Effects of Carrier Gas Flow Rate and ZSM-5 Catalyst on Yields and Quality of Bio-oil from Pyrolysis of Lignocellulosic Biomass Using a Fixed-bed Reactor

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ABSTRACT

This experimental process demonstrates the potential of advancing the technology of lignocellulosic-based biofuels. Maximized bio-oil yields and gasoline range aromatics were obtained from the pyrolysis of switchgrass biomass in a medium-scale fixed bed reactor (48.2 L). The reaction's final temperature was set at 520°C while the carrier gas flow rate was varied at (50 L min^{-1}, 75 L min^{-1} and 100 L min^{-1}) both without and with the use of the ZSM-5 catalyst. Bio-oil yields of 18.2%, 26.9%, and 34.1% were generated without catalyst. Using the ZSM-5 catalyst, bio-oil yields of 20.2%, 41.5%, and 47.7% were generated. At 75 L min^{-1}, 9.6% gasoline range organics (GROs) were detected without the catalyst and 12.4% aromatics were detected in the experiment with ZSM-5 catalyst. At 100 L min^{-1}, 10.5%, and 13.7% of aromatics were detected without and with ZSM-5 catalyst respectively. At 75 L min^{-1} 14.5% of oxygen content recorded without catalyst, and 5.6% with ZSM-5 catalyst. At 100 L min^{-1}, oxygen content was 10.4% without catalyst, and 8.6 % with ZSM-5 catalyst. The effects of carrier gas flow rate variations and a ZSM-5 catalyst on bio-oil yields and quality were experimentally demonstrated using a single-step thermochemical conversion process. This is a major development towards improving U.S energy security and achieving global CO_2 emissions mitigation targets.

Highlights of the Experiment

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- Increasing nitrogen (N_2) carrier gas flow rate resulted in enhanced bio-oil yields from pyrolysis of lignocellulosic biomass with maximum yield (wt%) of 34.1% obtained at 100 liters per minute (LPM) without using a catalyst.
- Incorporating ZSM-5 catalyst in switchgrass pyrolysis led to increased bio-oil yields (wt%) with a 47.74% maximum generated at 100 LPM.
- Using ZSM-5 catalytic pyrolysis improved GROs yield (wt%) with an average improvement of about 30% from bio-oil samples obtained without catalyst.
- Using ZSM-5 catalyst resulted in reduced oxygen content in upgraded bio-oil samples with the lowest of 5.58% recorded at 75 LPM.
- Medium-scale experimental fixed bed reactor (48.2 L) developed at Prairie View A&M University is optimally utilized at 75 LPM and 100 LPM.

INTRODUCTION

In the United States, 29% of carbon dioxide (CO_2) emissions come from the transportation sector, accounting for almost one-third of the country's emissions. This exceeds the CO_2 emissions from electricity generation (27%) and industrial sources (22%) [1].

Dedicated perennial energy crops such as switchgrass, crop residues, and forestry biomass are primary cellulosic biomass that could potentially displace 30% of the current petroleum consumption in the U.S. [2]. However, these energy resources have not been fully utilized where economic conversion routes to biofuels are unidentified. The traditional biochemical route for converting lignocellulosic biomasses into transportation fuels is comprised of four steps: pretreatment, enzymatic or acidic hydrolysis, fermentation and distillation [3]. Alternatively, thermochemical routes such as pyrolysis and catalytic pyrolysis require only one step to convert biomass to liquid bio-oil with enhanced quality. Maximizing the bio-oil yield and enhancing its quality in a single step are keys for the commercialization of lignocellulosic feedstock as biofuels.

Research Objectives

This research investigates making biofuel more available in the transportation sector by studying the conversion of lignocellulosic biomass (i.e., switchgrass) into bio-oil using pyrolysis and catalytic pyrolysis reactions. The objectives of this research are: 1) to determine the effects of carrier gas flow rates and ZSM-5 catalyst on bio-oil yields and quality, such as gasoline range aromatics ratio and oxygen content; and 2) to identify optimal carrier gas flow rates for the pyrolysis and catalytic pyrolysis processes of switchgrass in a medium-scale experimental fixed bed reactor (48.2 L). The implications are salient: large-scale implementation can lower the U.S dependence on foreign petroleum sources and substantially reduce CO_2 emissions.

Past Studies

A.V. Bridgewater demonstrated in the "Fast pyrolysis of Cassava rhizome in the presence of catalysts" that ZSM-5 was the most active catalyst from three other catalysts (Al-MCM-41, Al-MSU-F, MI-575) studied in producing aromatic hydrocarbons and reducing oxygenated lignin derivatives, thus improving bio-oil heating value and viscosity [4]. Olazar et al. studied the fast pyrolysis of pine saw dust with ZSM-5 in a spouted bed reactor and observed a yield of aromatics of 12% (carbon) [5]. This research also seeks to identify the amount of gasoline range aromatics from pyrolysis of switch grass in a medium-scale, experimental fixed-bed reactor over the ZSM-5 catalyst.

Table 1.
Research test matrix demonstrating parameters investigated
(**pyrolysis reaction temperature, flow rates, and ZSM-5 catalyst**).

Temperature ºC	*Flow Rate LPM*	*Catalyst*
520	50	No Catalyst
520	75	No Catalyst
520	100	No Catalyst
520	50	ZSM-5
520	75	ZSM-5
520	100	ZSM-5

METHODOLOGY

A medium volume (48.2 L) experimental fixed bed reactor was developed at Prairie View A&M University (see Figure 1) and used for pyrolysis and ZSM-5 catalytic pyrolysis experiments. Switchgrass was provided by Texas A&M University at College Station. Switchgrass was dried at 94°C to constant weight, and then ground to 0.5 mm particle size. Reaction final temperature was set at 520°C. The nitrogen (N_2) carrier gas flow rate was varied without catalyst and with ZSM-5 catalyst at 50 L min^{-1},75 L min^{-1}, and 100 L min^{-1} (see Table 1). Bio-oil yields were determined using Equations 1, 2, and 3. Bio-oil quality was determined using GC-MS (oxygen, carbon, hydrogen, nitrogen, and sulfur) and a Thermo-Scientific Flash 2000 elemental analyzer.

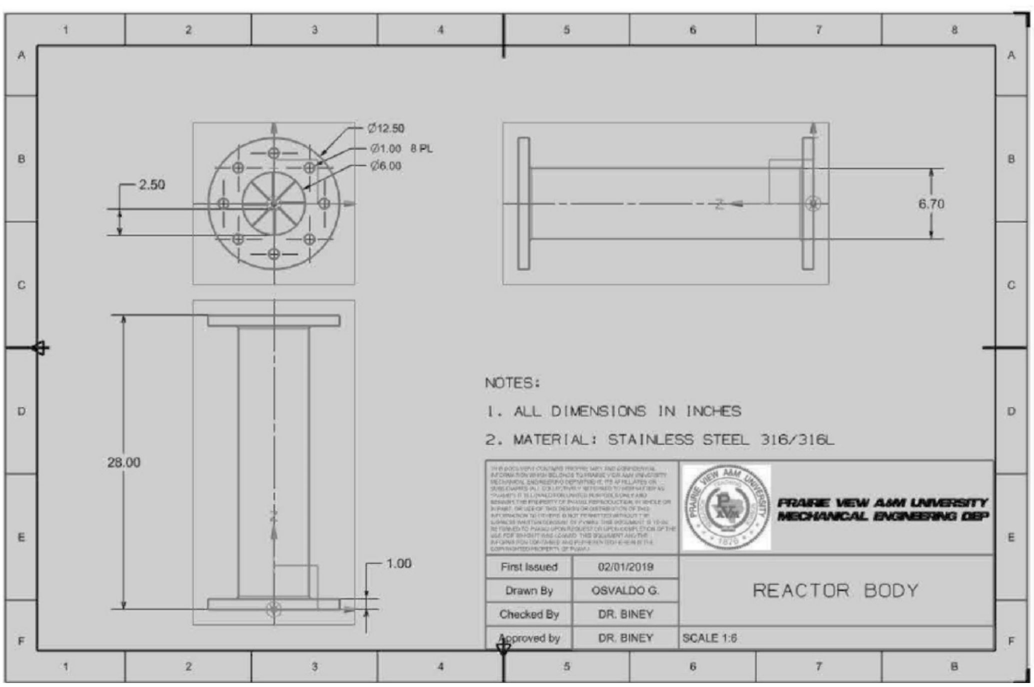


Figure 1. Dimensioned front, top, and side views of reactor.

Figure 1 shows detailed reactor dimensions with front, top, and side views. The reactor is made from a stainless-steel cylindrical case with a volume of approximately 48.2 L. The reactor has a 6" inner diameter and 26" height, not including top and bottom flanges which are each 1" in height.

$$\text{Bio-oil yield \%} = \text{Collected bio-oil mass} \div \text{Feedstock mass X } 100\% \quad (1)$$

$$\text{Bio-char yield \%} = \text{Collected bio-char mass} \div \text{Feedstock mass X } 100\% \quad (2)$$

$$\text{Bio-gas yield \%} = 100\% - (\text{Bio-oil yield \%} + \text{Bio char yield \%}) \quad (3)$$

RESULTS AND DISCUSSION

Bio-oil yields increased with increasing carrier gas flow rate. At 50 LPM without a catalyst, an 18.22% bio-oil yield was reported. Yields of 26.86% and 34.1% of bio-oil were generated by increasing the flow rate to 75 LPM, and 100 LPM respectively without a catalyst.

At a 50 LPM carrier gas flow rate with the ZSM-5 catalyst, a bio-oil yield of 20.15% was reported enhancing the yield by 1.93% without a catalyst. At 75 LPM with ZSM-5 catalyst, 41.5% of bio-oil yield was reported, demonstrating a 14.64% yield enhancement obtained at 75 LPM without a catalyst. At 100 LPM with the ZSM-5 catalyst, 47.74% of bio-oil yield was recorded, showing a 13.64% enhancement in bio-oil yield obtained at 100 LPM flow rate without catalyst.

Increasing carrier gas flow rate and incorporating the ZSM-5 catalyst in pyrolysis reaction led to increased bio-oil production, where bio-oil yield weight percent had increased linearly by varying the flow rates (through 50LPM, 75 LPM, 100 LPM) both with and without ZSM-5 catalyst.

Table 2 summarizes yield weight percentages obtained of bio-oil, bio-gas generated, bio-char, and bio-gas through varying carrier gas flow rate; the ZSM-5 catalyst was used for Research Experiments 1 through 6 (results shown graphically in Figures 2-4).

Figure 2.a. shows the variations in bio-oil, char, bio-gas, and bio-gas yields at 50 LPM, 75 LPM, and 100 LPM without catalyst. Bio-oil yield increased from 18.22% at 50 LPM to 26.86% at 75 LPM, and 34.1% at 100 LPM. This demonstrates an increased production of bio-oil with increased flow rates. Char weight percent decreased from 36.28% at 50

Table 2.

Pyrolysis byproducts at various flow rates with and without ZSM-5 catalyst.

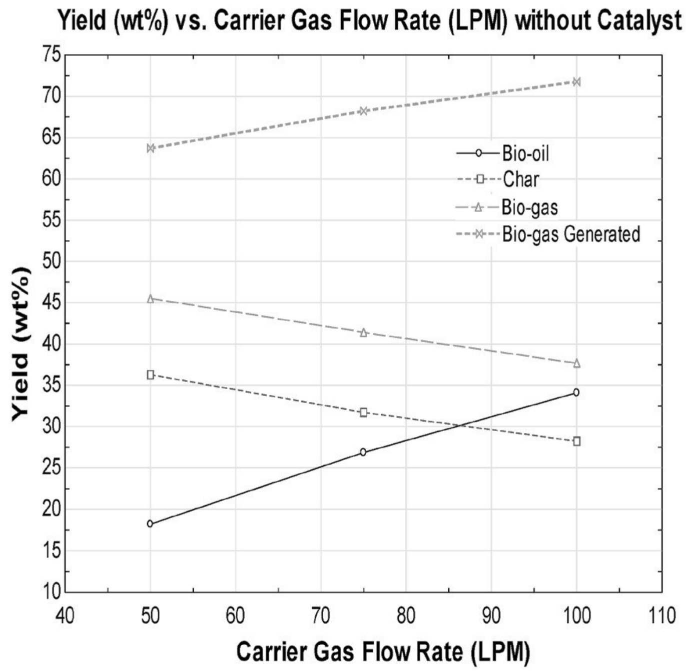
	Bio-oil yield (%)	*Char yield (%)*	*Bio-gas yield (%)*	*Bio-gas generated yield (%)*
1) 50 LPM, no catalyst	18.22	36.28	45.50	63.72
2) 75 LPM, no catalyst	26.86	31.74	41.40	68.20
3) 100 LPM, no catalyst	34.10	28.20	37.70	71.75
4) 50 LPM, with ZSM-5 catalyst	20.15	27.02	52.82	72.97
5) 75 LPM with ZSM-5 catalyst	41.50	32.10	26.40	67.90
6) 100 LPM with ZSM-5 catalyst	47.74	28.56	23.70	71.44

LPM to 31.74% at 75 LPM, and 28.2% at 100 LPM demonstrating a decrement of char production with increased flow rates. Bio-gas yields decreased from 45.5% at 50 LPM to 41.4% at 75 LPM, and 37.7% at 100 LPM.

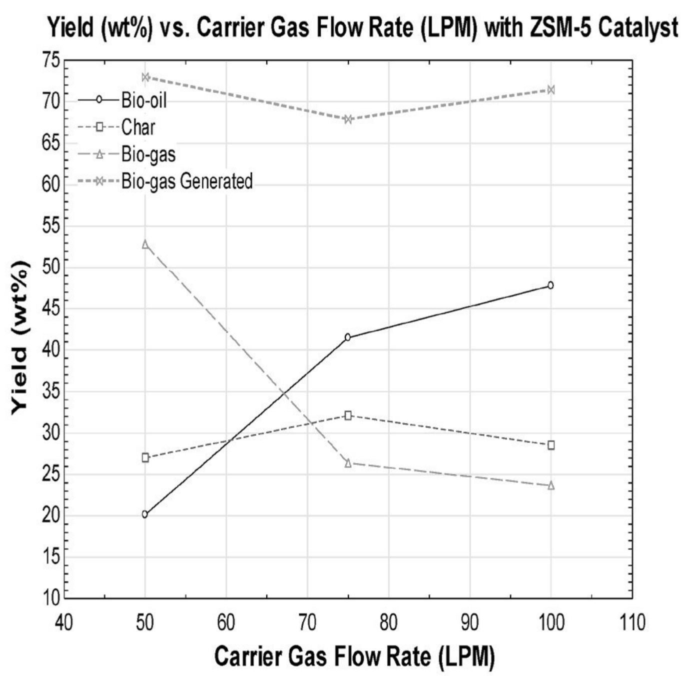
Figure 2.b. shows the variation of bio-oil, char, bio-gas, and bio-gas yields at 50 LPM, 75 LPM, and 100 LPM with the ZSM-5 catalyst. Bio-oil yield increased from 20.15% at 50 LPM to 41.5% at 75 LPM, and 47.74% at 100 LPM demonstrating an increased production of bio-oil with increased flow rates. Char weight percentage increased from 27.02% at 50 LPM to 32.1% at 75 LPM, and then decreased to 28.56% at 100 LPM. Bio-gas yield decreased from 52.82% at 50 LPM to 26.4% at 75 LPM and 23.7% at 100 LPM.

Figure 3.c. shows bio-oil yield (wt%) without catalyst vs. with ZSM-5 catalyst. Bio-oil increased by 1.93% when ZSM-5 catalyst was incorporated at 50 LPM, 14.64% when ZSM-5 catalyst was incorporated at 75 LPM, and by 13.64% when ZSM-5 was incorporated at 100 LPM.

Figure 3.d. shows bio-gas yield (wt%) without catalyst vs. with ZSM-5 catalyst. Bio-gas has increased by 7.3% when ZSM-5 catalyst was incorporated at 50 LPM, and then decreased by 15.0% when ZSM-5 catalyst was incorporated at 75 LPM, and by 14.0% when ZSM-5 was incorporated at 100 LPM.

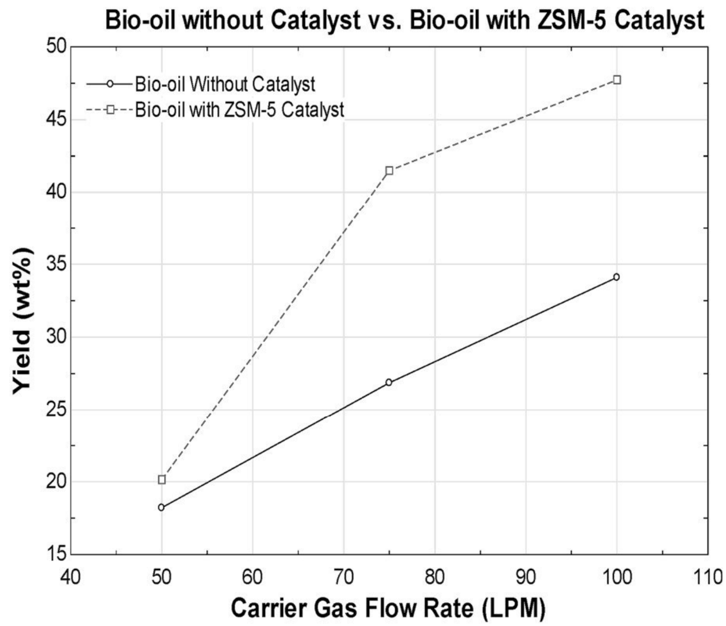


a) Yield (wt%) vs. carrier gas (LPM) without catalyst.

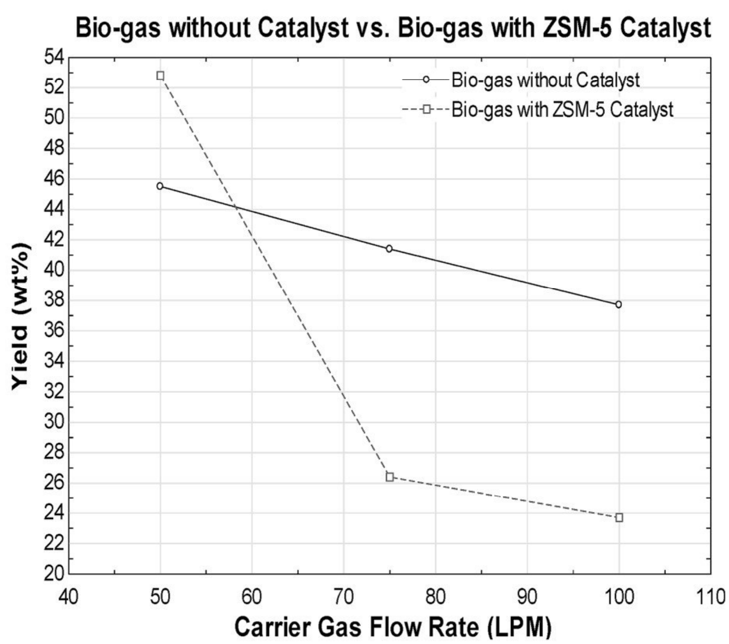


b) Yield (wt%) vs. carrier gas (LPM) with ZSM-5 catalyst.

Figure 2. Effects of N_2 carrier gas flow rate on bio-oil yield percentage.



c) Bio-oil yield (wt%) without catalyst vs. with ZSM-5 catalyst.



d) Bio-gas yield (wt%) without catalyst vs. with ZSM-5 catalyst.

Figure 3. Effects of ZSM-5 catalyst on bio-oil yield percentage.

Figure 4.e. demonstrates the amount of GROs obtained without catalyst vs. with the ZSM-5 catalyst at 75 LPM and 100 LPM. The figure shows that the aromatics percentage had increased by 2.82% when the catalyst was used at 75 LPM. The figure also shows an increment represented by 3.21% when the catalyst was used at 100 LPM.

Figure 4.f. shows oxygen (wt%) in bio-oil samples obtained at 75 LPM and 100 LPM without and with ZSM-5 catalyst. At 75 LPM without catalyst, 14.5% of oxygen was found in bio-oil samples. At 75 LPM with ZSM-5 catalyst, the percentage dropped significantly to 5.6%, demonstrating a decrement of about 10%. The utilization of the ZSM-5 catalyst resulted in a significant oxygen decrease, leading to an increased higher heating value (HHV). At 100 LPM without catalyst, oxygen (wt%) found in bio-oil samples was 10.41%. At 100 LPM with ZSM-5 catalyst, the oxygen (wt%) found in bio-oil samples was 8.64%; this demonstrates a decrease in the bio-oil content by about 2%.

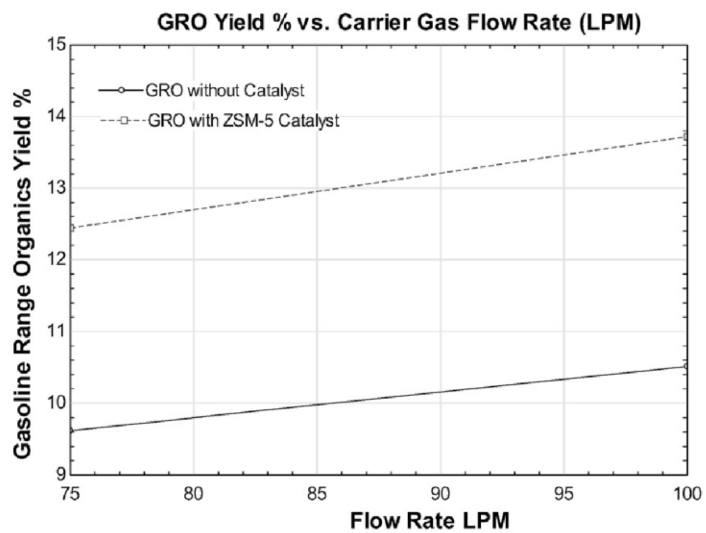
Table 3 shows the GROs obtained in bio-oil samples at 75 LPM without a catalyst, where the GC-MS data and the percent composition analysis confirmed that the GROs formed 9.62% of the total bio-oil composition.

Table 4 shows the GROs obtained in bio-oil samples at 75 LPM with ZSM-5 catalyst. The GC-MS data and the percent composition analysis confirm that the GROs formed 12.44% of the total bio-oil composition.

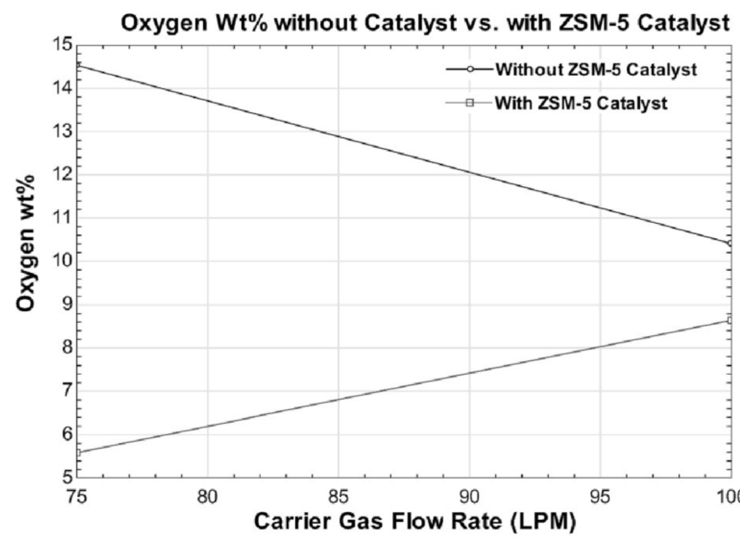
Table 5 shows the GROs obtained in bio-oil samples at 100 LPM without catalyst; the GC-MS data and the percent composition analysis confirmed that the GROs formed 10.51% of the total bio-oil composition.

Table 6 shows the GROs obtained in bio-oil samples at 100 LPM with the ZSM-5 catalyst. The GC-MS data and the percent composition analysis confirmed that the GROs formed 13.72% of the total bio-oil composition.

Table 7 shows the oxygen content of bio-oil samples with and without the ZSM-5 catalyst at 75 LPM and 100 LPM respectively.



e) Gasoline range aromatics (wt%) without catalyst vs. with ZSM-5 catalyst.



f) Oxygen (wt%) with and without ZSM-5 catalyst.

Figure 4. Effects of ZSM-5 catalyst on gasoline range organics yield percentage and oxygen content percentage.

Table 3. Composition of gasoline range organics detected in GC-MS data at 75 LPM without catalyst, GROcompoundnames,retentiontimesandmolecularweights.

Compound number	*RT (min)*	*Compound name*	*Mol. weight (amu)*	*Area/Total area*	*Percentage*
3	6.899	Styrene	104.063	0.014051	1.41%
6	7.814	Benzene, (1-methylethyl)-	120.094	0.006805	0.68%
7	8.589	Benzene, propyl-	120.094	0.005812	0.58%
8	8.799	Benzene, 1-ethyl-3-methyl-	120.094	0.030432	3.04%
9	8.974	Benzene, 1,2,3-trimethyl-	120.094	0.020778	2.08%
10	9.265	Benzene, 1-ethyl-2-methyl-	120.094	0.009536	0.95%
11	9.615	Benzene, 1,2,4-trimethyl-	120.094	0.025611	2.56%
12	10.343	Benzene, 1,2,3-trimethyl-	120.094	0.011398	1.14%

Table 4. Composition of gasoline range organics detected in GC-MS data at 75 LPM with ZSM-5 catalyst, GROcompoundnames,retentiontimesandmolecularweights.

Compound number	*RT (min)*	*Compound name*	*Mol. weight (amu)*	*Area/Total area*	*Percentage*
3	6.899	Styrene	104.063	0.014051	1.41%
6	7.814	Benzene, (1-methylethyl)-	120.094	0.006805	0.68%
7	8.589	Benzene, propyl-	120.094	0.005812	0.58%
8	8.799	Benzene, 1-ethyl-3-methyl-	120.094	0.030432	3.04%
9	8.974	Benzene, 1,2,3-trimethyl-	120.094	0.020778	2.08%
10	9.265	Benzene, 1-ethyl-2-methyl-	120.094	0.009536	0.95%
11	9.615	Benzene, 1,2,4-trimethyl-	120.094	0.025611	2.56%
12	10.343	Benzene, 1,2,3-trimethyl-	120.094	0.011398	1.14%

Table 5. Composition of gasoline range organics detected in GC-MS data at 100 LPM without catalyst, GROcompoundnames,retentiontimesandmolecularweights.

Compound number (#)	*RT (min)*	*Compound name*	*Mol. weight (amu)*	*Area/Total area*	*Percentage*
3	6.899	Styrene	104.063	0.010882	1.09%
5	7.814	Benzene, (1-methylethyl)-	120.094	0.006029	0.60%
6	8.589	Benzene, propyl-	120.094	0.004853	0.49%
7	8.805	Benzene, 1-ethyl-3-methyl-	120.094	0.026292	2.63%
8	8.974	Mesitylene	120.094	0.016861	1.69%
9	9.265	Benzene, 1-ethyl-2-methyl-	120.094	0.0082	0.82%
10	9.621	Benzene, 1,2,4-trimethyl-	120.094	0.022035	2.20%
11	10.343	Benzene, 1,2,3-trimethyl-	120.094	0.009899	0.99%

Table 6. Composition of gasoline range organics detected in GC-MS data at 100 LPM with ZSM-5 catalyst, GROcompoundnames,retentiontimesandmolecularweights.

Compound number	*RT (min)*	*Compound name*	*Mol. weight (amu)*	*Area/Total area*	*Percentage*
4	6.905	Styrene	104.063	0.016448	1.64%
5	6.98	Cyclohexanone	98.073	0.002979	0.30%
6	7.348	Ethanol, 2-butoxy-	118.099	0.007458	0.75%
7	7.814	Benzene, (1-methylethyl)-	120.094	0.007367	0.74%
8	8.589	Benzene, propyl-	120.094	0.00603	0.60%
9	8.805	Benzene, 1-ethyl-2-methyl-	120.094	0.031234	3.12%
10	8.98	Mesitylene	120.094	0.018082	1.81%
11	9.265	Benzene, 1-ethyl-2-methyl-	120.094	0.009506	0.95%
12	9.615	Benzene, 1,2,3-trimethyl-	120.094	0.026319	2.63%
13	10.344	Benzene, 1,2,3-trimethyl-	120.094	0.011741	1.17%

Table 7.

Represents a comparison between gasoline range organics % compositions

obtained at various flow rates with and without ZSM-5 catalyst.

Bio-oil samples at various flow rates, with and without ZSM-5 catalyst	*Gasoline range organics % composition*
75 LPM carrier gas flow rate without catalyst	9.62%
75 LPM carrier gas flow rate with ZSM-5 catalyst	12.44%
100 LPM carrier gas flow rate without catalyst	10.51%
75 LPM carrier gas flow rate without catalyst	13.72%

CONCLUSIONS

The medium-scale experimental fixed bed reactor (48.2 L), developed at Prairie View A&M University, is proven to effectively maximize bio-oil yields (wt%) from the pyrolysis of lignocellulosic biomass. Effects of carrier gas (N_2) flow rate variation demonstrated maximum bio-oil yield at 100 LPM with 34.1% (obtained without catalyst) at 520°C pyrolysis reaction temperature. Ex-situ ZSM-5 catalytic pyrolysis led to enhanced gasoline range aromatics with an average improvement of 30%, an oxygen content reduction of about 40%, and a maximized bio-oil yield of 47.74% generated at 100 LPM. Maximized bio-oil yield and enhanced GROs range aromatics qualities were obtained in a single step thermo-chemical process.

This validation of a medium-scale implementation paves the way towards commercialization of lignocellulosic biomass in the U.S transportation sector. Dedicated perennial energy crops such as switchgrass, crop residues, and forestry biomass could potentially displace 30% of the U.S current petroleum consumption if used as biofuels [2].

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References

[1] United States Environmental Protection Agency (2018). Sources of greenhouse gas emissions. https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions, accessed 9 June 2021.

[2] Schmer, M., Vogel, K., Mitchell, R. and Perrin, R. (2008). Net energy of cellulosic ethanol from switchgrass. *Proceedings of the National Academy of Sciences*, 105, pages 464-469. https://doi.org/10.1073/pnas.0704767105.

[3] Carlson, T., Vispute, T. and Huber, G. (2008). Green gasoline by catalytic fast pyrolysis of solid biomass derived compounds. *ChemSusChem*, 1, pages 397-400. https://doi.org/10.1002/cssc.200800018, accessed 23 October 2022.

[4] Pattiya, A., Titiloye, J. and Bridgwater, A. (2008). Fast pyrolysis of cassava rhizome in the presence of catalysts. *Journal of Analytical and Applied Pyrolysis*, 81, pages 72-9. https://doi.org/10.1016/j.jaap.2007.09.002.

[5] Olazar, M., Aguado, R., Bilbao, J. and Barona, A. (2000). Pyrolysis of sawdust in a conical spouted-bed reactor with a HZSM-5 catalyst. *AIChE Journal*, 46, pages 1,025-1,033. https://doi.org/10.1002/aic.690460514.

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