PRODUCTION OF LIQUID HYDROCARBONS FROM MILLET HUSK VIA CATALYTIC HYDRODEOXYGENATION IN NIO/AL$_2$O$_3$ CATALYSTS

NASIR ANKA GARBA[1], IBRAHIM K. MUDURU[2], MOHAMMED A. SOKOTO[2] & SANI M. DANGOGGO[2]
[1]Department of Chemistry, Federal University Gusau, Nigeria
[2]Department of Pure and Applied Chemistry, Usmanu Danfodiyo University Sokoto, Nigeria

ABSTRACT
A number of viable options are being explored for the production of energy to meet growing global energy demand. The research investigated the conversion of millet husk to liquid hydrocarbons. Furfural was produced from millet husk via a single-stage process that involved simultaneous hydrolysis and dehydration processes, and was subsequently converted to straight-chain hydrocarbons through aldol condensation and hydrodeoxygenation reactions. The hydrodeoxygenation of the aldol condensation product over NiO/Al$_2$O$_3$ (493 K, 30 bar and reaction time of 1 hour) yielded liquid hydrocarbons with the selectivity of 77.5%. The results indicate that millet husk could be a good substrate for furfural production, and could be a source of fuels and chemicals for industries.
Keywords: biofuels, hydrocarbons, furfural, aldol condensation, hydrodeoxygenation, millet husk, catalysis, FTIR, GC-MS, biomass.

1 INTRODUCTION

As concern grows over the twin challenges of climate change and energy security, a number of viable options are being explored for the production of energy to meet the global demand in a sustainable fashion. One of these options is biofuel production from renewable biomass. The exploitation of biomass for energy and biochemical production has been recognized as a viable option for adding value to lignocellulosic agricultural residues such as corn stover, wheat straw, rice husk/straw, and millet husk [1]. Lignocellulosic biomass consists of three major components: cellulose (40–50%), hemicellulose (25–35%), and lignin (15–20%) [2].

Biomass is a renewable resource of carbon produced from organic matter including agricultural residues. These materials can be converted to energy carrier and/or heat as well as liquid fuels by either thermochemical, physicochemical, or biological processes (Fig. 1). According to Mehdi et al. [3], biomass conversion can yield biodiesel, alcohols (ethanol/methanol), biogas, biomass-to-liquid, and hydrogen.

However, the renewable production of biofuels and chemicals will solely rely on biomass, since, among all the renewable resources, biomass is the only source of carbon [3]. A complete transition from petroleum to biomass feedstocks seems feasible for the production of biofuels and chemicals based on the current production volume of biomass; however, biomass feedstocks, being highly functionalized molecules, are significantly different from petroleum feedstocks that are generally unfunctionalized, presenting significant technological, economic, and environmental challenges [4], [5].

One of the main concerns in the large-scale production of biofuels and chemicals is the consumption of edible biomass such as corn, sugarcane, soybeans, and vegetables as feedstocks for biofuels generation. This issue has motivated researchers around the world to develop second-generation technologies for processing non-edible biomass (lignocellulosic biomass) so that the sustainable production of a new generation of fuels and chemicals can be achieved without affecting food supplies. In this respect, lignocellulosic biomass is
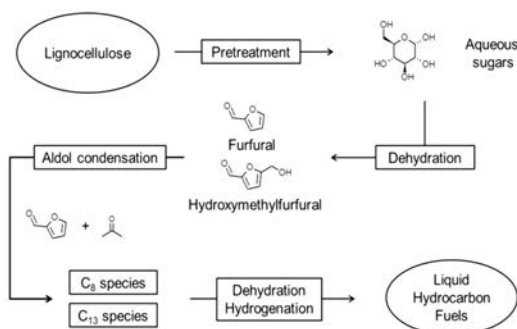
Figure 1: Biomass conversion process.

attractive since it is abundant and can be grown faster and more economically than food crops [1]. Lignocellulosic biomass consists of three major components: cellulose (40–50%), hemicellulose (25–35%), and lignin (15–20%) [2]. The aim of this research is to examine the potential of millet husk for the generation of hydrocarbons via an aqueous-phase process.

2 METHODOLOGY

Millet husk was first converted to furfural, which was further converted to hydrocarbon intermediates via aldol condensation. These were subsequently converted to liquid hydrocarbons with a selectivity of 77.5% by catalytic hydrodeoxygenation using NiO/Al_2O_3 at a 220ºC reaction temperature, and 30 bar for 1 hour.

2.1 Production of furfurals

Millet husk sample was collected, cleaned, dried, and stored in a dry place in the laboratory. A 5.0 g sample of dried millet husk was prepared and 5.0 g of sodium chloride (NaCl) was added to the sample and mixed in a clean beaker. The mixture was placed in a 250 cm^3 borosilicate glass tube reactor followed by the addition of 50 cm^3 of diluted sulfuric acid (H_2SO_4). The reactor was placed upright inside a furnace and connected to a water condenser. A distillation process was then carried out based on the chosen variables of acid concentration, temperature, and reaction times. The organic portion of the distillate was then extracted with dichloromethane using a separating funnel, and the solvent was removed using a rotary evaporator at 40ºC. The resultant solution was analyzed using a Fourier transform infra-red (FTIR) spectrometer [6].

2.2 Aldol condensation

The aldol condensation of furfural with acetone was performed using a flat-bottomed flask of 250 cm^3 capacity equipped with a magnetic stirrer. Then, 10 cm^3 of the distilled furfural was mixed with 5 cm^3 of acetone in the ratio of 2:1, and was subsequently transferred into the reactor, where 50% water/ethanol was added to the mixture. The reactor was heated at 85ºC and 20 cm^3 of 4M NaOH was added to the mixture with vigorous stirring (500 rmp/min) for 30 min [7]. The resulting mixture was filtered and washed three times with ethanol to remove excess NaOH. Any crystalline products that had formed were dissolved in ethyl acetate. The products were analyzed using a FTIR and ultraviolet–visible spectroscopy at a wavelength of 200 nm and 400 nm, respectively [8].

2.3 Hydrodeoxygenation

Hydrodeoxygenation of the aldol product was carried out at 493 K in a 316 L stainless steel tubular reactor. Then, 30 cm^3 of the aldol adduct and 1.8 g NiO/Al$_2$O$_3$ catalyst was transferred into the reactor and the reactor was purged with nitrogen gas. The reactor was pressurized with hydrogen at up to 30 bars and heated to 493 K for 1 hour. The liquid product obtained at the end of the reaction was then filtered and analyzed by gas chromatography and mass spectrometry (GC–MS) [9].

3 RESULTS AND DISCUSSION

A Cary 630 FTIR machine was used to identify the furfural produced. The results are presented in Tables 1–3.

Table 1: FTIR spectral analysis of the produced furfural.

Class of hydrocarbons	Functional group	Wavenumber (cm^{-1})
Aldehyde	C=O	1720–1740
	C-H	2700–2900
Aromatic	C-H	3000–3100
	C=C	1450–1600
Ether	C-O	1000–1300

Table 2: FTIR spectral analysis of the aldol adducts.

Class of hydrocarbons	Functional group	Wavenumber (cm^{-1})
Ketone	C=O	1700–1725
Alkenes	C-H	3080–3140
	C=C	1630–1670
Aromatic	C-H	3000–3100
	C=C	1450–1600
Ether	C-O	1000–1300

Table 3: Compositions of hydrodeoxygenated products.

Name of hydrocarbon	Molecular formula	% peak area
Decane	C$_{10}$H$_{22}$	13.59
3-methyltridecane	C$_{10}$H$_{22}$	12.01
Tetradecane	C$_{14}$H$_{30}$	5.36
Pentadecane	C$_{14}$H$_{30}$	6.13
Hexadecane	C$_{15}$H$_{32}$	17.48
Hexadecane	C$_{16}$H$_{34}$	12.52
Eicosane	C$_{20}$H$_{42}$	10.41
Docosane	C$_{22}$H$_{46}$	13.59

As shown in Fig. 2, a strong absorption was shown by the IR spectrum at 1669 cm^{-1}, which corresponds to the absorption of conjugated carbonyl (C=O). The C=O absorption is lower than the usual absorption of aldehyde due to internal hydrogen bonding, which occurs in conjugated unsaturated aldehyde, and conjugation lowers the vibrational frequency of carbonyl compounds. The presence of the aldehyde group was proven with the existence of two weak absorptions gained at 2848 cm^{-1} and 2812 cm^{-1}, as observed in the standard furfural that indicated moderate intense stretching of aldehydic C-H, which is attributable to Fermi resonance between the fundamental aldehydic C-H stretching and the first overtone of the aldehydic C-H bending vibration [11]. Moreover, strong peaks from 1570 cm^{-1} to 1466 cm^{-1} indicated inactive stretching of C=C from the aromatic ring, and strong peaks at 1020 cm^{-1} indicated the C-O stretching vibration. These IR spectrum changes were also compared with that of the standard furfural spectrum, and that of Alonso et al. [12] and Ong and Sashikala [6].

The IR spectrum of the furfural-acetone dimer obtained is shown in Fig. 3. The frequency of the main absorption bands illustrated that the (C-H) vibrational frequency appears at 3142 and 3121 cm^{-1}, which correspond to the sp^2 vibration in the furan ring. The stretching absorbance (C=O) observed at 1603 cm^{-1} infers the carbonyl group, and a sharp stretching absorbance band at 1013 cm^{-1} probably indicates C-O stretching for cyclic C-O-C linkage of furfural. The peaks at 1553 cm^{-1} and an overtone at 2116 cm^{-1} may be as a result of C=C stretching vibration in the furan unit. Similarly, the lower broad absorption at 3401 cm^{-1} could be due to the presence of O-H vibration, which could be attributed to the absorption of the solvent that remained in the product. The spectrum observed was similar to those reported by Gharbi et al. [13] and Gandini [14].

The results presented in Table 3 show the distribution of the alkanes obtained from the hydrodeoxygenation of aldol adducts. The products were mainly liquid hydrocarbons with a carbon range of C$_{10}$–C$_{22}$. The total relative peak area of the products was 77.50%, with hexadecane and decane being the major products, each of which accounts for 17.48% and 13.59%, respectively. Based on GC–MS data, the liquid phase also contains significant amounts of two other alkanes larger than C$_{16}$ – eicosane and docosane – which could be formed due to a decomposition and polymerization reaction. In the liquid phase, other than alkanes, there were some other organic oxygenates identified by the GC–MS, including ethanol, 2-oxepanone, and acetic acid, which are most likely byproducts. The results obtained
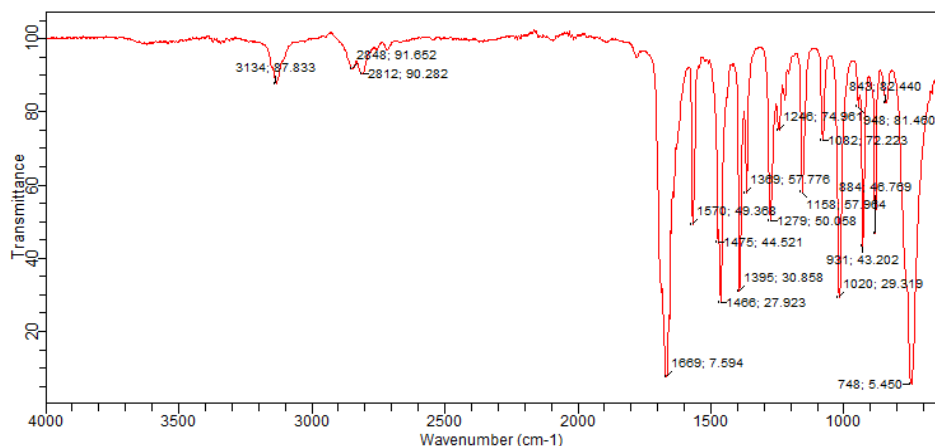

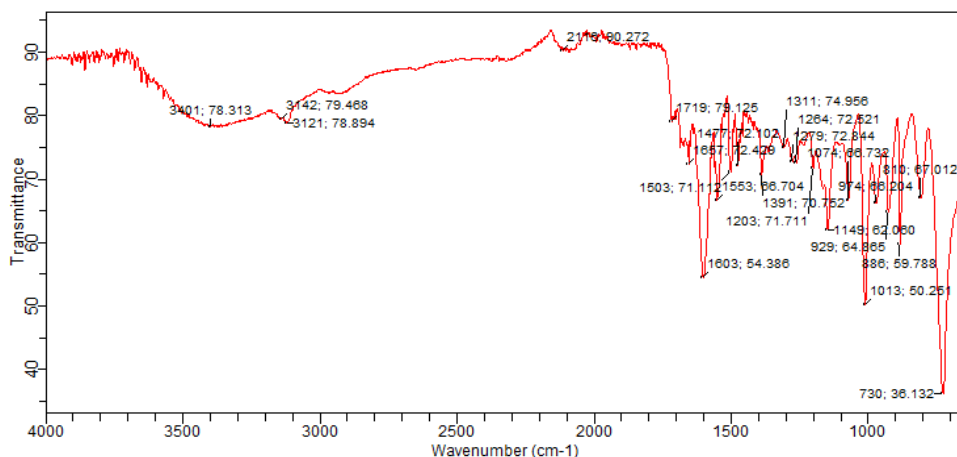Figure 2: FTIR spectrum of the furfural produced from millet husk.

Figure 3: FTIR spectrum of the aldol adduct.

by Rong et al. [15] showed an overall experimental yield of 76% liquid alkanes (jet fuel range), which corresponds to a weight-percent yield of 0.46 kg of alkanes per kg of xylose (monomer and oligomers) in the hemicelluloses extract. Other results obtained by Faba et al. [9] also reported 21.5% of tridecane from the hydrodeoxygenation of furfural-acetone condensation adducts over Pt/Al₂O₃ catalysts. The hydrodeoxygenation step could also be improved with improvements in the catalysts and reactor design. The straight alkanes produced could be further upgraded via the hydroisomerization process to form branched alkanes.

4 CONCLUSION

The study demonstrated the conversion of millet husk to liquid hydrocarbons via an aqueous phase process. Millet husk was converted to furfural and the produced furfural was further converted to hydrocarbon intermediate via aldol condensation, which was subsequently converted to liquid hydrocarbons with selectivity of 77.5% by catalytic hydrodeoxygenation using NiO/Al₂O₃ at a 220ºC reaction temperature, 30 bar for 1 hour. Thus, millet husk could be a good substrate for furfural production and could be a source of biofuel and biochemical for industries. The transformation potential of millet husk provides a new and useful process for the development of biofuels from waste lignocelluloses biomass.

REFERENCES

[1]   Roman-Leshkov, Y. & Dumesic, J.A., Solvent effects on fructose dehydration to 5-hydroxymethylfurfural in biphasic systems saturated with inorganic salts. *Top Catal*, **52**, pp. 297–303, 2009.
[2]   Gurbuz, E.I., Alonso, D.M., Bond, J.Q. & Dumesic, J.A., Reactive extraction of levulinate esters and conversion to γ-valerolactone for production of liquid fuels. *ChemSusChem*, **4**(3), pp. 357–361, 2011.
[3]   Mehdi, H., Fabos, V., Tuba, R., Bodor, A. & Mika, L.T., Integration of homogeneous and heterogeneous catalytic processes for a multi-step conversion of biomass: from sucrose to levulinic acid, γ-valerolactone, 1,4 pentanediol, 2-methyltetrahydrofuran and alkanes. *Green Chem*, **10**, p. 238, 2008.

[4]   Rao, R.S., Baker, R.T. & Vannice, M.A., Furfural hydrogenation over carbon-supported copper. *Catal Lett*, **60(**1–2), pp. 51–57, 1999.

[5]   Kunkes, E.L., Simonetti, D.A., West, R.M., Serrano-Ruiz, J.C., Gartner, C.A. & Dumesic, J.A., Catalytic conversion of monofunctional hydrocarbons and targeted liquid-fuel classes. *Science*, **322**, pp. 417–421, 2008.

[6]   Ong, H.K. & Sashikala, M., Identification of furfural synthesized from Pentosan in rice husk. *J Trop Agric & Fd Sc*, **35(**2), pp. 305–312, 2007.

[7]   Fakhfakh, N., Cognet, P., Cabassud, M.Y. & Rioios, M.D., Stoichio-kinetic modeling and optimization of chemical synthesis: application to the aldolic condensation of furfural on acetone. *Chem Eng Process*, **47**(3), pp. 349–362, 2008.

[8]   Martinez, A., Rodriquez, M.E., York, S.W., Preston, J.F. & Ingram, L.O., Use of UV absorbance to monitor furans in diluted acid hydrolysates of biomass. *Biotechnol Prog*, **16**, pp. 637–641, 2000.

[9]   Faba, L., Diaz, E., Vega, A. & Ordonez, S., Hydrodeoxygenation of furfural-acetone condensation adducts to tridecane over platinum catalysts. *Catalysis Today*, **269**, pp. 132–139, 2015.

[10]   Choudhary, V., Sandler, S.I. & Vlachos, D.G., Conversion of xylose to furfural using Lewis and Bronsted acid catalyst in aqueous media. *ACS Catal*, **2**(9), pp. 2022–2028, 2012.

[11]   Pavia, D.L., Lampman, G.M. & Kriz, G.S., *Introduction to Spectroscopy*, 3rd ed., Thomson Learning Inc., 2001.

[12]   Alonso, D.M., Wettstein, S.G., Bond, J.Q., Root, T.W. & Dumesic, J.A., Production of biofuels from cellulose and corn stover using alkylphenol solvents. *ChemSusChem*, **4**, pp. 1078–1081, 2011.

[13]   Gharbi, S., Afli, A. & Gandini, A., Polyamides incorporating furan moieties. Synthesis, characterization and properties of a homologous series. *Polymer International*, **50**, p. 509, 2001.

[14]   Gandini, A., Furans as offspring of sugars and polysaccharides and progenitors of a family of remarkable polymers: a review of recent progress. *Polymer Chemistry*, **1**, p. 245, 2010.

[15]   Rong, X., Ayyagari, V., Subrahmanyam, H.O., Wei, Q., Peter, V.W., Hemant P. & Huber, G.W., Production of jet and diesel fuel range alkanes from waste hemicellulose-derived aqueous solutions. *J RSC*, **140**, pp. 77–84, 2010.