

Comparative Kinetic and Pyrolytic Studies of D-Glucose Using Formulated Red Mud, Sand, and HZSM-5

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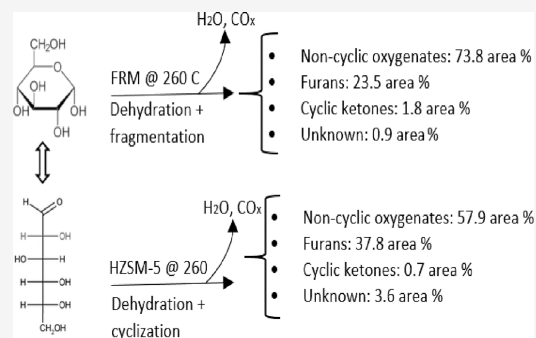


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ABSTRACT: The catalytic pyrolysis of D-glucose (DG) was conducted using a thermogravimetric analyzer (TGA) and formulated red mud (FRM) as the catalyst to determine the kinetic parameters of DG decomposition in the presence of the catalyst. The FRM reduced the overall activation energy (45.58–87.35 kJ/mol) of DG conversion compared to sand (45.27–112.00 kJ/mol). The trend of the frequency factor (A) for the catalytic pyrolysis (first-order reaction: $78.1\text{--}1.14 \times 10^8 \text{ s}^{-1}$) and non-catalytic pyrolysis (first-order reaction: $7.10\text{--}2.08 \times 10^7 \text{ s}^{-1}$) of DG was different, which indicated different reaction mechanisms. Compared to the sand and HZSM-5 catalyst, the FRM altered the thermal decomposition profile of the DG and promoted its decomposition at lower reaction temperatures. The thermogravimetric analyses showed that at 260 °C, the FRM catalyst converted more DG (50% conversion) than the HZSM-5 (44% conversion) and sand (35% conversion), which was in agreement with its activation energy. Furthermore, the DG decomposition was studied in a fixed-bed reactor using catalytic and non-catalytic pyrolysis conditions. The FRM promoted the formation of low-molecular-weight compounds (acetic acid and formic acid, CO_2 , formaldehyde, and CO) and hindered the formation of furans. The HZSM-5 catalyst promoted the formation of furans.



1. INTRODUCTION

Due to its low cost and abundance, lignocellulosic biomass has been extensively studied for biofuel production.^{1–3} However, the conversion process of biomass to biofuels still has challenges and is still under development.^{4,5} Lignocellulosic biomass consists of cellulose (23–53%), hemicellulose (20–35%), and lignin (10–25%).⁶ These components are structurally different from each other and therefore have different thermal degradation temperatures.⁷ For instance, cellulose and hemicellulose decompose into mostly mono- and oligosaccharides during pyrolysis.⁸

The main product of the fast pyrolysis of lignocellulosic biomass is a liquid product called biooil. This liquid has high viscosity, high oxygen content, high water content, and low stability.^{2,9,10} Catalytic pyrolysis can improve the properties of the biooil by converting the reactive species in the latter to either gases consisting mainly of $\text{C}_1\text{--C}_5$ hydrocarbons alongside carbon monoxide and carbon dioxide or shorter chain liquid organic molecules.¹¹ Several kinetic studies have been conducted for the catalytic pyrolysis of different types of lignocellulosic biomass to develop potential catalysts that can lower the activation energy required to convert the biomass and improve the quality of biooil produced from its catalytic pyrolysis. For instance, Nisar and his team studied the catalytic pyrolysis of different biomass such as almond shell waste using the zinc oxide catalyst,¹² cobalt-impregnated sesame stalk biomass,¹³ sugarcane bagasse using the copper oxide catalyst,¹⁴ juice-squeezed grapefruit waste using nickel oxide,¹⁵ de-oiled

karanja (*Pongamia pinnata* L.) seed press cake using the anthill catalyst,¹⁶ and peanut shells using the termite hill catalyst.¹⁷ All catalysts studied lowered the activation energies required to convert hemicellulose, cellulose, and lignin and improved the biooil quality by lowering the amount of oxygenated compounds in it.

To better understand the catalytic pyrolysis mechanisms of lignocellulosic biomass, it is important to study the catalytic pyrolysis of its different components separately. Cellulose is the major polymer in lignocellulosic biomass and is a homopolymer of glucose molecules connected via $\beta(1 \rightarrow 4)$ glycosidic bonds.¹⁸ The catalytic pyrolysis of glucose has been investigated in the literature, and the most common catalyst used was zeolite. For instance, aqueous glucose solutions were converted into hydrocarbons after being passed through an HZSM-5 fixed-bed reactor.¹⁹ Haniff and Dao reported that at temperatures above 292 °C, the catalytic pyrolysis of glucose using ZSM-5 and modified ZSM-5 catalysts (Mn-ZSM-5 and Zn-ZSM-5) promoted the polymerization of the carbohydrate feed, which resulted in a low hydrocarbons yield.²⁰

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In a more recent study of the catalytic fast pyrolysis of glucose using HZSM-5,²¹ it was reported that the process involves two steps; below 300 °C, the decomposition of glucose via retro-aldol condensation yielded a variety of small oxygenates consisting of low-molecular-weight ketones and aldehydes. Above 300 °C, furans and anhydrous sugars were the major products of the glucose dehydration. Additionally, the higher temperature resulted in the formation of hydrocarbons inside the HZSM-5 catalyst. Coke formation on the surface of the catalyst was observed in parallel with the aromatics production. Recently, Cheng et al. used the density functional theory to study the products of cellulose catalytic pyrolysis over the ZSM-5 catalyst, and they used glucose as a model compound.²² Among their findings, they reported that the glucose was converted into 5-hydroxymethylfurfural (5-HMF), which was then converted into furfural (FF), and then the FF was converted into benzene inside the ZSM-5 catalyst pores. They also reported that the complex catalytic reaction system was highly dependent on the electrophilicity of the acid sites on the ZSM-5 catalyst.

The major cost of biofuel production from biomass is directly related to the energy efficiency of the biomass conversion process as well as the catalyst cost and efficiency. Therefore, reducing the cost of the catalyst is a step toward achieving the economically feasible biofuel production process. Substantial effort has been put into the screening of pyrolysis catalysts to identify catalysts that are cheap and can improve the quality of the pyrolysis biooil. Red mud, a byproduct of the Bayer process for processing bauxite ore to produce alumina, has been extensively investigated as a pyrolysis catalyst,^{23–27} and its performance was compared to that of the HZSM-5 catalyst.^{25,28–31} Red mud is produced as a slurry that is subsequently dumped into evaporation ponds where it becomes a red solid residue as the water evaporates with time. Yathavan and Agblevor reported that both the red mud and HZSM-5 catalysts produced low-viscosity biooils with a high calorific value compared to the conventional fast pyrolysis of the same biomass.²⁸ In fact, the red mud catalyst produced biooil that was less viscous (>2-fold) and had higher energy content (HHV) than the one produced using the commercial HZSM-5. To understand the mechanisms of the catalytic pyrolysis of biomass using the red mud catalyst, it is necessary to investigate the catalytic pyrolysis of its major polymers as well as their corresponding building blocks (glucose, xylose, mannose, lignols, etc.) and identify the origins of the chemicals present in the final catalytic pyrolysis biooil. By doing so, it will be possible to predict the composition of the red mud catalytic biooil based on the composition of the biomass (content of cellulose, hemicellulose, and lignin) used.

The red mud catalyst was reported to retain its catalytic activity after regeneration.²⁸ In contrast, the ZSM-5 catalyst is known to experience irreversible deactivation due to alkali and alkaline earth metal oxides present in biomass.^{32–34} Therefore, the red mud catalyst is a potential competitor to the synthetic and expensive HZSM-5. Although the reaction pathways of the HZSM-5-catalyzed pyrolysis of biomass,^{22,35–38} cellulose, hemicelluloses, and lignin, as well as their respective model compounds (glucose, xylose, and guaiacol), have been extensively studied, there is very little published literature on the reaction pathways of the cheaper and more effective competitor, red mud.

In this paper, the catalytic pyrolysis of D-glucose (DG) using sand, formulated red mud (FRM), and HZSM-5 was

conducted. This study was divided into two sections: (1) determination of the kinetic parameters of the DG decomposition in the presence of sand (as a reference) and in the presence of FRM and (2) studying the effect of the FRM and HZSM-5 in a fixed-bed reactor on the pyrolysis product distribution as well as the composition of the pyrolysis gases and liquid.

2. MATERIALS AND METHODS

2.1. Catalysts. The FRM and HZSM-5 catalysts used in this study were from the same batches used by Agblevor et al.³⁹ and Yathavan,¹¹ respectively. Prior to each experiment, the sand and the catalysts were dried at 105 °C overnight and sieved to a particle size of $125 < d_p < 180 \mu\text{m}$. The FRM was suspended in deionized water (5 g of FRM + 50 mL of deionized water), and the pH of the slurry was measured using an InLab Expert PRO-ISM electrode (Mettler-Toledo, LLC, OH, USA). Since the FRM particles used for this study were smaller than those used by Agblevor et al.³⁹ ($180 < d_p < 450 \mu\text{m}$), the specific surface area of the FRM ($125 < d_p < 180 \mu\text{m}$) was measured using a Quantachrome Monosorb (Quantachrome Instruments, Boynton Beach, FL). The surface area of the HZSM-5 catalyst was also measured to confirm what was reported by Yathavan.¹¹

2.2. Thermogravimetric Analysis and Kinetic Parameters. DG was purchased from Fisher Scientific (Fair Lawn, NJ, USA) and used as is for all experiments. The thermogravimetric analysis of the DG was conducted using a TA Instruments thermogravimetric analyzer (TGA) Q500 (TA Instruments, New Castle, DE, USA). About 10 mg of DG was mixed with 10 mg of sand, FRM, or HZSM-5. The sample was then loaded into a platinum pan and heated from room temperature to 700 °C under 100 mL/min of nitrogen gas. At the end of the TGA analysis, the remaining solid residue consisted of DG residue + sand, DG residue + FRM, or DG residue + ZSM-5. The kinetic study was conducted for the DG-sand and DG-FRM mixtures. Therefore, four different heating rates (5, 10, 15, and 20 °C/min) were used.

2.3. Catalytic Pyrolysis of DG. The DG pyrolysis setup is shown in Figure 1. It consisted of a stainless steel tubular reactor (210 mm ×

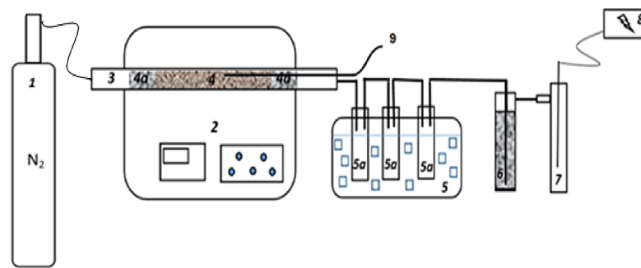


Figure 1. Schematic diagram of the pyrolysis unit: (1) nitrogen source, (2) furnace, (3) tubular reactor, (4) 1:1 ratio of glucose and catalyst/sand mixture, (4a) glass wool, (5) ice bath, (5a) condenser, (6) cotton filter, (7) electrostatic precipitator, (8) AC power source, and (9) thermocouple.

11 mm ID) containing 3 g of DG mixed with 3 g of sand, FRM, or HZSM-5. The mixture was sandwiched between two pieces of glass wool on both ends of the reactor. Ultrahigh-purity nitrogen (99.99%) was used as the sweeping gas at a flow rate of 100 mL/min. The reactor and its content were placed inside an STF 1200 tube furnace (Across International, Livingston, NJ, USA) and heated at a heating rate of 15 °C/min from room temperature to 260 °C (held for 7 to 10 min) for the DG-FRM. The heating rate of 15 °C/min was chosen because it was the highest heating rate that did not cause excessive foaming of the DG. When the reactor was heated at 20 °C/min, the DG foaming during pyrolysis blocked the outlet of the reactor. For the DG-sand and DG-HZSM-5 experiments, a heating rate of 15 °C/min was used from room temperature to 260 °C and then held at that

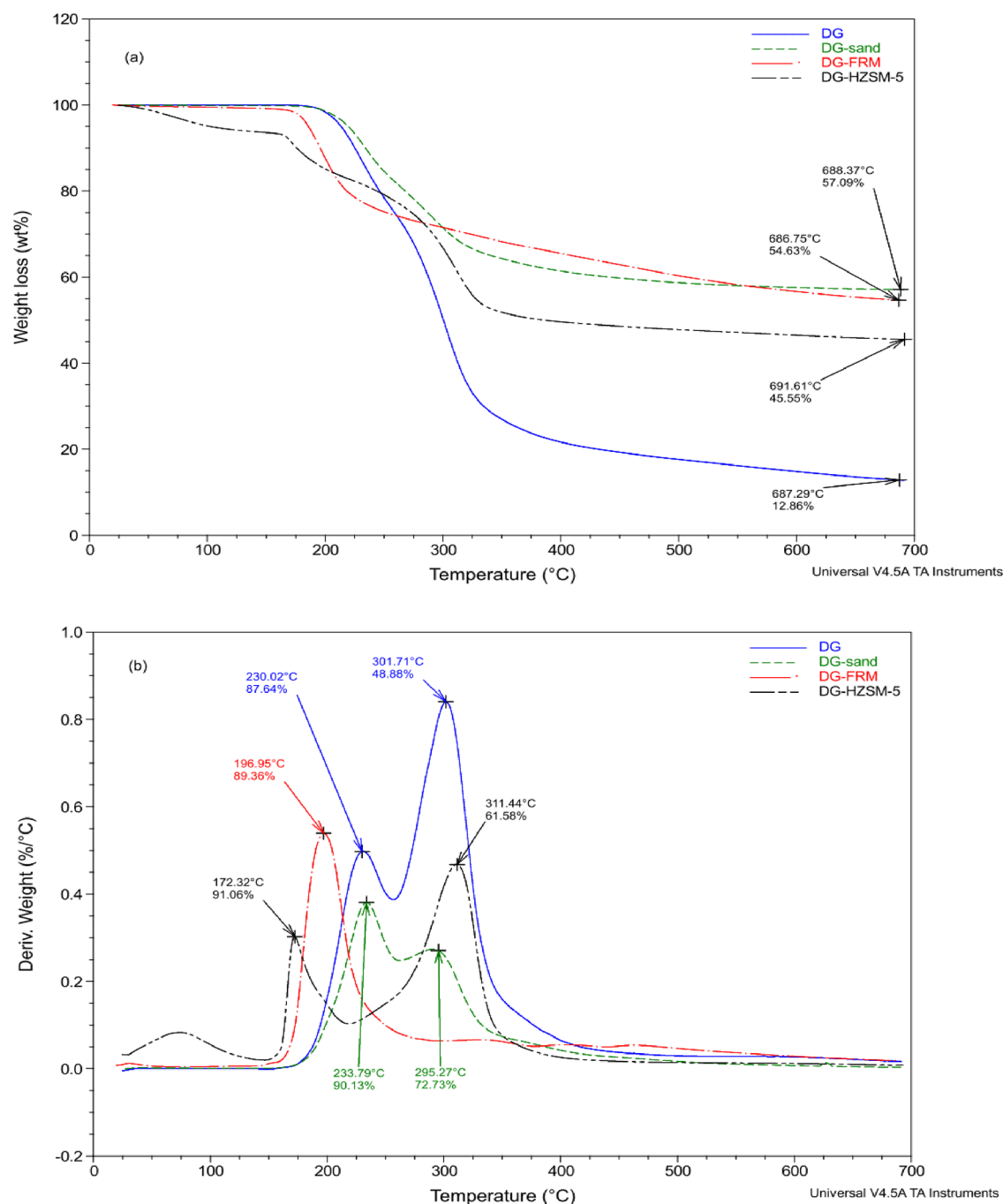


Figure 2. Effect of the FRM, HZSM-5, and sand on the (a) TGA curves and (b) DTG curves of the DG.

temperature for 7 to 10 min. Subsequently, the reactor was heated from 260 to 400 °C and held at that temperature for 7 to 10 min before cooling the reactor to room temperature under a nitrogen gas flow of 100 mL/min. The choice of the reaction temperature at which the biooil samples were collected was based on the TGA thermograms. For example, the DTG peak of the DG-FRM sample started at 150 °C and ended at 260 °C; therefore, the pyrolysis temperature for DG-FRM was set at 260 °C to collect the biooil corresponding to the DTG peak. For the DG-sand pyrolysis, the first biooil sample was collected at 260 °C and the second sample was collected between 260 and 400 °C. When the desired reaction temperature was reached, the sample was maintained at that temperature for 7 min or until the white pyrolysis vapors disappeared (~7 to 10 min).

During each experiment, the pyrolysis vapors were passed through a series of three condensers (glass bottles) placed into an ice bath.

The aerosol particles along with the pyrolysis gases were passed through a cotton filter and then an electrostatic precipitator (ESP) to trap any aerosols formed. The pyrolysis gases were passed through an exhaust tube and then into a fume hood. Most of the biooil was collected in the first condenser. The weights of condenser #2 and #3 as well as the ESP and the cotton filter remained roughly the same. Biooil and pyrolysis gas samples were collected from room temperature to 260 °C for the catalytic pyrolysis and from room temperature to 260 °C and then from 260 to 400 °C for the non-catalytic experiments. As for the pyrolysis gases, they were collected at the desired reaction temperatures using Tedlar Bags Push Lock Valve, 1 liter gas bags (SUPELCO, Bellefonte, PA, USA). To determine the pyrolysis solid yields for the non-catalytic pyrolysis of DG, two experiments were conducted; during the first one, the DG-sand sample was heated from room temperature to 260 °C, and then the reactor was cooled to room temperature. For the second experiment,

a new DG-sand sample was heated from room temperature to 400 °C, and then the reactor was cooled to room temperature. The pyrolysis product yields were calculated by mass balance, and all pyrolysis experiments were replicated. The pyrolysis gas product yield was calculated by difference.

2.4. Biooil Analysis. **2.4.1. Water Content of the Biooil.** The water content of the biooils was measured using a volumetric Karl Fischer titrator, which consisted of a Metrohm 701 KF Titrino (Brinkmann Instruments, Inc., NY, USA) connected to a 703 titration stand. The titration reagent was Hydranal composite-5. About 0.02 to 0.03 g of the biooil samples was injected into the titration pot containing methanol. The injected biooil sample was titrated using the Hydranal composite-5 titration reagent, and the water content was determined as the weight percent of the sample.

2.4.2. Chemical Composition of the Biooil. The chemical composition of the biooil was determined using a Shimadzu GC–MS system (Shimadzu Scientific Inc., Columbia, MD, USA) consisting of a GC-2010 connected to a GC/MS-QP2010S. The GC was equipped with a Phenomenex ZB-5HT Inferno capillary column (30 m × 0.32 mm × 0.25 μm). The carrier gas was high-purity helium (99.99%) at a flow rate of 2 mL/min. The GC injector temperature was set to 250 °C, and the split ratio was 30. The temperature program of the GC oven was set as follows: heated from 40 to 250 °C at 15 °C/min, then ramped at 50 °C/min to 300 °C, and held for 7.5 min. Regarding the mass spectrometer, the ion source was set at 200 °C and the solvent cut time was 1.5 min. The ionization energy was 70.0 eV, and the analysis was performed in EI mode over a scanning range (*m/z*) of 10 to 350 amu. The biooil samples were dissolved in methanol (~0.02 g of biooil/g of methanol) prior to analysis. The injection volume was 3 μL. The individual peaks were integrated, and the corresponding compounds were identified. The reported chemicals had a 75% match or higher, and all peaks that had a lower match percentage were added to the unidentified group. Since all GC–MS samples were prepared in a similar manner, relative quantitation of the biooil compounds was possible. The GC–MS quantitation was based on the biooil organic phase yield, and the results were reported on a water-free basis.

3. RESULTS AND DISCUSSION

3.1. Catalysts. The specific surface areas of the FRM and HZSM-5 were 101 and 121 m²/g, respectively. The pH of the FRM slurry was 9.5. More physicochemical properties of the FRM and HZSM-5 catalysts can be found in the work of Agblevor et al.³⁹ and Yathavan,¹¹ respectively. Briefly, the FRM is an alkaline catalyst with pore size and pore volume of 10 Å and 0.3 cm³/g, respectively, and has an acidity of 0.095 mmol/g.³⁹ The HZSM-5 is an acidic catalyst (acidity: 2.39 mmol/g).¹¹ The pore size and pore volume of the HZSM-5 were not measured for this study. The specific surface area of the HZSM-5 catalyst was 19.8% higher than that of the FRM. The pore size of the FRM catalyst is 10 Å,³⁹ which is significantly higher than what was reported in the literature for ZSM-5 (5–6.36 Å).^{40–42} The kinetic diameter of a DG molecule is about 8.6 Å,^{40,43} which means that it can easily enter the pores of the FRM but not the pores of the HZSM-5. Therefore, the conversion of the DG molecules using FRM should be higher than its conversion using the HZSM-5 catalyst because the DG molecule can be converted on the surface and inside the pores of the FRM, but can only be converted on the surface of the HZSM-5 catalyst, not inside its pores.

3.2. Thermogravimetric Analysis and Kinetic Parameters for DG-FRM. The thermogravimetric analyses of the DG-FRM and DG-HZSM-5 were conducted to study the decomposition behavior of DG in the presence of the FRM catalyst. DG-sand experiments were also performed to determine the non-catalytic parameters of the thermal

degradation of DG. Figure 2 shows the effect of sand, HZSM-5, and FRM on the thermal decomposition of the DG. The pure DG (PDG) sample without heating medium or catalyst produced a thermogram that was similar to those reported in the literature.^{21,44,45} The PDG thermogram had two major decomposition peaks: the first peak (230 °C) corresponded to the dehydration and decarboxylation of the PDG, and the second peak (301.71 °C) corresponded to the further dehydration and decomposition of the PDG.²¹ The solid yield of the PDG experiment was 12.86 wt % at 700 °C. The 50–50% mixture of sand and DG exhibited a similar decomposition pattern as the PDG. The solid yield from the DG-sand mixture (14.18%) was similar to that from the PDG experiment. Furthermore, the DG-sand mixture showed a shift in the DTG first peak to a higher temperature (233.79 °C), whereas the second peak shifted to a lower temperature (295.27 °C). The order of peak intensity of the PDG was reversed when DG was mixed with sand. These changes in the thermograms of the DG-sand sample compared to the PDG sample suggested that the addition of sand affected the decomposition of DG, possibly due to an improved heat transfer from the sand particles to the DG particles. The TGA and DTG curves of the DG-HZSM-5 sample looked similar to what was reported in the literature²¹ but were slightly different from those of sand and PDG. For the DG-HZSM-5, the first peak shifted to a lower temperature (172 °C) compared to the 230 and 233 °C for the PDG and DG-sand, respectively. The second peak of the DG-HZSM-5 was at 311 °C compared to 301 and 296 °C of the PDG and DG-sand, respectively. The weight loss at the first peak was similar for all three samples but at the second peak weight loss was different for the three samples. The PDG lost 51%, the DG-sand lost 28%, while the DG-HZSM-5 lost 38% (Figure 2).

The TGA profile of the DG-FRM mixture was completely different from that of the PDG, the DG-sand, and the DG-HZSM-5 samples. The decomposition curve of the DG-FRM mixture showed one major weight loss centered at 196.95 °C. This temperature was lower than that of the first DTG peak (233.79 °C) from the DG-sand sample. Also, when the FRM catalyst was used, the weight loss at 260 °C was 15% higher than the DG-sand experiment. Therefore, the FRM catalyst promoted the thermal decomposition of the DG at lower reaction temperatures compared to the PDG, DG-sand, and DG-HZSM-5. The solid yield (9.26 wt %) of the DG-FRM run at 700 °C was lower than that of the DG-sand and PDG runs. To perform a visual inspection of the catalytic and non-catalytic pyrolysis solid product, DG-sand and DG-FRM samples were heated to 260 °C using the TGA instrument and then cooled to room temperature. The DG-sand sample was a shiny, brown, solid (Figure 3), whereas the DG-FRM sample was a brown fluffy solid that was not as shiny as the DG-sand residue (Figure 3). Similar residues were observed by Ponder and Richards when they pyrolyzed glucose samples and glucose mixed with additives (NaCl and NaOH).⁴⁶ They reported that the NaOH-treated glucose sample experienced more vigorous boiling when heated.⁴⁶ At 700 °C, the DG-HZSM-5 sample showed greater weight loss than the DG-sand and DG-FRM samples because of the loss of water from the HZSM-5 catalyst itself in addition to weight loss from the glucose decomposition, as shown by the following investigation. To show the origin of the higher weight loss of the DG-HZSM-5 compared to the DG-FRM and DG-sand samples, the TGA/DTG analysis of the fresh HZSM-5,

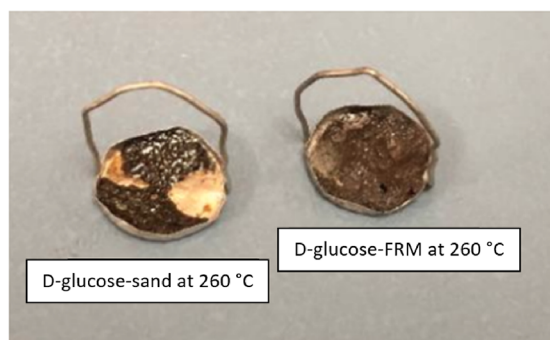


Figure 3. TGA solid residue of the DG-sand (1:1 ratio) and DG-FRM (1:1 ratio) at 260 °C under nitrogen atmosphere.

FRM, and sand was conducted, and the thermograms are shown in Figure S1 (Supporting Information). As the TGA temperature increased from room temperature to 700 °C, the HZSM-5 lost 12.5 wt % of its initial weight, whereas the FRM lost only 1.56 wt %, and the sand did not experience any weight loss. The DTG curve of the HZSM-5 showed one major weight loss peak centered at 99.94 °C, which was due to the physisorbed water on the catalyst.

The calculated solid residues from the DG-sand, DG-FRM, and DG-HZSM-5 at 700 °C were 14.18, 10.81, and 3.6 wt %, respectively. The DG-HZSM-5 had the lowest solid residue yield, which was probably due to further decomposition of the DG sample at high temperatures. Carlson et al. reported that the carbon yield of coke from the pyrolysis of glucose with ZSM-5 decreased with the increasing temperature.²¹

To calculate the pyrolysis kinetic parameters, the thermograms were analyzed using a differential method.^{47–50} This method gives multiple frequency factors at different reaction rates (first-, second-, and third-order reactions) and different conversions. Furthermore, the differential method provides multiple activation energy values as a function of the substrate conversion. The variation of the activation energy as a function of the conversion allows for a more detailed analysis of samples that have multiple weight loss stages. In contrast, the Kissinger method assumes that the substrate thermal decomposition is a first-order reaction and yields a single activation energy and frequency factor value.^{16,17,51} The Kissinger method does not give enough kinetic details about the thermal decomposition of the DG, which is known to have two weight loss stages, each of which requires different activation energies.

The first parameter calculated was the conversion (X), as shown in eq 1:

$$X = \frac{m_0 - m}{m_0 - m_\infty} \quad (1)$$

where m_0 is the initial mass of the sample, m is the mass of the sample at different time points, and m_∞ is the mass of the sample at the end of the experiment.

Once the conversion values were calculated, the conversion rate (dX/dt) was calculated using eq 2:

$$\frac{dX}{dt} = kf(X) \quad (2)$$

where k is the reaction rate constant (s^{-1}) and $f(X)$ is a temperature-independent conversion function. k was calculated using the Arrhenius equation (eq 3):

$$k = A \times \exp\left(\frac{-E}{R \times T}\right) \quad (3)$$

where A , E , R , and T represent the pre-exponential factor (s^{-1}), the apparent activation energy (kJ/mol), the universal gas constant (J/mol.K), and the pyrolysis temperature (K), respectively.

$f(X)$ was expressed by eq 4:

$$f(X) = (1 - X)^n \quad (4)$$

where n is the apparent reaction order.

After substituting eqs 3 and 4 into eq 2 and applying the natural logarithm to it, we get eq 5:

$$\ln\left(\frac{dX}{dt}\right) = \ln[A^*(1 - X)^n] - \frac{E}{R} \times \frac{1}{T} \quad (5)$$

The apparent energy of activation E was calculated (at different fixed conversion values) from the slope of the curve where $\ln(dX/dt)$ was plotted against $1/T$ where the intercept $\ln[A^*(1 - X)^n]$ is constant. The intercept $\ln[A^*(1 - X)^n]$ was used to calculate the pre-exponential factor A at different conversion values and at different reaction orders (0, 1, and 2).

The variation of the apparent activation energies (E) as a function of the conversion (X) for the DG-sand mixture is shown in Table 1. For a conversion range of 5 to 80%, the E values varied between 45.27 and 112.00 kJ/mol, whereas the pre-exponential factor was between $4.98 \times 10^{+01}$ and $4.55 \times 10^{+07} s^{-1}$. The activation energies corresponding to the first and second DTG peaks of the DG-sand mixture were approximately 45.27 and 45.92 kJ/mol, respectively. These values were lower than the activation energies (105.49 and 216.84 kJ/mol) of glucose reported by Cui et al. using the Coats–Redfern method.⁴⁵ Furthermore, our activation energy values were lower than those reported by Gao et al. where the initiation of the first and second weight losses required on average 118.2 and 89.8 kJ/mol, respectively.⁴⁴ The significant difference in the activation energies from our experiments and those reported in the literature was most likely due to the fact that our DG samples were mixed with sand (1:1 ratio), which improved the heat transfer to the DG particles; therefore, less energy was required to initiate the first and second weight

Table 1. Calculated Kinetic Parameters for the Pyrolysis of DG-Sand

conversion (wt %)		5	10	20	30	40	50	60	70	80
E (kJ/mol)		45.27	74.79	63.16	55.53	45.92	86.89	111.61	112	70.28
pre-exponential factor										
n	0	$7.42 \times 10^{+01}$	$1.67 \times 10^{+05}$	$8.15 \times 10^{+03}$	$8.69 \times 10^{+02}$	$4.98 \times 10^{+01}$	$3.42 \times 10^{+05}$	$4.55 \times 10^{+07}$	$2.00 \times 10^{+07}$	$6.40 \times 10^{+02}$
	1	$7.81 \times 10^{+01}$	$1.85 \times 10^{+05}$	$1.02 \times 10^{+04}$	$1.24 \times 10^{+03}$	$8.30 \times 10^{+01}$	$6.84 \times 10^{+05}$	$1.14 \times 10^{+08}$	$6.67 \times 10^{+07}$	$3.20 \times 10^{+02}$
	2	$8.23 \times 10^{+01}$	$2.06 \times 10^{+05}$	$1.27 \times 10^{+04}$	$1.77 \times 10^{+03}$	$1.38 \times 10^{+02}$	$1.37 \times 10^{+06}$	$2.84 \times 10^{+08}$	$2.22 \times 10^{+08}$	$1.60 \times 10^{+04}$

Table 2. Calculated Kinetic Parameters for the Pyrolysis of DG-FRM

conversion (wt %)		5	10	20	30	40	50	60	70	80
E (kJ/mol)		52.17	79.71	87.35	83.79	70.87	50.92	54.98	46.65	45.58
pre-exponential factor										
n	0	$1.05 \times 10^{+03}$	$2.54 \times 10^{+06}$	$1.66 \times 10^{+07}$	$4.75 \times 10^{+06}$	$9.75 \times 10^{+04}$	$1.75 \times 10^{+02}$	$1.03 \times 10^{+02}$	$4.81 \times 10^{+00}$	$1.42 \times 10^{+00}$
	1	$1.11 \times 10^{+03}$	$2.83 \times 10^{+06}$	$2.08 \times 10^{+07}$	$6.79 \times 10^{+06}$	$1.63 \times 10^{+05}$	$3.50 \times 10^{+02}$	$2.58 \times 10^{+02}$	$1.60 \times 10^{+01}$	$7.10 \times 10^{+00}$
	2	$1.16 \times 10^{+03}$	$3.14 \times 10^{+06}$	$2.60 \times 10^{+07}$	$9.69 \times 10^{+06}$	$2.71 \times 10^{+05}$	$7.00 \times 10^{+02}$	$6.45 \times 10^{+02}$	$5.35 \times 10^{+01}$	$3.55 \times 10^{+01}$

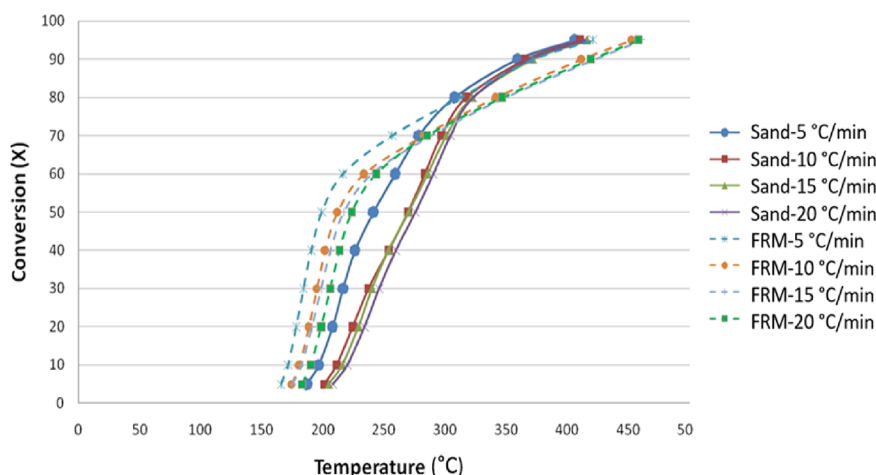


Figure 4. Conversion variation as a function of the reaction temperature for different heating rates.

losses. It is also important to mention that the two methods have different assumptions and use different equations, which could have contributed to the significant difference in the results. The effect of sand on the weight loss of DG can be seen in Figure 2. When the TGA temperature reached 260 °C, the DG-sand sample lost about 35% of the DG initial weight, whereas the PDG sample lost only 25% of the DG initial weight. Clearly, the presence of sand improved the conversion of DG due to the improved heat transfer from the sand particles into the DG particles. However, when the reaction temperature reached 370 °C, both the DG-sand and PDG samples lost about 80% each, which can be seen by the parallel slopes of both curves between 370 and 700 °C.

The evolution of the apparent activation energy and pre-exponential factor of the decomposition of the DG-FRM sample is shown in Table 2. For conversion between 5 and 80%, the apparent activation energies of DG in the presence of FRM were between 45.58 and 87.35 kJ/mol. The pre-exponential factor range was between $1.42 \times 10^{+07}$ and $1.66 \times 10^{+07} \text{ s}^{-1}$. Compared to sand, the use of FRM reduced the overall activation energy required to convert the DG. Additionally, at 260 °C, the DG-FRM sample lost 50% of the DG initial weight compared to 35% loss using sand, which further proved that the use of the FRM catalyst promoted the conversion of the DG at temperatures below 300 °C. The activation energy values for the DG-FRM sample were significantly lower than what was reported in the literature for glucose conversion using different catalysts. For instance, Cheng et al. reported that the use of HZSM-5 significantly lowered the activation energy of glucose conversion to FF.²² They used the density functional theory to calculate the activation energy of the glucose conversion to FF and to benzene over HZSM-5. The activation energy ranged from 7.78 to 147.61 kJ/mol (1.86 to 35.28 kcal/mol).

At conversion below 40%, the pre-exponential factor at different reaction orders for the DG-sand samples was lower than that of the FRM-DG samples. This could be explained by the fact that the decomposition of the DG took place at higher temperatures in the presence of sand than it did in the presence of FRM. Therefore, the number of volatile molecules at conversion below 40% was smaller for the DG-sand run, which meant that there were fewer molecules per unit volume; hence, the probability of those molecules colliding and reacting was lower than the case of DG-FRM samples. In contrast, the higher conversion of the DG in the presence of the FRM at conversion below 40% meant that there were more volatile molecules available to react. Therefore, the pre-exponential factor of the DG-FRM experiments was higher than that of the DG-sand experiments. The conversion variation as a function of the reaction temperature for the DG-sand and DG-FRM is shown in Figure 4. At temperatures below 300 °C, the conversion of DG in the presence of the catalyst was higher than that of the non-catalytic experiments, which further confirms that the FRM facilitated the thermal decomposition of the DG compared to sand.

3.3. Pyrolysis of DG-Sand: Effect of the Reaction Temperature on the Pyrolysis Product Distribution. To understand the chemistry behind the DG-FRM thermogram (Figure 2), the composition of the volatile matter was investigated by collecting biooil and pyrolysis gas samples at different temperatures during the pyrolysis experiments. The pyrolysis product distribution is shown in Figure 5. The pyrolysis gas product composition can be found in Table S1 of the Supporting Information. At a low temperature (260 °C), the major product of the DG-sand pyrolysis was a black/dark brown solid residue (64.5 wt %). The total liquid and pyrolysis gas yields were 20.4 and 15.1 wt %, respectively. The relatively higher solid yield obtained from the DG-sand pyrolysis at 260 °C was most likely due to the slow heating rate that promoted

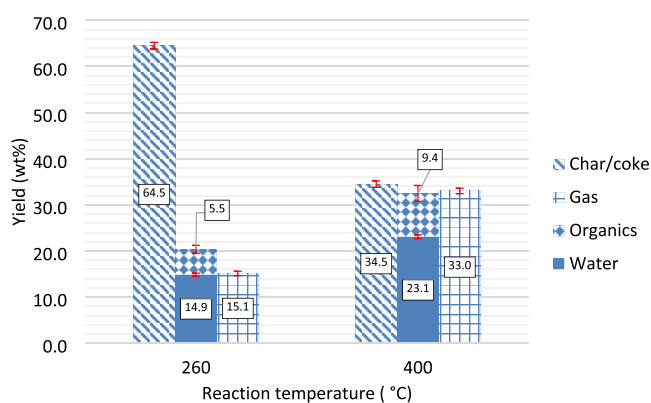


Figure 5. Pyrolysis product distribution for the DG-sand mixture at 260 and 400 °C (*: gas yield calculated by difference).

the dehydration of DG and promoted the solid formation as the reaction temperature increased from room temperature to 260 °C. Paine et al. explained the char formation during glucose pyrolysis as a result of pyrosynthetic condensation that was initiated at lower pyrolysis temperatures at or adjacent to the reactive carbonyl carbon (C-1) of the acyclic glucose.⁵²

The water content of the pyrolysis liquid was 75.6 wt %, and CO₂ accounted for 86.2 wt % of the total pyrolysis gas produced. The water and the CO₂ were probably due to the decomposition of DG and the primary pyrolysis products (anhydrous sugars). The production of water and CO₂ during the first DTG peak of DG was in agreement with the literature.²¹ Furthermore, the slow heating rate allowed for extensive dehydration of the DG in the reactor,⁵³ which explains the high water content of the pyrolysis liquid.

As the reaction temperature increased to 400 °C, the DG-sand pyrolysis solid product yield decreased by 46.5%, whereas the liquid and pyrolysis gas yields increased by 59.3 and 118.5%, respectively. The water content of the biooil increased by 55.0%, and the major pyrolysis gas products were CO₂ and CO (86.2 and 29.72 mol %, respectively). The deoxygenation reactions were favored in the following order: dehydration > decarboxylation > decarbonylation. The decrease in solid content and increase in the liquid and gas products as the reaction temperature increased were expected. In fact, at low reaction temperatures, the acyclic DG can undergo pyrosynthetic condensation, which results in the formation of char via aldol condensation reactions initiated by the reactive carbonyl group (C-1) of the acyclic DG molecule.⁵² The terminus of the DG chains would be dangling from the char surface. These dangling DG ends on the char can persist to higher reaction temperatures compared to the acyclic DG itself. The decrease in the solid yield and increase in the gas yield as the reaction temperature increased from 260 to 400 °C could be explained by the cracking of those dangling ends to produce low-molecular-weight liquid oxygenates and non-condensable gases. Therefore, the second peak of the DG-sand DTG curve was attributed to char/solid residue decomposition.

When comparing the pyrolysis solid yields to the solid yields calculated from the TGA curves, it was clear that the solid yields from the TGA at 260 and 400 °C (69.6 and 39.1 wt %, respectively) were higher than those from the fixed-bed reactor pyrolysis experiments for the DG-sand (64.5 wt % at 260 °C and 34.5 wt % at 400 °C). This difference was probably due to the fact that during the fixed-bed reactor pyrolysis experiments, the reactor temperature was held at 260 °C and at 400 °C for 7

to 10 min in order to collect enough liquid products at each reaction temperature. Consequently, the sample in the reactor underwent further decomposition; hence, the solid yields from the fixed-bed reactor pyrolysis experiments were lower than those calculated from the TGA curve.

3.4. Catalytic Pyrolysis of DG: Effect of the Catalyst on the Pyrolysis Product Distribution. The catalytic pyrolysis product distribution is shown in Figure 3. The pyrolysis gas product composition can be found in Table S2 of the Supporting Information. HZSM-5 was used for comparison. At 260 °C, the solid, total liquids, and pyrolysis gas yields of the DG-FRM experiment were 50.5, 22.5, and 27.0 wt %, respectively. In contrast to the DG-sand pyrolysis, the catalytic pyrolysis solid product decreased by 21.7%, while the total liquids and pyrolysis gas yields increased by 10.3 and 78.8%, respectively. These results indicated that the FRM catalyst promoted both the decomposition of the DG into liquid products and the cracking of the organic vapors into pyrolysis gas. These results corroborated the finding from the TGA analysis where the FRM promoted the decomposition of the DG at a low temperature compared to sand. The water content of the catalytic biooil was 80.3 wt % of the total liquid product, which was about 21% higher than the non-catalytic pyrolysis at 260 °C. The increase in water content in the pyrolysis liquid product could be due to the relatively high sodium content of the FRM.³⁹ In fact, the addition of alkali metal such as sodium to glucose can increase the dehydration rate by a factor of $10 \times 10^{+08}$.⁵⁴ The sodium in red mud comes from NaOH, which is a chemical used during the Bayer process to extract aluminum from its bauxite. The excess NaOH from the bauxite treatment ends up in the red mud slurry. The latter is discarded into evaporation ponds, where the water evaporates, leaving behind a NaOH-rich solid residue known as red mud.

The pyrolysis gas product from the DG-FRM at 260 °C consisted mainly of CO₂, which increased by more than 11-fold (mol % basis) compared to the DG-sand experiment. The formaldehyde content increased by more than 151-fold (mol % basis) compared to the DG-sand pyrolysis. During the DG-FRM pyrolysis, the content of C₁, C₂, and C₃ gaseous compounds increased by more than 13-fold (mol % basis) compared to the DG-sand pyrolysis. These results indicated that at 260 °C, the FRM promoted the formation of C₁–C₃ gaseous compounds. The effect of the FRM on the DG was expected since the former is known to promote dehydration, decarboxylation, and decarbonylation of lignocellulosic biomass and its primary pyrolysis vapors to produce liquid and gas products.^{28,29,55}

The presence of basic additives, such as NaHCO₃ and CH₃COONa, during the pyrolysis of glucose has been reported to promote the nonselective cleavage of carbon–carbon bonds in the glucose, which would promote the formation of low-molecular-weight compounds.⁵⁶ Furthermore, Ponder and Richards reported that the addition of NaOH as the catalyst during the pyrolysis of glucose resulted in an increase of C₁–C₃ compounds at the expense of anhydrous sugars and furan derivatives.⁴⁶ Since the FRM is an alkaline material (pH 9.5) and it has relatively high sodium content, it promoted the carbon–carbon bond breakage of the DG and promoted the formation of liquid and gaseous low-molecular-weight compounds. In addition to the catalytic activity of NaOH, transition metal oxides such as Fe₂O₃ and TiO₂ contributed to the reactivity of the FRM. In fact, the highly reactive oxygen in these two metal oxides was reported

to promote the cleavage of the C–C bond, which promoted the formation of low-molecular-weight compounds and non-condensable gases.^{57,58} Furthermore, alumina can promote the cracking of larger molecules,⁵⁹ which would result in the formation of lower-molecular-weight compounds as well as pyrolysis gases.

The yields from the DG-HZSM-5 pyrolysis are shown in Figure 6 and Table S2. The solid yield was comparable to that

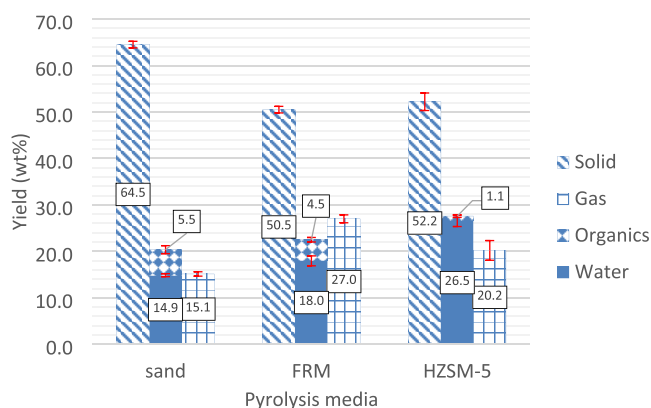


Figure 6. Catalytic pyrolysis product distribution for the DG-FRM, DG-sand, and DG-HZSM-5 at 260 °C (*: gas yield calculated by difference).

of the DG-FRM pyrolysis, whereas the gas yield from the HZSM-5 experiment was 25.9% lower than that of the FRM. The HZSM-5 resulted in the production of more water (47.2% increase) and less organics (75.6% decrease) compared to the FRM. The pyrolysis gas product from the DG-HZSM-5 experiment consisted mainly of CO₂ (85.54%) and CO (11.23%), whereas the formaldehyde content was very low (0.15%). The FRM catalyst was more effective than the HZSM-5 since the former produced less solid and more organic liquid and gas than the latter. This difference in pyrolysis product distribution between the FRM and HZSM-5 was an indication that the two catalysts have different catalytic pathways. While the HZSM-5 is a well-studied acidic catalyst, limited literature is available about the FRM and its catalytic pathways. Another indication of difference in catalytic pathways is the CO/CO₂ ratio. The HZSM-5 had a higher CO/CO₂ ratio (0.53) compared to the FRM (0.14). The difference in the catalytic pathways between the FRM and HZSM-5 could be due to the difference in acidity and pore size. The HZSM-5 catalyst used in this study has a surface area of 121 m²/g and an acidity of 2.390 mmol/g,¹¹ whereas the FRM is an alkaline catalyst (pH 9.5) that has a surface area of 101 m²/g and an acidity of 0.095 mmol/g.³⁹

The comparison of the solid yields from the pyrolysis experiments at 260 °C to those calculated from the TGA curves for sand, FRM, and HZSM-5 at 260 °C indicated a similar trend. The TGA solid yields followed the order sand > HZSM-5 > FRM, which was similar to the pyrolysis result trend. However, the pyrolysis solid yield values were lower than those obtained from the TGA curves. The solid yields calculated from the TGA curves for DG-sand, DG-FRM, and DG-HZSM-5 were 69.6, 55.7, and 57.8 wt %, respectively, compared to the pyrolysis experiment yields of 64.5, 50.5, and 52.2 wt %, respectively. These differences were probably because during pyrolysis, the DG-sand, DG-FRM, and DG-HZSM-5 were held at 260 °C for 7 to 10 min in order to

collect enough liquid products in the condensers. It is worth mentioning that as the TGA temperature increased to 700 °C, the solid yield trend for sand, FRM, and HZSM-5 changed to the following order: sand > FRM > HZSM-5.

3.5. Catalytic Pyrolysis of DG: Effect of the DG-to-FRM Ratio on the Pyrolysis Product Distribution. The pyrolysis product distribution from the DG-FRM pyrolysis at 260 °C using different DG-to-FRM ratios is shown in Figure 7.

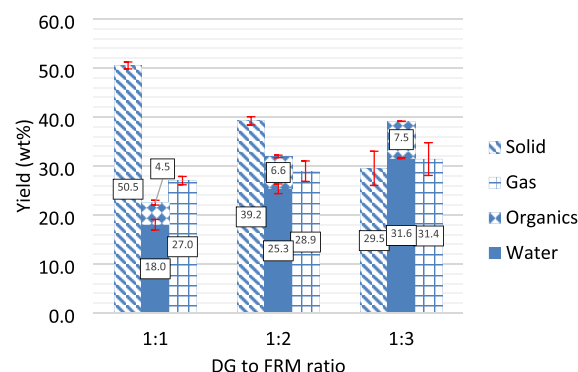


Figure 7. Effect of the DG-to-FRM ratio on the catalytic pyrolysis product distribution at 260 °C.

The pyrolysis gas product composition can be found in Table S3 of the Supporting Information. A decreasing DG-to-FRM ratio from 1:1 to 1:3 resulted in a decrease in the solid yield from 50.5 to 29.5 wt %, respectively. All other pyrolysis products increased as the ratio decreased from 1:1 to 1:3. This was probably due to the increased surface area/catalytic sites available to vapors, which resulted in further cracking via dehydration, decarboxylation, and decarbonylation. The pyrolysis gas product of the DG-FRM pyrolysis at different DG-to-FRM ratios is shown in Table S3. As the ratio decreased from 1:1 to 1:3, the CO and CO₂ content increased by 75.1 and 25.0% (mol % basis), respectively, which confirmed that the FRM promoted the decarbonylation and decarboxylation reactions. The C₁, C₂, and C₃ gaseous compounds increased, whereas the C₄ hydrocarbons decreased with the decreasing ratio of DG to FRM. The formaldehyde content decreased as the DG:FRM ratio decreased, whereas the acetaldehyde content increased. The CO/CO₂ ratio increased as the DG-to-FRM ratio decreased and was always less than one, which means that the FRM promotes the decarboxylation more than the decarbonylation reaction.

3.6. Analysis of the Biooils. During the GC/MS analysis, the samples were heated to 300 °C and held at that temperature for about 7.5 min. To estimate the nonvolatile fraction content in the catalytic and non-catalytic biooils collected at 260 °C, the samples were analyzed using TGA (Figure S3a,b in the Supporting Information). At 300 °C, the solid residues of the DG-sand, DG-FRM, and DG-HZSM-5 biooils were 5.67, 3.68, and 0.52 wt %, respectively. Consequently, more than 94 wt % of the catalytic and non-catalytic biooils consisted of volatile GC-detectable compounds. It is worth mentioning that the DTG peaks in Figure S3a (Supporting Information) were due mostly to water evaporation. However, the peaks were centered around different temperatures, which suggested that the chemical composition of the catalytic and non-catalytic biooils was different.

3.6.1. Effect of the Reaction Temperature on the Chemical Composition of the DG-Sand Pyrolysis. The composition of the volatile fraction of the DG-sand biooil (organic fraction) at 260 and 400 °C is shown in Figures 8 and

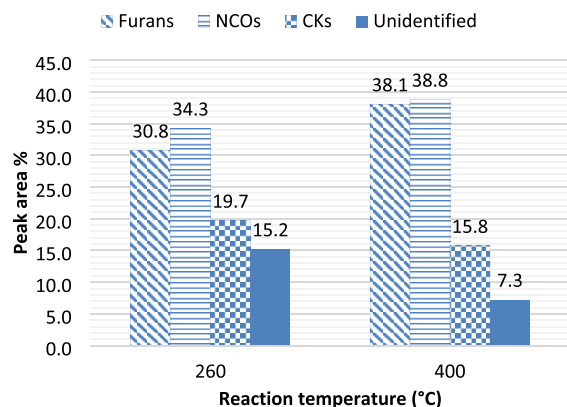


Figure 8. Major chemical groups in the DG-sand pyrolysis liquid at 260 and 400 °C.

9. In total, 13 chemical compounds were identified in the organic phase of the DG-sand biooil sample produced at 260 °C (Figure 9a). It consisted of a mixture of three main groups of compounds: (1) noncyclic oxygenates (NCOs), mainly formic acid (FA) and acetic acid (AA), (2) furans such as FF and 2-furanmethanol (2-FM), and (3) cyclic ketones (CKs) such as levoglucosenone (LGO), butyrolactone, and 4H-pyran-4-one,2,3-dihydro-3,5-dihydroxy-6-methyl- (4HPDD). The NCOs were the major chemical group at 34.3%, followed by furans at 30.8%, and finally the CKs accounted for 19.7%. The composition of the non-catalytic biooil at a low temperature (260 °C) was different from what has been reported by Gao et al.⁴⁴ They reported that the main product of the glucose fast pyrolysis at 300 °C was levoglucosan (about 55%). In our case, the main chemicals present in the organic phase were FA (18.3%), FF (20.2%), and 4HPDD (14.0%). No levoglucosan (LGA) was present in the biooil, and only 1.1% of levoglucosenone was detected. This could be due to the longer residence time (~6.13 s on average) of the pyrolysis vapors in the reactor, which resulted in further dehydration of levoglucosan into levoglucosenone and the formation of the more-stable furans as well as the NCOs. It is worth noting that 4HPDD and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (2,5-DHF) are two common products of the caramelization reaction of glucose.⁶⁰ These two 6-carbon compounds were formed by dehydration and rearrangement of the acyclic glucose during the DG-sand experiment.

When the reaction temperature of the DG-sand experiment increased to 400 °C, a total of 16 chemical compounds were detected (Figure 9b). Both the furan and NCO contents increased by 23.7 and 13.3%, respectively, whereas the CK content decreased by 19.8%. The increase in the NCO content was a result of further thermal cracking of DG promoted by the higher reaction temperature. In fact, the increase in the NCO content was most likely due to the Grob fragmentation of the C₃, C₄, and C₅ chains dangling from the char surface. Those dangling termini on the surface of the char can persist into a higher temperature domain than the acyclic glucose itself; hence, their thermal cracking produced some of the NCOs and non-condensable gases. Paine et al. reported that although half of the FA comes from C-1, all carbons of the glucose molecule

contributed to the formation of FA with C-5 being the lowest contributor.⁵² As for the AA formation, most carbons of the DG contributed to its formation with C-1 and C-2 being the major contributors (48%).⁵²

The increase in the furan content was most likely due to the dehydration of anhydrous sugars.^{21,61} Furthermore, the pyrolysis solid product observed at 260 °C most likely consisted of unreacted DG and polyfurfuryl alcohol (PFA) resin. The latter is readily formed from furfuryl alcohol in the presence of an acidic catalyst or in an acidic environment.⁶² Since acetic acid and formic acid accounted for about 27.4% of the organic phase of the biooil, they could have promoted the formation of such resin. PFA would eventually start to break down as the reaction temperature increases to give rise to furanic compounds. Guigo et al. reported that at 350 °C, the scission of the PFA resin resulted in the production of furanic compounds without ring opening.⁶³

The decrease in the CKs with the increasing temperature was probably due to the decomposition of the caramelization products (4HPDD and 2,5-DHF accounting for 17.6% of the CKs) due to the higher reaction temperature.

It is worth mentioning that 2-(2-ethoxy-1-methoxyethyl)-furan (2-EMF), a compound that has 9 carbon atoms, was detected in the DG-sand pyrolysis liquid at 260 and 400 °C. Such a product was not reported in the literature.^{21,44,46,61} This compound was believed to originate from FF via the mechanism described by Ren et al.⁶⁴ Briefly, β -methoxy-(S)-2-furanethanol is formed by the breakage of the C=O bond of FF and its rearrangement.⁶⁴ Then, it underwent further reactions to produce 2-EMF. To prove such hypothesis, the pyrolysis of FF using sand was conducted at 260 °C. The chemical composition of the organic phase is shown in Table 3. The major chemical compound detected in the pyrolysis liquid was 2-EMF (77.6%). Other compounds detected included acetol (13.3%), 5-MF (5%), acetylfuran (1.4%), and 2-butenedioic acid, 2-methyl-, (E) (1.1%).

3.6.2. Effect of the Catalyst on the Chemical Composition of the DG Pyrolysis. The composition of the DG-FRM as well as the DG-HZSM-5 biooils at 260 °C is shown in Figures 10 and 11 and Figure S2 (Supporting Information). The FRM results were displayed alongside the DG-sand and DG-HZSM-5 liquid composition for comparison. Compared to the DG-sand pyrolysis liquid, the DG-FRM had more NCOs (111.5% increase) and less furans (30.3% decrease). In the DG-FRM pyrolysis liquid, the CK content decreased by more than 10-fold. The increase in the NCOs was attributed to the basicity of the FRM catalyst, which promoted the cleavage of the carbon–carbon chains of the DG.^{46,56,65} The decrease in furans in the catalytic liquid product was probably due to the scarcity of the C₄, C₅, and C₆ fragments in the liquid. The significant decrease in the CK content in the catalytic pyrolysis liquid was due to the absence of the caramelization products 4HPDD and 2,5-DHF. This is because the FRM catalyst reduced the energy barrier for dehydration and carbon–carbon bond breakage, which resulted in the predominance of the C₁, C₂, and C₃ compounds at the expense of the higher-molecular-weight ones such as furans and CKs. In fact, Ponder and Richards reported that the fast pyrolysis of glucose for 30 min at 270 °C in the presence of basic additives promoted the C₁–C₃ products and suppressed the production of furans and anhydrosugars.⁴⁶ One of the additives they used was NaOH, which promoted the formation of low-molecular-weight oxygenates such as glycolaldehyde, acetol, acetic acid, and

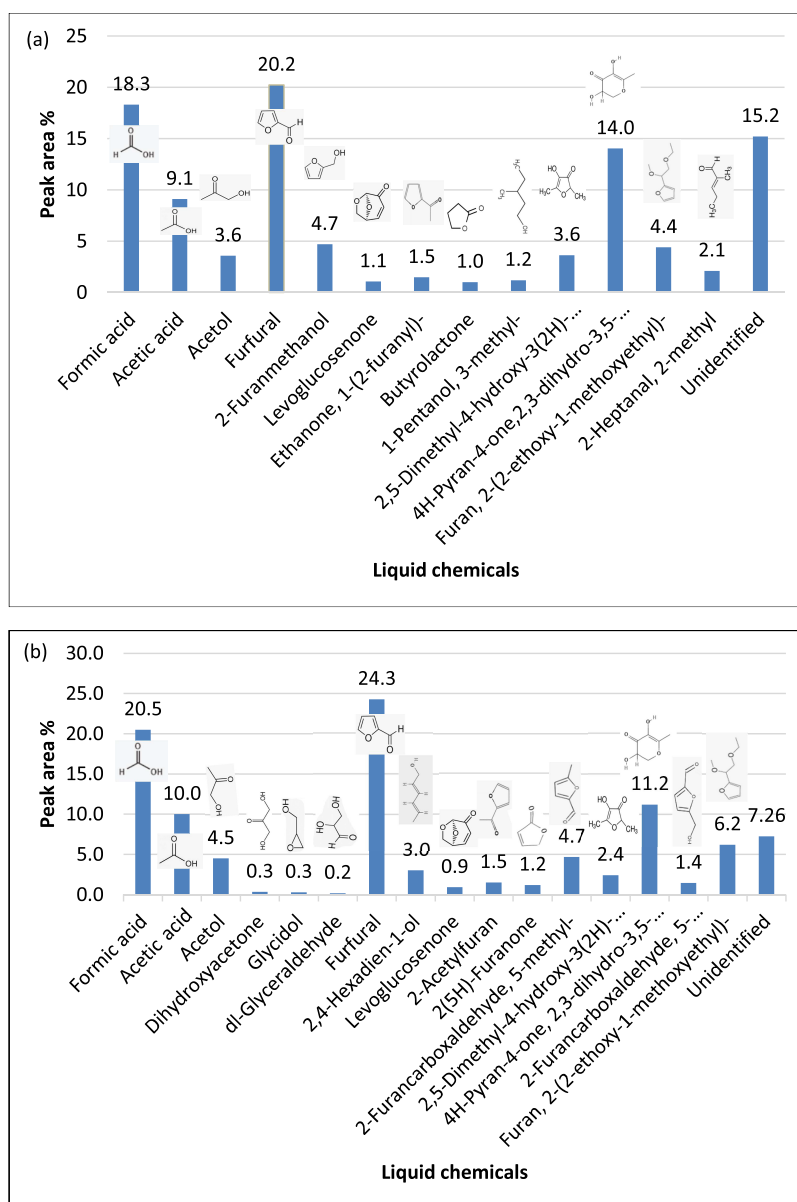


Figure 9. Chemical composition (GC-MS) of the DG-sand biooil collected at (a) 260 °C and (b) 400 °C.

Table 3. Chemical Composition of the Liquid Phase from the Furfural-Sand Pyrolysis at 260 °C

chemical compound	peak area %
acetol	13.3
2-butenedioic acid, 2-methyl-, (E)	1.1
ethanone, 1-(2-furanyl)	1.4
2-(2-ethoxy-1-methoxyethyl)furan	77.6
2-furancarboxaldehyde, 5-methyl	5.0
unidentified	1.5

formic acid at the expense of FF, 5-HMF, and anhydrosugars. The FRM has a relatively high content of NaOH and the pH of the FRM water slurry was 9.5, which confirms the basicity of the FRM catalyst.

Additionally, Houminer et al. studied the effect of basic additives on the pyrolysis of glucose.⁵⁶ They reported that the basic additives resulted in a nonselective and easier breakage of the glucose carbon-carbon bonds, which would promote the

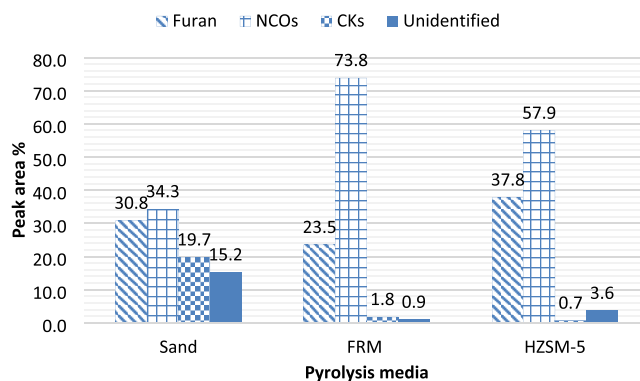


Figure 10. Major chemical groups in the DG-sand, DG-FRM, and DG-HZSM-5 pyrolysis liquids at 260 °C.

formation of the NCOs at the expense of the furanic compounds during the DG-FRM pyrolysis reaction. In contrast, the same authors reported that when glucose was

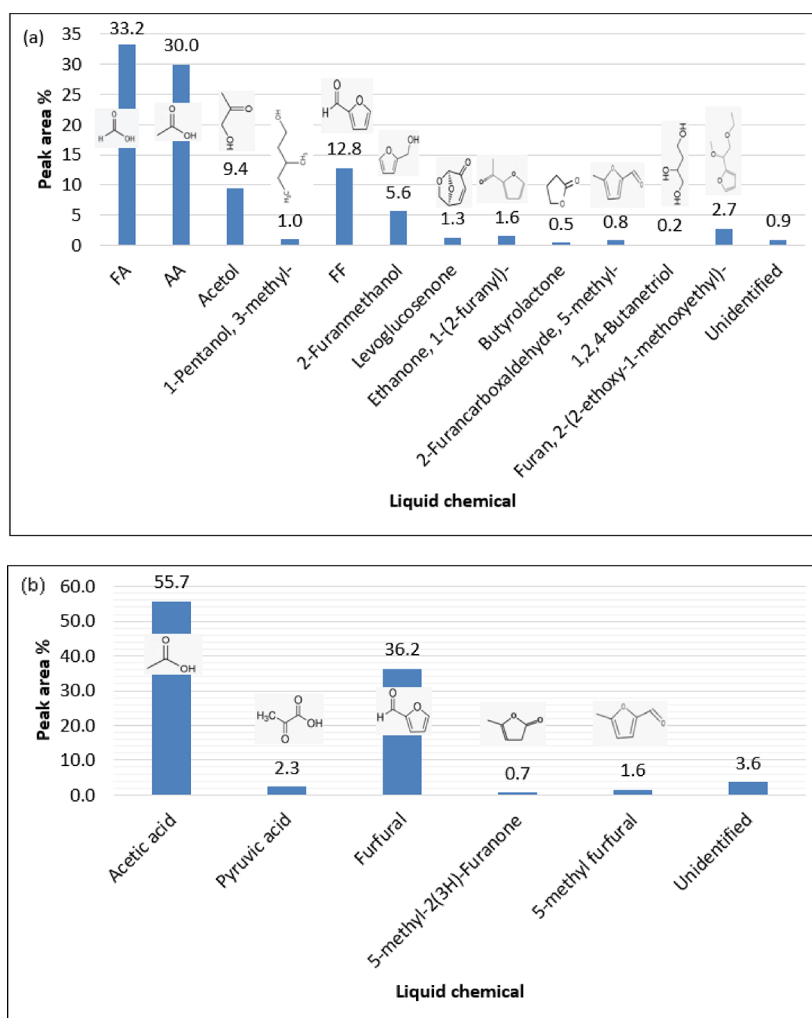


Figure 11. Chemical composition (GC–MS) of the (a) DG-FRM and (b) DG-HZSM-5 biooil collected at 260 °C.

pyrolyzed at 160 and 260 °C in the presence of an acidic additive (NaHSO_4), the latter inhibited the fragmentation reaction. Kroh reported that unlike the basic additives that tend to promote fragmentation, acidic additives/conditions promoted the dehydration and cyclization reactions.⁶⁵ These results would explain the lower NCO content and higher furan content of the DG-HZSM-5 liquid compared to the DG-FRM one (Figure 10). Carlson et al. reported that at low reaction temperatures (<300 °C), the main pyrolysis products were C_2 and C_3 compounds and the addition of HZSM-5 to the glucose lowered the temperature at which those low-molecular-weight compounds were produced.²¹ However, the presence of furans, especially FF, was not observed in their studies. This could be due to two factors: the properties of HZSM-5 used and/or the residence time of the vapors in the reactor.

Another factor that might have contributed to the difference in the HZSM-5 and FRM catalytic biooil composition was the catalyst pore size. As mentioned earlier (Section 3.1), the pore size of the FRM (~10 Å) was significantly bigger than what was reported in the literature for ZSM-5 (5–6.36 Å); therefore, the DG molecules (kinetic diameter ~8.6 Å) can access the FRM pores and undergo further reaction inside those pores. This could lead to further cracking of the primary pyrolysis vapors and the production of low-molecular-weight compounds. In contrast, the DG cannot access the pores of the

HZSM-5 catalyst, unless it was cracked on the surface of the catalyst first, and then the fragments with a kinetic diameter that is less than 5 Å can enter the HZSM-5 pores and undergo further cracking and/or react with other fragments present in those pores. Furthermore, the difference in acidity between the FRM and HZSM-5 catalysts was believed to be a contributor to the difference in their catalytic activity. In fact, Paasikallio et al.⁶⁶ used the same batch of zeolite catalysts that was used in our study. They reported that the HZSM-5 (from BASF) had three types of acid sites: weak (LT), medium (MT), and strong (HT) acid sites. The abundance of the LT, MT, and HT in the ZSM-5 was about 0.3–0.4, 0.9–1, and 1–1.1 mmol/g, respectively.⁶⁶ In contrast, the fresh FRM had an acidity of 0.095 mmol/g, which was significantly lower than that of the HZSM-5 catalyst. Acidic catalysts were reported to promote dehydration and cyclization reactions,⁶⁵ which would explain the higher water and furan content in the HZSM-5 catalytic biooil compared to that of the FRM catalytic one. Furthermore, the FRM had a basicity of 0.015 mmol/g. Basic catalysts were reported to promote the carbon–carbon bond breakage^{46,65} and hinder the formation of furans and anhydrous sugars.⁴⁶

It is worth mentioning that the FRM catalyst promoted the formation of acids (63.2%; Figure 11a) compared to the non-catalytic pyrolysis (27.4%; Figure 9a) of DG. In contrast, the

red mud-catalyzed pyrolysis of pinyon–juniper wood¹¹ reduced the carboxylic acid content in the biooil compared to the non-catalytic pyrolysis. This difference in biooil composition between the DG catalytic biooil and the pinyon–juniper catalytic biooil suggested that (1) glucose was most likely not an intermediate product during the red mud-catalyzed pyrolysis of pinyon–juniper biomass and/or (2) the acid compounds from the catalytic cracking of glucose in pinyon–juniper may have reacted with other compounds in the pyrolysis vapors. The differences in biooil composition from the FRM-catalyzed pyrolysis of DG and that of the pinyon–juniper biomass were due to the complexity of the latter. In fact, the pinyon–juniper biomass contains glucose molecules that are in a polymer form (cellulose) and in a heteropolymer form (hemicellulose). Therefore, the study of the FRM-catalyzed pyrolysis of the glucose polymer and heteropolymer is needed to understand the influence of the $\beta(1 \rightarrow 4)$ glycosidic bonds in cellulose as well as the heteroenvironment of the DG molecule in hemicellulose on the biooil composition. Our next paper will investigate the FRM-catalyzed pyrolysis of cellulose, and the third paper will report on the FRM catalytic pyrolysis of hemicellulose.

3.6.3. Effect of the DG-to-FRM Ratio on the Chemical Composition of the DG Pyrolysis. To understand the effect of the FRM catalyst on the DG pyrolysis, the DG-FRM pyrolysis was conducted at 260 °C using different DG-to-FRM ratios (DG:FRM = 1:1, 1:2, and 1:3). The total mass of DG + FRM was kept at 6 g to avoid the interference of the heat transfer effect. Therefore, the 1:1, 1:2, and 1:3 ratios meant 3 g DG + 3 g FRM, 2 g DG + 4 g FRM, and 1.5 g DG + 4.5 g FRM, respectively. The chemical composition of the pyrolysis liquid for the different DG-to-FRM ratios is shown in Figure 12. The

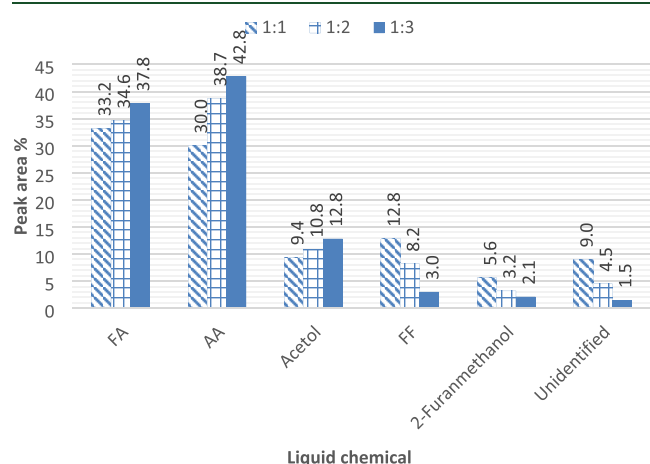


Figure 12. Effect of the DG-to-FRM ratio on the chemical composition of the DG pyrolysis liquid at 260 °C.

focus was on five compounds, i.e., FA, AA, acetol, FF, and 2-FM, which accounted for more than 90% of the pyrolysis liquid organic phase. As expected, higher FRM content resulted in an increase in the NCOs (FA, AA, and acetol) and hindered the production of furans (FF and 2-FM). This further confirmed that the FRM promoted the carbon–carbon bond cleavage to produce NCOs and hindered the formation of furans. Interestingly, the selectivity to AA exhibited the largest increase (42.7% increase) compared to only 13.9% increase of the FA selectivity. The FF and 2-MF content decreased by 76.6 and 62.5%, respectively.

4. CONCLUSIONS

The addition of FRM to DG produced a thermogram that was different from all thermograms reported in the literature. The FRM reduced the activation energy needed to convert the DG to degradation products. Compared to sand and HZSM-5, the use of FRM for the catalytic pyrolysis of DG resulted in a lower solid residue yield and a higher gas yield. These findings indicated that the catalytic pathways of the FRM were different from those of the sand and HZSM-5. The major compounds produced during the FRM-catalyzed pyrolysis of DG were low-molecular-weight oxygenates (NCOs), CO₂, and CO.

The single DTG peak observed during the pyrolysis of DG-FRM was due to the decomposition of DG into C₁–C₃ liquid and gaseous compounds. Consequently, less C₄–C₆ fragments were present to undergo pyrosynthetic condensation to form char/solid residue. The FRM was able to break down the DG at low reaction temperatures compared to the more expansive HZSM-5 catalyst. Compared to the HZSM-5, the effectiveness of the FRM (in addition to the fact that 60 wt % of it is a waste material) made it a more attractive catalyst for the catalytic pyrolysis of lignocellulosic biomass. This is because the use of the FRM catalyst would lower the overall cost of biooil production by lowering the catalyst preparation cost.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c04325>.

Thermogravimetric (TGA and DTG) analysis of the sand, FRM, and HZSM-5 in Figure S1, typical chromatograms from the GC/MS analysis of the DG catalytic biooils in Figure S2, pyrolysis gas product composition for the non-catalytic and catalytic pyrolysis of DG in Tables S1–S3, and thermogravimetric (TGA and DTG) analysis of the catalytic and non-catalytic biooils in Figure S3 (PDF)

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Notes

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