies around the World, Office of the Bioeconomy Council: Berlin, Germany (2018)

11. Lokko, Y., Heijde, M., Schebesta, K., Scholtès, P., Van Montagu, M.: M. Giacca. Biotechnology and the bioeconomy—Towards inclusive and sustainable industrial development. New biotechnol 40, 5–10 (2018)

12. Kluts, I., Wicke, B., Leemans, R., Faaij, A.: Sustainability constraints in determining European bioenergy potential: A review of existing studies and steps forward. Renew. Sust. Energ. Rev. 69, 719–734 (2017)

13. Haase, M., Rösch, C., Ketzer, D.: GIS-based assessment of sustainable crop residue potentials in European regions. Biomass Bioenergy 86, 156–171 (2016)

14. Hamelin, L., Borzęcka, M., Kozak, M., Pudelko, R.: A spatial approach to bioeconomy: Quantifying the residual biomass potential in the EU-27. Renew. Sust. Energ. Rev. 100, 127–142 (2019)

15. Parliament, E.: Proposal of a directive on transition to second generation biofuels.(2019)

16. Conway, R.: US Biobased Products Market Potential and Projections Through 2025, USDA Report (2008) 720–166
17. Golden, J.S., Handfield, R.B., Daystar, J., McConnell, T.E.: An economic impact analysis of the US biobased products industry: A report to the Congress of the United States of America. Ind. Biotechnol. 11(4), 201–209 (2015)

18. L. Marelli, Padella, M., Edwards, R., Moro, A., Kousoulidou, M., Giuntoli, J., ... Garcia-Lledo, L. The impact of biofuels on transport and the environment, and their connection with agricultural development in Europe. (2015)

19. Garcia-Condado, S., Lopez-Lozano, R., Panarello, L., Cerrani, I., Nisini, L., Zucchini, A., et al.: Assessing lignocellulosic biomass production from crop residues in the European Union: Modelling, analysis of the current scenario and drivers of interannual variability. GCB Bioenergy 11(6), 809–831 (2019)

20. Xiong, S.J., Ohman, M., Zhang, Y.F., Lestander, T.: Corn Stalk Ash Composition and Its Melting (Slagging) Behavior during Combustion. Energ. Fuel 24(9), 4866–4871 (2010)

21. Ma, H.H., Zhang, B.X., Zhang, P., Li, S., Gao, Y.F.: X. M. Hu. An efficient process for lignin extraction and enzymatic hydrolysis of corn stalk by pyrrolidinium ionic liquids. Fuel Process. Technol. 148, 138–145 (2016)

22. Fan, X.H., Ji, Z.Y., Gan, M., Chen, X.L., Jiang, T.: Integrated assessment on the characteristics of straw-based fuels and their effects on iron ore sintering performance. Fuel Process. Technol. 150, 1–9 (2016)

23. Akhlaghi, M., Boni, M.R., De Gioannis, G., Muntoni, A., Polettini, A., Pomi, R., et al.: A parametric response surface study of fermentative hydrogen production from cheese whey. Bioresour. Technol. 244, 473–483 (2017)

24. D. Bourguignon. Advanced biofuels: Technologies and EU policy: EPRS, the European Parliamentary Research Service; 2017

25. Moreno, A.D., Alvira, P., Ibarra, D., Tomáš-Pejó, E.: Production of Ethanol from Lignocellulosic Biomass. In: Fang, Z., Smith, J.R.L., Qi, X. (eds.) Production of Platform Chemicals from Sustainable Resources, pp. 375–410. Springer Singapore, Singapore (2017)

26. Thorenz, A., Wietschel, L., Stindt, D., Tuma, A.: Assessment of agroforestry residue potentials for the bioeconomy in the European Union. J Clean. Prod. 176, 348–359 (2018)

27. Kamm, B., Gruber, P.R., Kamm, M.: Biorefineries-industrial processes and products; 2006

28. Wietschel, L., Thorenz, A., Tuma, A.: Spatially explicit forecast of feedstock potentials for second generation bioconversion industry from the EU agricultural sector until the year 2030. J Clean. Prod. 209, 1533–1544 (2019)

29. Laird, D.A., Brown, R.C., Amonette, J.E., Lehmann, J.: Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels Bioprod. Bior. 3(5), 547–562 (2009)

30. Cheng, S., D’cruz, I., Wang, M., Leitch, M., Xu, C.: Highly efficient liquefaction of woody biomass in hot-compressed alcohol – water co-solvents. Energ Fuel 24(9), 4659–4667 (2010)

31. Song, C., Hu, H., Zhu, S., Wang, G., Chen, G.: Nonisothermal catalytic liquefaction of corn stalk in subcritical and supercritical water. Energ Fuel 18(1), 90–96 (2004)
32. Wang, W.Z., Zhang, Q.K.: Research Progress in Atmospheric Pressure Catalytic Liquefaction Technology of Biomass. Contemporary Chemical Industry 42(12), 1726–1728 + 1761 (2013)
33. Li, M.Y., Sun, J.J., Li, L.T.: J. W. Huang. Liquefaction of Corn Stover in Ethanol /Water Co-solvent for Bio-oil Production [J]. Biomass Chemical Engineering 52(02), 23–28 (2018)
34. Yan, L., Yang, N., Pang, H., Liao, B.: Production of levulinic acid from bagasse and paddy straw by liquefaction in the presence of hydrochloride acid. CLEAN−Soil, Air, Water 36(2), 158–163 (2008)
35. Wang, Y., Zhang, Q.K.: Study on the process of liquefaction of corn stalk by using phosphorus acid as catalyst. Contemporary Chemical Industry 44(5), 932–934 + 938 (2015)
36. Tan, Z.H., Zhang, Q.K., Zhao, S.L., Li, P.: Study on the Liquefaction of Corn Stalk by Using Phosphotungstic Acid as Catalyst. Journal of Jilin Agricultural University 34(1), 90–93 + 108 (2012)
37. Zhai, Q., Li, F., Wang, F., Feng, J., Jiang, J., Xu, J.: Ultrafine grinding of poplar biomass: effect of particle morphology on the liquefaction of biomass for methyl glycosides and phenolics. Cellulose 26(6), 3685–3701 (2019)
38. Wei, B., Chen, F., Li, Z., Cheng, Y.: Liquefaction of fermentation residue of corn stover in polyhydric alcohols. Chem. Indus. For. Prod. 34(5), 53–59 (2014)
39. Yao, Y.: Combined liquefaction of wood and starch in a polyethylene glycol-glycerin blended solvent. Mokuzai Gakkaishi 39, 930–938 (1993)
40. Chen, F., Lu, Z.: Liquefaction of wheat straw and preparation of rigid polyurethane foam from the liquefaction products. J. Appl. Polym. Sci. 111(1), 508–516 (2009)
41. Liu, H., Hu, H., Jahan, M.S., Ni, Y.: Furfural formation from the pre-hydrolysis liquor of a hardwood kraft-based dissolving pulp production process. Bioresour. Technol. 131, 315–320 (2013)
42. Jin, Y., Ruan, X., Cheng, X., Lü, Q.: Liquefaction of lignin by polyethyleneglycol and glycerol. Bioresour. Technol. 102(3), 3581–3583 (2011)
43. Czernik, S., Bridgwater, A.: Overview of applications of biomass fast pyrolysis oil. Energ. Fuel 18(2), 590–598 (2004)
44. Özbay, N., Apaydin-Varol, E., Uzun, B.B., Pütün, A.E.: Characterization of bio-oil obtained from fruit pulp pyrolysis. Energy 33(8), 1233–1240 (2008)
45. Islam, M.R., Tushar, M., Haniu, H.: Production of liquid fuels and chemicals from pyrolysis of Bangladeshi bicycle/rickshaw tire wastes. J. Anal. Appl. Pyrol. 82(1), 96–109 (2008)
46. Wu, L., Guo, S., Wang, C., Yang, Z.: Production of alkanes (C7–C29) from different part of poplar tree via direct deoxy-liquefaction. Bioresour. Technol. 100(6), 2069–2076 (2009)
47. Lu, Q., Li, W.Z., Zhu, X.-F.: Overview of fuel properties of biomass fast pyrolysis oils. Energy Convers. Manag. 50(5), 1376–1383 (2009)
48. Wang, L., Bai, X., Yi, W., Kong, F., Li, Y., He, F., et al.: Characteristics of bio-oil from plasma heated fluidized bed pyrolysis of corn stalk. Transactions of the Chinese Society of Agricultural Engineering 22(3), 108–111 (2006)
49. Heng, M., Sun, S., Sun, P., Chen, J.: Analysis by GC-MS of bio-oil produced from paulownia direct liquefaction in hot-compressed water without catalyst. Kezaisheng Nengyuan/Renewable Energy Resources 28(6), 48–53 (2010)

50. Kurimoto, Y., Koizumi, A., Doi, S., Tamura, Y., Ono, H.: Wood species effects on the characteristics of liquefied wood and the properties of polyurethane films prepared from the liquefied wood. Biomass Bioenergy 21(5), 381–390 (2001)

51. Zheng, H., Lu, Z., Fan, L., Huang, B., Liao, Y., Hu, Y.: Liquefaction of fir sawdust catalyzed by [Psmim]HSO4 and characterization of liquefaction products. Chem. Indus. For. Prod. 34(2), 91–96 (2014)

52. Zeng, C., Zheng, H., Lv, J., Chen, X., Huang, B.: Liquefaction of fir sawdust in supercritical ethanol with dissolved phosphotungstic acid, BioResour. 10 (4) (2015) 7738–7751

53. Cao, C.Y., Li, Z.Q.: Y. F. Su. Research on Hydro-liquefaction Products of Corn Stalk. Paper Sci Technol 31(2), 33–36 (2012)

54. Liu, S.Y., Yang, G.F.: C. J. Su. Observation and analysis on micro-structure of corn straw briquette fuels. J Therm. Sci. Technol. 8(3), 277–282 (2009)

55. Balat, M.: Production of bioethanol from lignocellulosic materials via the biochemical pathway: A review. Energy Convers. Manag. 52(2), 858–875 (2011)

**Figures**

![Figure 1](image)

**Figure 1**

Effect of reaction time on liquefaction rate
Figure 2
Effect of reaction temperature on liquefaction rate

Figure 3
Effect of catalyst dosage on the liquefaction rate
Figure 4

Effect of liquid solid ratio on the liquefaction rate

Figure 5

GC-MS total ion flow diagram of biofuel oil prepared with polyethylene glycol as a liquefaction agent
Figure 6

Comparison of liquefaction residue and biofuel oil A: liquefaction residue; B: raw material; C: liquefaction biofuel oil
Figure 7

(a) SEM of the raw material; (b) SEM of the liquefaction residue

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.
• GraphicAbstract.docx