Kinetic study and catalytic pyrolysis of D-glucose using Formulated red mud catalyst

Hamza Abdellaoui[a], Foster A. Agblevor[a]

a: Utah State University (Logan, UT, USA)

Abstract

Pyrolysis and catalytic pyrolysis of D-(+)-Glucose (DG) was conducted using a thermogravimetric analyzer and formulated red mud (FRM) as catalyst to determine the kinetic parameters of DG decomposition in the presence of the catalyst. Compared to sand, the FRM altered the thermal decomposition profile of the DG and promoted its decomposition at lower reaction temperature. The activation energy of the DG-FRM experiment ranged between 45.58 kJ/mol and 87.35 kJ/mol compared to 45.27 kJ/mol and 112.00 kJ/mol for the DG-sand experiment. The catalytic pyrolysis yields of liquid, gas, and solid at 260 °C were 22.5 wt.%, 27.0 wt.%, and 50.5 wt.%, respectively. By contrast, the liquid, gas, and solid yields from the non-catalytic pyrolysis were 20.4 wt.%, 15.1 wt.%, and 64.5 wt.%, respectively at 260 °C, and 32.5 wt.%, 33.0 wt.%, and 34.5 wt.% for the liquid, gas, and solid, respectively at 350 °C. The organic fraction of the catalytic biooil consisted of a mixture of non-cyclic oxygenates (NCOs: 73.8%) and furans (24.2 %). The organic fraction of the non-catalytic biooil consisted of NCOs (34.3 %), furans (38.3 %), and Cyclic ketones (CKs: 15.6 %). It appears that the catalytic cracking of DG over the FRM proceeded via the cleavage of the C-C bonds in DG and its thermal decomposition products on the lattice oxygen sites of transition metal oxides (Fe_2O_3, TiO_2) and the Lewis acid sites of alumina on the surface of the FRM, which resulted in the production of low molecular weight intermediate compounds (such as AA and FA) and non-condensable pyrolysis gases.

Introduction

- Due to its low cost and abundance, lignocellulosic biomass has been the center of attention as feedstock for biofuel production.

- Cellulose is the major (23-53%) polymer in lignocellulosic biomass and is a homopolymer of glucose molecules connected via a β(1→4) glycosidic bond

- 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**.

- The pyrolysis of glucose as model compound has been extensively investigated in the literature.

- In literature, red mud was extensively investigated as a pyrolysis catalyst and compared to the HZSM-5 catalyst

- Very little information about the reaction pathways of red mud catalyst is available.

- The composition of red mud varies depending on the collection site, therefore, a commercially produced reformulated red mud (FRM) was used in this study.

- FRM: 60 wt % red mud, 30 wt % colloidal alumina, and 10 wt % colloidal silica.
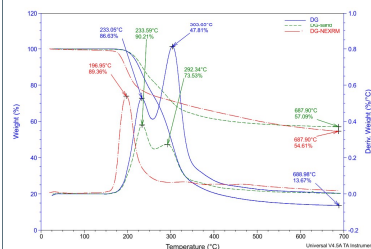
Results

Figure 1: Effect of the FRM and sand on the thermogravimetric analysis of the DG.

Table 1: Pyrolysis and catalytic pyrolysis products distribution

	DG-sand		DG-FRM
	260 ℃	**350 ℃**	**260 ℃**
Char/coke	64.5 ± 0.71	34.5 ±0.71	50.5 ±0.70
Organic liquid	5.5 ±0.86	9.4 ±1.72	4.5 ±0.50
Water	14.9 ± 0.32	23.1 ±0.43	18.0 ±1.1
Gas*	15.1 ±0.50	33.0 ±0.60	27.0 ±0.85

*: Calculated by difference

Results cont.

Table 2: Calculated kinetic parameters for the pyrolysis of D-(+)-Glucose using sand

Conversion (%)		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	112.00	70.28
Pre-Exponential factor										
n	0	7.42E+01	1.67E+05	8.15E+03	8.69E+02	4.98E+01	3.42E+05	4.55E+07	2.00E+07	6.40E+02
	1	7.81E+01	1.85E+05	1.02E+04	1.24E+03	8.30E+01	6.84E+05	1.14E+08	6.67E+07	3.20E+03
	2	8.23E+01	2.06E+05	1.27E+04	1.77E+03	1.38E+02	1.37E+06	2.84E+08	2.22E+08	1.60E+04

Table 3: Calculated kinetic parameters for the pyrolysis of D-(+)-Glucose using FRM

Conversion (%)		5.00	10	20	30	40	50.00	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	1.05E+03	2.54E+06	1.66E+07	4.75E+06	9.75E+04	1.75E+02	1.03E+02	4.81E+00	1.42E+00
	1	1.11E+03	2.83E+06	2.08E+07	6.79E+06	1.63E+05	3.50E+02	2.58E+02	1.60E+01	7.10E+00
	2	1.16E+03	3.14E+06	2.60E+07	9.69E+06	2.71E+05	7.00E+02	6.45E+02	5.35E+01	3.55E+01

(1) Nitrogen source, (2) furnace, (3) tubular reactor, (4) 1:1 ratio of glucose and red mud blend, (4a) glass wool, (5) ice bath, (5a) condenser, (6) filter, (7) Electrostatic precipitator, (8) AC power source, (9) Thermocouple
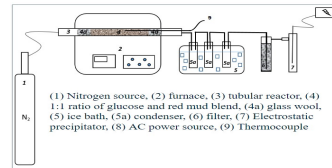
Figure 2 : Schematic diagram of the pyrolysis unit.
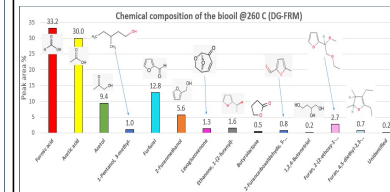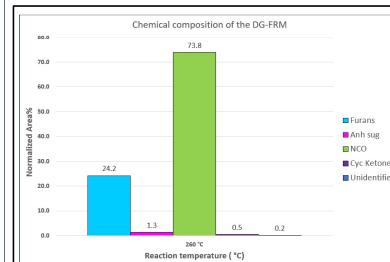

Figure 3 : Chemical composition of the DG-FRM biooil at different pyrolysis temperatures
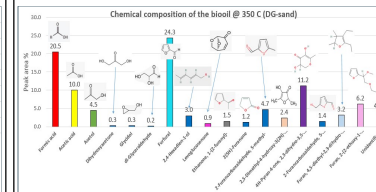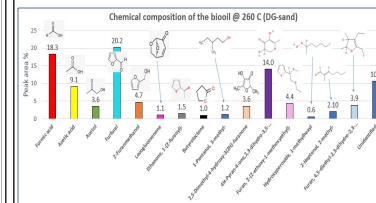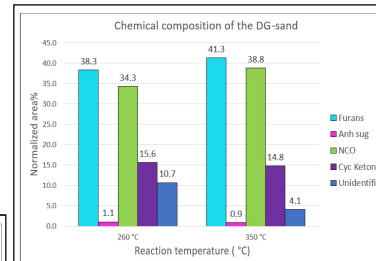

Figure 4 : Chemical composition of the DG-sand biooil at different pyrolysis temperatures

Discussion

- When the FRM was used, the weight loss at 260 C increased by almost 10%.

- The activation energy, at 80% conversion, of the catalytic pyrolysis of D-glucose using FRM was 35.15 % lower than that of its slow pyrolysis using sand.

- The char and organic liquid yields decreased, whereas the gas yield increased after using the catalyst at 260 C, and CO_2 was the major gas (98.5% using FRM and 76.1% using sand).

- The organic fraction of the non-catalytic biooil consisted of 34.3 % non-cyclic oxygenates, 38.3 % furans, and 15.6 % cyclic ketones.

- The organic fraction of the catalytic biooil consisted of 73.8 % non-cyclic oxygenates and 24.2 % furans.

- The main products of the catalytic biooil collected at 260 C were formic acid (33.2 %) and acetic acid (30.0 %)

- The main product of the non-catalytic biooils were furfural and formic acid (20.2 % and18.3 %, respectively at 260 C and 24.3 % and 20.5 %, respectively at 350 C).

- The content of the C6 or higher compounds was 7 % In the catalytic biooil and 32.4 % And 34.6 % in the non-catalytic biooils at 260 C and 350 C.

Conclusions

- The FRM promoted the thermal decomposition of the DG and altered its thermogram, which was a result of catalytic activity.

- The FRM inhibited the formation of furans and promoted the production of NCOs.

- The lattice oxygen sites as well as the Lewis acid sites on the surface of the FRM promoted the cleavage of the C-C bonds in the DG, which resulted in the increase of NCOs and non-condensable gases content.

Acknowledgements