Catalytic Fast Pyrolysis of Soybean Straw Biomass for Glycolaldehyde-Rich Bio-oil Production and Subsequent Extraction

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ABSTRACT: In this study, soybean straw (SS) as a promising source of glycolaldehyde-rich bio-oil production and extraction was investigated. Proximate and ultimate analysis of SS was performed to examine the feasibility and suitability of SS for thermochemical conversion design. The effect of the co-catalyst ($CaCl_2$ + ash) on glycolaldehyde concentration (%) was examined. Thermogravimetric-Fourier-transform infrared (TG-FTIR) analysis was applied to optimize the pyrolysis temperature and biomass-to-catalyst ratio for glycolaldehyde-rich bio-oil production. By TG-FTIR analysis, the highest glycolaldehyde concentration of 8.57% was obtained at 500 °C without the catalyst, while 12.76 and 13.56% were obtained with the catalyst at 500 °C for a 1:6 ratio of SS-to-$CaCl_2$ and a 1:4 ratio of SS-to-ash, respectively. Meanwhile, the highest glycolaldehyde concentrations (%) determined by gas chromatography–mass spectrometry (GC–MS) analysis for bio-oils produced at 500 °C (without the catalyst), a 1:6 ratio of SS-to-$CaCl_2$, and a 1:4 ratio of SS-to-ash were found to be 11.3, 17.1, and 16.8%, respectively. These outcomes were fully consistent with the TG-FTIR results. Moreover, the effect of temperature on product distribution was investigated, and the highest bio-oil yield was achieved at 500 °C as 56.1%. This research work aims to develop an environment-friendly extraction technique involving aqueous-based imitation for glycolaldehyde extraction with 23.6% yield. Meanwhile, proton nuclear magnetic resonance (¹H NMR) analysis was used to confirm the purity of the extracted glycolaldehyde, which was found as 91%.
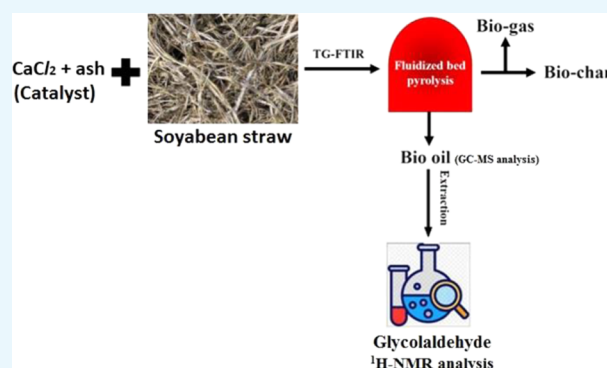
1. INTRODUCTION

Glycolaldehyde (GA), as one of the important chemical compounds found in bio-oil, is an effective meat-browning agent, which delivers smoky flavors.[1−4] Based on its specific characteristics, many companies, especially "Red Arrow Products Company", produce a variety of food-flavoring compositions that effectively strive with comparable products known as "liquid smoke".[3,5] GA could be among the ideal candidates for synthetic browning of food products at the industrial scale.[5−8] Bio-oil composition mainly depends on the nature of biomass feedstock, pyrolysis temperature, and catalyst used.[9] In the literature, GA formation is attributed to thermal decomposition of the cellulose.[10−12] Ultimately, a higher cellulose fraction (%) in biomass could result in a higher GA (%). In this context, we selected soybean straw (SS) due to its rich cellulosic fraction (37.3%) as compared to the other biomass reported earlier, such as wood chips (31.8%), grape residues (17.2%), rice husks (24.3%), olive husks (18.5%), wheat straw (27.3%), and rice straw (27%).[13,14] Additionally, development of catalytic fast pyrolysis (CFT) necessitates tools that can precisely determine the composition of the bio-oil. This requires a better selection of pyrolysis

temperature and biomass-to-catalyst ratio, as the composition of the bio-oil is strongly linked with the temperature and concentration of the catalyst used. However, no such efforts were made to address this challenge. In the present work, we have developed a very simple and cost-effective tool, i.e., thermogravimetric-Fourier-transform infrared (TG-FTIR) analysis, to optimize the pyrolysis temperature and biomass-to-catalyst ratio for bio-oil production with a rich concentration of the desired chemicals such as GA.

Catalytic fast pyrolysis (CFT) is a promising technique and significantly alters the composition of the resulting bio-oil. However, a systematic understanding of the effect of a catalyst on the chemical speciation due to pyrolysis has been comparatively unexplored. Previously, extensive efforts have been made towards GA production via catalytic pyrolysis.

Varhegyi et al. (1989) examined the effects of NaCl, MgCl$_2$, ZnCl$_2$, and FeSO$_4$ on pyrolysis.[15] These inorganic compounds were observed to facilitate the production of smaller molecules such as GA. Jensen et al. (1998) examined the effect of KCl on wheat straw pyrolysis and found that the presence of KCl resulted in low interaction between the biomass constituents, which led to formation of smaller molecules such as GA.[16] Similar observations were also found on pyrolysis of the rice hull,[17] sunflower stem,[18] olive bagasse,[19] and palm oil. However, the yield of GA has always been a serious challenge. Kostetskyy et al. (2020) observed that water contents could serve as a catalyst to facilitate GA production via pericyclic fragmentation reactions, and reduce the undesired reactions.[5] However, it seriously affects the efficiency and performance of the instrument. In this aspect, we proposed a novel catalyst, namely a mixture of mineral salts and ash (CaCl$_2$ + ash), to effectively enhance the GA (%) in soybean straw-derived oil. It was hypothesized that C2−C3 scission of the glucose intermediate produced GA during pyrolysis.[20,21] In our proposed catalyst, ash contents along with minerals (CaCl$_2$) decrease the activation energy and facilitate the primary thermal decomposition, mainly of cellulose, resulting in production of GA.

Furthermore, GA extraction is highly challenging, as bio-oil is a complicated chemical mixture.[2,3] Due to the high consumption of solvents, column chromatography is not economically feasible. Moreover, direct distillation is not favorable because bio-oils have poor thermal stability.[22] Extensive research has been done on the isolation of GA from bio-oil;[23−25] however, the non-environment-friendly nature and regeneration challenge of amine due to the formed Schiff base turned it into a tedious and unsafe extraction method.[26,27] Vitasari et al. (2012b) developed a process to recover GA from bio-oil based on multiple evaporation and condensation steps.[28,29] However, the multi-step scheme involving evaporation and condensation enhances the economic cost of the process. Herein, we have proposed a novel efficient extraction to isolate GA from bio-oil. We utilized the aqueous-phase extraction method based on the fact that GA can be collected in the aqueous phase because of its high polarity. Aqueous-based imitation turns this into highly environment-friendly technique.

In the present work, we report soybean straw (SS) as a promising source of glycolaldehyde-rich bio-oil. The comparative chemical analysis of TG-FTIR and gas chromatography−mass spectrometry (GC−MS) empowers the researchers to optimize the pyrolysis temperature, and the biomass-to-catalyst ratio by TG-FTIR analysis. Such discovery is essential to endow the process design with cost-effective biomass conversion technologies. Moreover, development of a low-cost and easily prepared catalyst (CaCl$_2$ + ash) along with the environment-friendly extraction technique makes this study highly helpful to flourish the food industry.

2. RESULTS AND DISCUSSION

2.1. Physicochemical Properties.
To evaluate the potential of SS as a biomass feedstock for the thermochemical conversion processes, the sample was first subjected to ultimate analysis and proximate analysis, the results of which along with the biomass fraction and HHV are shown in Table 1. The highly volatile matter contents (73.61%) of SS make it highly feasible for liquid product (bio-oil) formation via pyrolysis. Additionally, its lower ash contents (5.03%) reflect its

Table 1. Ultimate Analysis and Composition of Dry SS Biomass

Proximate Analysis (wt %)	
volatile matters	73.61
moisture	6.77
ash	5.03
fixed carbon	14.59
Ultimate Analysis (wt %, dry basis)	
carbon (C)	53.68
hydrogen (H)	5.38
oxygen (O)	37.17
nitrogen (N)	2.59
sulfur (S)	1.17
higher heating value (MJ/kg)	18.23
Composition of SS	
cellulose	37.3
hemicellulose	25.53
lignin	34.29

suitability for application to pyrolysis biomass feedstock as high ash contents mainly cause agglomeration, slagging, and fouling, while they also limit heat and mass transfer.[31,32] The moisture content of SS was found as 6.77%. Ultimately, these features make it a viable feedstock for pyrolysis, as a moisture content less than 10% is considered suitable for pyrolysis.[33]

The ultimate analysis confirmed that SS has high contents of carbon (53.68%), resulting in higher combustion enthalpy (18.96 MJ/Kg) as compared to already reported biomass such as *mango peel* (16.41 MJ/Kg), *castor residue* (14.43 MJ/Kg), *camel grass* (15.00 MJ/Kg), *arduno donax* (17.20 MJ/Kg), *miscanthus gigantus* (17.80 MJ/Kg), *para grass* (15.04 MJ/Kg), and *giant reed* (17.20 MJ/Kg).[31−35] The high oxygen contents (37.17%) are mainly associated with SS's numerous oxygenated functional groups as confirmed by FTIR analysis (Figure S1 and Table 2),[32,33] and biomass components (Table 2) such as lignin (34.29%), hemicellulose (25.53%), and cellulose (37.3%).

Table 2. Functional Groups as Assigned to Specific Wavenumbers for FTIR Analysis of Soyabean Straw

functional group	wavenumber (cm^{-1})	assigned peaks
−OH, N−H	3334	alcohol, amine
−C−H	2900 and 2847	methylene group (lipids)
−C=O	1670	aromatic conjugate
−C=C−	1640	alkene
aromatic −C=C−	1450−1410	aromatic conjugation
−C−O	1365	organic acid
−C−O−C−	1270	ethers
−C−C−	1220	alkanes
−C−O, C−O−H	1080 and 1025	alcohols, esters, polysaccharides

Higher nitrogen (N) and sulfur (S) contents in biomass are undesirable for thermochemical conversion design.[32] First, these elements result in formation of high-energy bonds, such as Ce−S, He−N, Ce−N, and He−S, and hence enhance the endothermicity of the reaction, making the biomass unfeasible for pyrolysis. Second, these elements contribute to the greenhouse effects and acid rain. Ultimately, the lower contents of N (2.59%) and S (1.17%) in SS reflect its environment-friendly nature and feasibility for thermochemical conversion design.
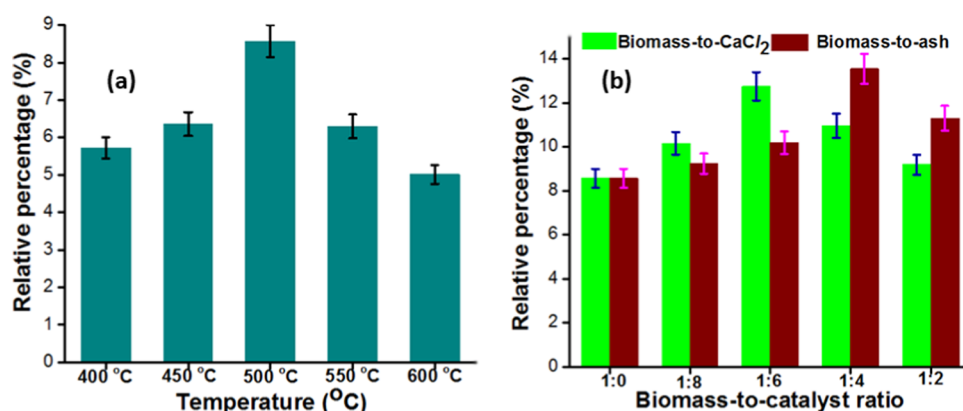
Figure 1. Relative percentage (%) of GA calculated by TG-FTIR analysis at (a) different temperatures and (b) different biomass-to-catalyst ratios calculated at 500 °C.
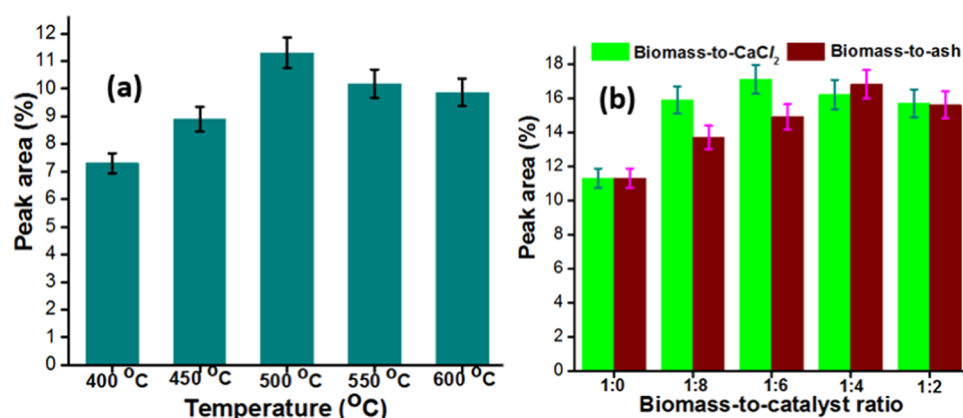

Figure 2. GA (%) in terms of the peak area calculated by GC−MS analysis of the bio-oil produced at (a) different temperatures and (b) different biomass-to-catalyst ratios at 500 °C.

2.2. Optimization of the Biomass-to-Catalyst Ratio for GA-Rich Bio-oil Production.

Bio-oil composition strongly fluctuates with pyrolysis temperature and catalyst concentration. Glycolaldehyde (GA) is an organic compound having two functional groups: a hydroxyl and an aldehyde group with a molar mass of 60.052 g/mol, similar to acetic acid. By integrating the corresponding area of the FTIR spectra at a specific temperature, we can get further insight into the relative concentration (%) of the desired chemicals.[9,36,37] For this, the TG-FTIR spectra at different temperatures (400−600 °C) were taken and are shown in Figure S2. Moreover, CH_4, CO_2, H_2O, $HOCH_2COH$, $HCOOH$, C_6H_5OH, CH_3CH_2OH, and C═C are identified as the main pyrolytic products from biomass pyrolysis. According to the characteristic wavenumbers of the pyrolytic products, CH_4 (3045−2875 cm^{-1}), CO_2 (2240−2335 cm^{-1}), H_2O (1750−1250 cm^{-1}), $HOCH_2COH$ (1900−1603 cm^{-1}), $HCOOH$ (1200−1100 cm^{-1}), C_6H_5OH (1400−1200 cm^{-1}), CH_3CH_2OH (1100−1000 cm^{-1}), and C═C (1600−1450 cm^{-1}) were apparently observed in the FTIR spectrum.

Furthermore, the total integrated area of the FTIR spectrum and relative percentage contents (%) at different temperatures (400−600 °C) and ratios of biomass-to-catalyst are given in Table S1a−c. As can be seen from Figure 1a, GA (%) increased with increasing pyrolysis temperature and showed a maximum concentration of 8.57% at 500 °C. Beyond this temperature, GA (%) was observed to decrease as 6.30 and 5.01% at 550 and 600 °C, respectively. For catalytic pyrolysis,

the catalyst and biomass were mechanically mixed. The biomass quantity was strictly controlled to 0.20 mg for TG-FTIR analysis. The solid catalyst quantity was varied from 2.5 to 10 mg (such as 2.5, 3.33, 5, or 10 mg) and added to the biomass physically to obtain biomass-to-catalyst ratios of 1:8, 1.6, 1:4, and 1:2, respectively. As can be seen from Figure 1b, GA (%) increased with increasing ratios of $CaCl_2$ and ash to biomass individually. However, it showed a maximum at 1:6 and 1:4 biomass-to-$CaCl_2$ and biomass-to-ash ratios, with values of 12.76 and 13.56%, respectively.

2.3. Bio-oil Production and GC−MS Analysis.

To study the consistency and authenticity of the GC-MS analysis, we produced bio-oils at each temperature and ratio of biomass-to-catalyst as of the TG-FTIR analysis. The composition of each resulted bio-oil is shown in Table S2a−c. It is obvious from Figure 2a that the bio-oil produced at 500 °C has the highest GA (%) of 11.3%. Moreover, for catalytic pyrolysis, the catalyst was mixed with the biomass mechanically and sent to the fluid reactor for bio-oil production.

The biomass quantity for each experiment was kept at 2 g. The corresponding catalyst quantity was varied from 0 to 1 g (such as 0, 0.25, 0.33, 0.5, or 1.0 g) to ensure the biomass-to-catalyst ratio of 1:0, 1:8, 1:6, and 1:2, similarly to the TG-FTR analysis. Interestingly, GA concentration was found to be the highest, 17. 1 and 16.8%, for 1:6 ratio of biomass-to-$CaCl_2$ and 1:4 ratio of biomass-to-ash, respectively, after which it started to decrease (Figure 2b). Hence, we finally produced the bio-oil using 1:6:4 ratio of biomass-to-$CaCl_2$-to-ash, by which GA was

found to be increased up to 20.23%. Hence, the consistency of this GC−MS analysis proves TG-FTIR as an efficient technique to optimize the pyrolysis temperature and catalyst ratio for bio-oil production with a high concentration of desired chemicals such as GA. Additionally, the GA (%) produced as a result of $CaCl_2$ + ash application was found to be higher than that produced with other catalysts used already, such as $Ca(OH)_2$ (13%), $CaCO_3$ (14%), $Ca(NO_3)_2$ (12.8%), $CaHPO_4$ (8.7%), and $MgCl_2$ (9.3%),[38] which confirms that $CaCl_2$ + ash could be an efficient catalyst to enhance the GA (%) during fast pyrolysis of biomass. The $CaCl_2$ + ash decreases the activation energy and facilitates the primary thermal decomposition mainly of cellulose, resulting in selective production of small molecules such as GA. Additionally, the presence of sodium and potassium contents as the strong cracking agents in ash facilitates selective C2−C3 scission of the glucose intermediate, resulting in increased GA (%) of up to 20.23%. This observation demonstrates the efficiency and superiority of our proposed catalyst.

2.4. Effect of Temperature on Product Distribution.

Temperature has a significant effect on product distribution.[39,40] The relationship between the product distribution and temperature was examined and is shown in Figure 3.
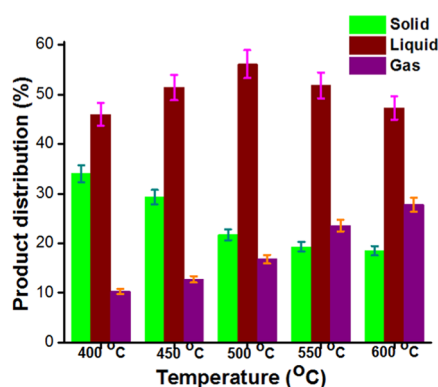

Figure 3. Effect of temperature on product distribution (%).

The liquid oil yield increased from 46% (400 °C) to 56.1% (500 °C), and then decreased to 51.8% (550 °C) and 47.1% (600 °C), and the maximum was reached at 500 °C as 56.1%. Meanwhile, with increase of temperature, the gases' yield increased continuously from 10.3% (400 °C) to 27.8% (600 °C), which might be due to the secondary reaction maximization. This also shows that at higher temperature, more biomass was converted into gases and less was converted into liquids.[41] However, the char yield was decreased continuously from 34 to 18.5% as the temperature was increased from 400 to 600 °C.

2.5. Extraction of Glycolaldehyde.

De Haan and his co-workers have extensively studied the glycolaldehyde extraction from bio-oil.[26−29] Due to the stable glycolaldehyde-bisulfite adduct formation, direct glycolaldehyde extraction from the bio-oil using sodium bisulfite is not appropriate.

Therefore, water extraction of bio-oil is considered to be efficient as the initial step, where mainly glycolaldehyde and some other polar compounds are also recovered in the aqueous phase. Glycolaldehyde was extracted using the scheme shown in Figure 4, and an overall glycolaldehyde yield of 23.6% (percentage of its initial mass in the feed) was achieved from the proposed process.

The high stability of products formed during extraction, such as Schiff base, and the low distribution coefficient of glycolaldehyde in solvents such as 1-octanol, TOA in 2-ethyl-hexanol etc. are the main challenges in enhancing the yield of GA. Thus, exploring of new solvents with high distribution coefficients of these oxygenates may introduce new extraction options. Moreover, the purity of glycolaldehyde was determined by ^1H NMR analysis of the extracted glycolaldehyde, which shows 91% purity (Figure 5), while the peaks present at 2.1, 2.7, 5.21, and 8 ppm might be due to impurities.

3. CONCLUSIONS

This study reports soybean straw (SS) as a promising source of glycolaldehyde-rich bio-oil production associated with rich cellulosic chemical composition (37.3%). The high volatile
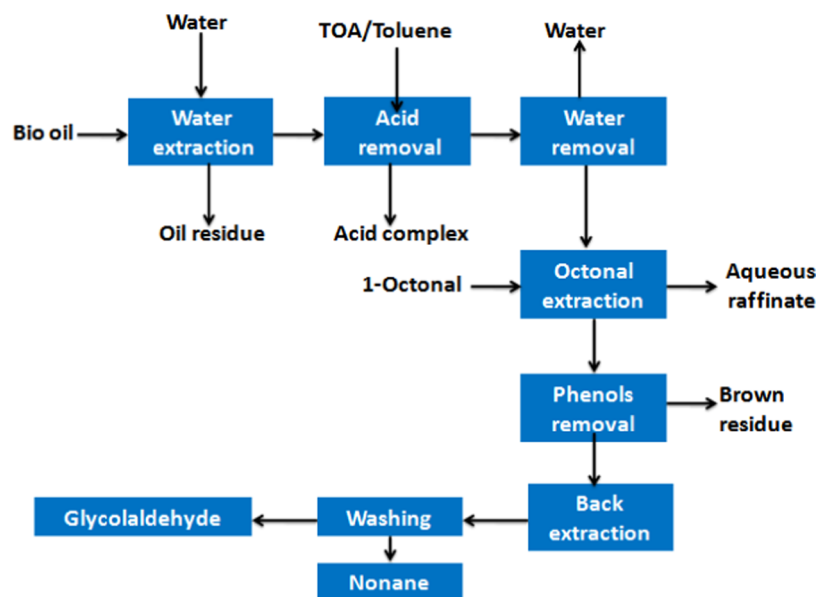

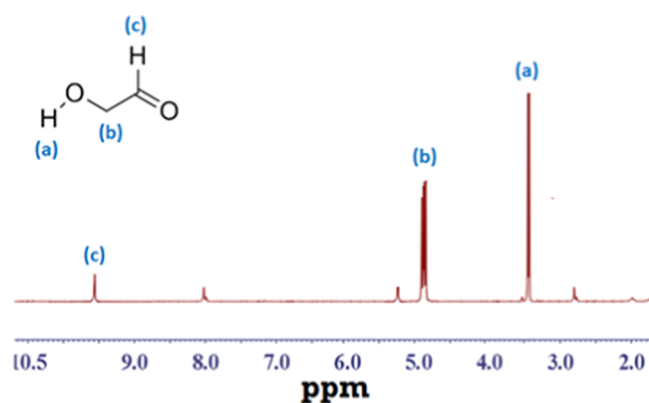**Figure 4.** Scheme used for GA extraction.

Figure 5. ^{1}H NMR of the extracted GA.

matter contents (73.61%), lower ash (5.03%) and moisture contents (6.77%), and high contents of carbon (53.68%) confirm the suitability of SS for thermochemical conversion design. Moreover, from the comparative analysis of TG-FTIR and GC−MS, it can be concluded that TG-FTIR analysis can be applied to optimize the pyrolysis temperature and biomass-to-catalyst ratio for high-quality bio-oil production because of its having a high concentration of desired chemicals such as GA. Furthermore, 20.23% of GA was obtained in the bio-oil produced using the co-catalyst ($CaCl_2$ + ash) at 1:6:4 ratio of biomass-to-$CaCl_2$-to-ash, which confirms the efficiency of our proposed catalyst for GA-rich bio-oil production. Additionally, the aqueous-based imitation of our proposed extraction technique reflects its environment-friendly nature along with an enhanced extraction yield and efficiency of 23.6 and 91%, respectively.

4. MATERIALS AND METHODS

4.1. Pyrolysis Process. The soybean straw (SS) sample was obtained from Suzhou, China. The sample was washed with tap water to remove surface contamination. Then, it was re-washed with distilled water and kept in an oven for 5 h at 80 °C for drying. Fully dried samples were further ground using a blender with stainless blades to reduce the particle size, while the samples were finally sieved with a particle size of ~250 to avoid any mass and heat transfer limitations.
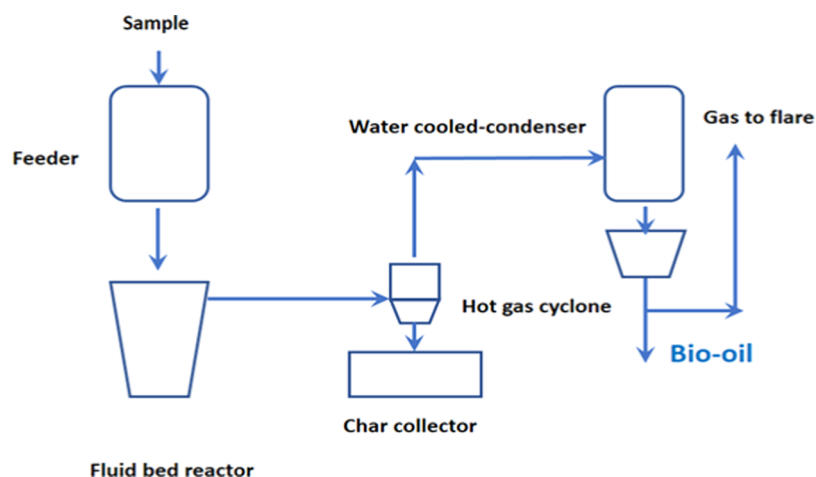
The experimental system for bio-oil production using fluidized bed pyrolysis is shown in Figure 6. Nitrogen gas (N_2) was heated externally and thoroughly flowed in a reactor with a flow rate of 0.6 kg/h. The silica sand (diameter = 256 mm) was positioned in the fluidized bed reactor. Bio-oils were produced at different temperatures (400−600 °C) without catalyst and with biomass-to-catalyst ratios of 1:8, 1:6, 1:4, and 1:2 (at 500 °C). The oil, char, and gas were obtained after experiment completion. Gaseous products were condensed into liquid and were collected in liquid collectors. The ASTM D5373 method was followed for ultimate analysis using a LECO CHNS-932 analyzer. The high heating value (HHV) was measured using a bomb calorimeter (Sundy SDC 5051). Biomass fraction was determined by a method introduced by Ranzi and co-workers.[30] All of the experiments were repeated thrice to confirm our results' reproducibility, and experimental errors were at ± 5% of the mean values.

4.2. Preparation of Ash. Soybean straw ash was prepared by the following method as reported by NREL (Sluiter et al., 2008). Air oxidation of as-received SS was performed at 570 °C in a furnace for about 6 h. The residue left was applied as ash for our research work, while the X-ray florescence (XRF) technique was used to determine the composition of ash (Table 3).

Table 3. Composition of Soyabean Straw Ash

compounds	contents (%)
Fe_2O_3	1.78
Al_2O_3	5.07
SiO_2	66.29
CaO	5.98
SO_3	0.51
MgO	5.03
K_2O	7.36
Na_2O	3.28
P_2O_5	1.87
SrO	0.29
TiO_2	0.17
BaO	0.06

4.3. TG-FTIR Analysis. A TGA (Q600 SDT, TA instrument) coupled with an FTIR spectrometer (Nicolet6700) was applied for SS pyrolysis. About 20 mg of the

Figure 6. Experimental setup for bio-oil production.

SS sample was pyrolyzed from 400 to 600 °C without the catalyst and at 500 °C with different biomass-to-catalyst ratios such as 1:8, 1:6, 1:4, and 1:2, and the FTIR spectra were recorded continuously.

4.4. GC−MS Analysis. GC−MS analysis was performed to determine the bio-oil composition, especially GA (%), in terms of peak area. The GC−MS instrument was designed with a PerkinElmer Clarus 680 Gas Chromatograph, a Clarus 600T Mass Spectrometer, a capillary column made of Elite-5MS30 with a film thickness of m 0.25 mm 0.25 lm, an injector temperature of 280 °C, carrier gas (helium) with a flow rate of 1.5 mL/min, 1:33 split ratio, an ion source of a 70 eV EI at 250 °C, and an MS scan range of m/z 50−600. After keeping the oven at 60 °C for 2 min, it was ramped at 4 °C/min to 250 °C, keeping 20 min as the dwell time.

4.5. Extraction of Glycolaldehyde. Glycolaldehyde (GA) was extracted from bio-oil using the multi-stage extraction scheme as shown in Figure 4. The scheme consists of (1) phase separation of bio-oil by adding distilled water in bio-oil, i.e. aqueous phase and organic phase; (2) extraction of the bio-oil-derived aqueous phase using tri-n-octylamine (TOA) in 2-ethyl-1-hexanol; (3) subsequent evaporation to remove most water and thereby to increase the GA concentration in the TOA-aqueous mixture; (4) extraction of glycolaldehyde from the glycolaldehyde-enriched aqueous mixture using 1-octanol polar solvent; (5) evaporation to enhance the GA yield by removing the brown color from the mixture caused by the phenolic groups; (6) back extraction using water to separate the GA from 1-octanol; and (7) complex washing by nonane to get glycolaldehyde.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04717.

IR spectra; TG-FTIR analysis; GC−MS analysis (PDF)

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✉M.H.T. and R.M.I. contributed equally to the work and are co-first authors. M.B.H. and A.K. prepared the manuscript draft and did the editing. H.A., Y.A.-T., M.I., and H.A.R. provided funding for the sample analysis and characterization, and contributed to the manuscript writing. X.C. supervised this work.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

SS	soybean straw
GA	glycolaldehyde
TG-FTIR	thermogravimetric-Fourier-transform infrared analysis
GC−MS	gas chromatography−mass spectrometry
^{1}H NMR	proton nuclear magnetic resonance
HHV	higher heating value
CaCl$_2$	calcium chloride
ASTM	American society for testing and materials
CFT	catalytic fast pyrolysis

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