

Catalytic Conversion of Furfural from Hemicellulose of *Citrullus colocynthis* (Melon) Seed Husk to Liquid Hydrocarbons

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Abstract: As concern over the twin challenges of climate change and energy security intensifies, numerous potential methods are being investigated for the production of energy and chemicals to satisfy global demand in an environmentally friendly manner. In light of this, catalytic conversion of furfural from hemicelluloses of *Citrullus colocynthis* (melon) seed husk to liquid hydrocarbons over NiO/SiO₂ was investigated. Furfural was produced by acid-catalyzed hydrolysis/dehydration of melon seed husk at temperature (220°C), acid concentration (10% H₂SO₄), and reaction time (55 minutes) which was subsequently converted to liquid hydrocarbons via furfural-acetone condensation followed by hydrodeoxygenation of furfural-acetone adduct. FT-IR spectrum of the produced furfural showed absorption at 1670 cm⁻¹ and 2800 cm⁻¹ indicating a conjugated carbonyl functional group and aldehydic hydrogen. The hydrodeoxygenation was carried out in a stainless-steel reactor at 150°C for 8 hours and 2bar hydrogen. The NiO/SiO₂ catalyst for the hydrodeoxygenation reaction was prepared by the wet impregnation method. XRF analysis of the NiO/SiO₂ revealed a percentage metal Composition of 73.939% SiO₂ and 24.641% NiO. The hydrodeoxygenation using NiO/SiO₂ in water at 150°C for 8 hours yielded liquid hydrocarbons with 86.61% hydrocarbons yield (C₉-C₁₂) and 1.46% 2-propenylidenecyclobutene. The result revealed that *Citrullus colocynthis*. (Melon) seed husk is a good source for liquid hydrocarbons production and could be used as a feedstock in industries for fuels and the production of the like chemicals.

Keywords: Furfural; Hemicellulose; Melon seed; Liquid Hydrocarbons; Hydrodeoxygenation.

I. INTRODUCTION

Global population growth and the depletion of fossil fuel reserves have led to an increase in the demand for fuel and chemicals. Political concerns over energy security and environmental issues brought on by CO₂ emissions and the ensuing global warming have also contributed to these problems. Diverse renewable energy sources have been investigated to create sustainable procedures in order to address issues [1].

For lignocellulosic biomass like maize stover, wheat straw, rice husk/straw, and millet husk to be more valuable, biomass can be utilized for energy and biochemical synthesis [2].

Therefore, using melon seed husk as a feedstock for clean energy, fuels and power production offers an alternate, but perhaps more effective, waste disposal option. This can be achieved by converting the furfural from hemicelluloses of *Citrullus colocynthis*(melon) seed husk (MSH) to liquid hydrocarbons which are found in the hemicelluloses of agricultural waste.

Citrullus colocynthis (Melon) is a tropical herbaceous, tendrill-bearing, vine plant of the *cucurbitaceae* family commercially cultivated in various regions in Africa (more especially Northern Part of Nigeria). It is an essential perennial cash crop cultivated for its fruits and oil-bearing seeds, the fruits are ovoid-shaped and weigh an average of 1.5kg. The mesocarp comprises numerous brown-colored oval shaped, dorsoventrally flattened seeds enclosed in a brittle cortex. The seeds contain a white, soft textured oil-rich kernel that is typically dehulled for processing into melon seed oil (MSO) [5].

The cultivation and extraction of vegetable oil from melon seeds generates large quantities of lignocellulosic waste known as Melon Seed Husk (MSH). With the growing culinary and medicinal importance of melon seeds, it is estimated that the cultivation and extraction of melon seed oil will result in increased waste over the coming years [4]. This will present further waste disposal and management challenges for the communities reliant on the crop for livelihood. In addition, current strategies for the disposal and management of agricultural wastes such as melon seed husk are considered inefficient, unsustainable, and environmentally hazardous [5].

The utilization of melon seed husk (MSH) as fuel feedstock for biomass and bioenergy applications is a potential solution for the current waste management and address fossil fuels challenges [5]. For hydrodeoxygenation reaction, the selection of catalyst plays an important role. Among different metal loading, the noble metal such as platinum (Pt) and palladium (Pd) have been revealed as suitable metals for hydrogenation reaction [6]. Furthermore, since hydrodeoxygenation (HDO) of biofuel is expected to be a large-scale process, employment

of noble metal-based catalysts could significantly raise production costs. However, the high prices of these noble metals failed to impress the industrial scope. As a consequence, the development of non-noble metal catalysts seems more rational. Thus, it seems more reasonable to use Ni-based catalyst for bio-fuel production via HDO owing to its lower cost. [6]

Apart from the active metal, the support material is also the key factor determining the catalytic performance. In the past, Al_2O_3 was widely used as catalyst support for HDO due to its cheap cost, excellent texture, and suitable acidity. However, coke formation tends to occur because of the induction of acid sites during HDO [6]. Catalyst activity usually disappeared swiftly because large amount of coke formed during the HDO reaction process. Worse, part of Al_2O_3 can be transformed into boehmite under hydrothermal conditions because alumina is known to be metastable under hydrothermal conditions, which usually leads to a decrease in catalytic activity [6][17]. To overcome these drawbacks, one of the major challenges in HDO reaction is to find suitable catalyst support. Recently numerous support materials such as active carbon, ZrO_2 , and TiO_2 were explored [7].

SiO_2 is an inert material with excellent hydrothermal stability and had been used as a catalyst support in the HDO of organic compounds. For example, Pt catalyst supported on SiO_2 was used in the HDO of cresol and guaiacol, obtaining high hydrocarbon yields [8].

The use of SiO_2 was reported to increase the activity of the catalyst by activating oxy-compounds and decreasing carbon deposition on the surface [9]. The crystal structure of SiO_2 is relatively stable in water and organic solvent. Hence, the reaction under the liquid phase is favorable. Sitthisa *et al.*, (2011) [10], investigated SiO_2 -supported Ni and Ni-Fe bimetallic catalysts for the conversion of furfural under 1 bar H_2 in the 210–250°C temperature range. Furfuryl alcohol and furan were primary products over monometallic Ni/ SiO_2 , resulting from hydrogenation and decarbonylation of furfural. Comparatively, 2-MF yields greatly increased with reduced yields of furan and C4 products using Fe-Ni bimetallic catalysts. Results proved that the addition of Fe suppressed the decarbonylation activity of Ni while promoting C=O hydrogenation (at low temperatures) and C-O hydrogenolysis (at high temperatures). To overcome these problems mentioned above, thus, in this research work, an inexpensive non-sulfided HDO catalyst was prepared by impregnation using the pristine transition metal Ni (nickel) as the active component and the common SiO_2 (silica) as support. The principal aim is to convert diverse hemicellulose derived furfural of melon seed husk into liquid hydrocarbons via Hydrodeoxygenation (HDO).

Several works were reported by the literature on the production of liquid hydrocarbons and effect of reaction conditions from lignocellulosic biomass, such as Concorbs [17] and Millet husk [2]. To the best of our knowledge there is no published information in literature on the production of

liquid hydrocarbons from Furfural of Hemicelluloses of *Citrullus Colocynthis L.*(Melon) Seed Husk, therefore this research intends to produce liquid hydrocarbons from Furfural obtained from Hemicelluloses of *Citrullus Colocynthis L.*(Melon) Seed Husk via Hydrodeoxygenation using NiO/ SiO_2 as a catalyst.

II. MATERIALS AND METHODS

2.1 Chemical and Solvent

The chemical and solvent used are Sulphuric acid (97%, BDH), Sodium Chloride (99%, LOBA) Sodium Sulphate (99.0%, LABTECH) Sodium hydroxide (97.0%, LOBA) Dichloromethane (99.0%, EMD) Acetone (99.0%, LOBA), Ethanol (95.0%, Kermel), Ethyl acetate (99.5%, LOBA), Hydrated Nickel nitrate (99.9%, EMD) and Silica (99.5, LOBA).

2.2 Sample Collection and Treatment

The melon seed husk was obtained from locally melon seed processing centre in Nguru local government area of Yobe State, Nigeria. The collected sample was dried under the sun in a dry place, ground, sieved then stored in a dry place.

2.3 Instrumentation

FT-IR Analysis of Furfural Produced and Furfural Acetone Adduct

The produced furfural and aldol adduct were analyzed using Carry630 Model FT-IR Spectroscopy. The transmission rate was set in the range of 4000-650 cm^{-1} at a resolution of 4 cm^{-1} . A drop of the sample was placed on a thin film positioned in the standard sample compartment of the FT-IR and the spectral data was obtained. The prepared NiO/ SiO_2 catalyst was characterized using X-ray Fluorescence (XRF) and The Fourier transform infrared (FT-IR) Spectroscopy. The Fourier transform infrared (FT-IR) spectroscopic analysis of the prepared NiO/ SiO_2 was carried out using M530 model Spectroscopy. The transmission rate was set in the range of 4000-600 cm^{-1} at a 4 cm^{-1} resolution value. The sample was compressed into a thin, clear pellet using a hydraulic press, mixed with alkali halide potassium bromide (KBr), and then put in the spectrometer's standard sample compartment where spectrum data was collected. The XRF analysis of the NiO/ SiO_2 was carried out using ARL QUANT'X EDXRF ANALYSER SN9952120 Model. The sample was compressed in to a thin, clear pellet using a hydraulic press, mixed with potassium bromide (KBr), and then put in the usual sample compartment of the XRF equipment to get the peaks of the elemental compositions. The GC-MS analysis of the hydrodeoxygenated product was carried out on Agilent Technologies GC 7890B, MSD 5977A. The injection volume was 1 μl and the inlet temperature was maintained at 230°C. The oven temperature was programmed initially at 80°C for 5 min and then programmed to 300°C at the rate of 6°C and holding the temperature for 15 min and the total run time was 45 min. The MS transfer line was maintained at 250°C, the source temperature was maintained at 230°C, and the MS

Quad at 150°C. The ionization mode was set at 70eV. Total Ion Count (TIC) was used to evaluate for compound identification and quantitation. The spectrum of the separated compound was compared with the database of the spectrum of known compounds saved in the NIST02 Reference Spectral Library.

2.4 Methods

2.4.1 Catalyst Preparation

Preparation of NiO/SiO₂ (NiS)

Impregnation of Nickel in the Silica support, The NiO/SiO₂ was prepared by dissolving 2.96g of nickel(II)nitrate (Ni(NO₃)₂·6H₂O) in water added with 5.96g of Silica (SiO₂) composite stirred for 24 hours at room temperature, after filtration the precipitate obtained was dried at 120°C overnight followed by Calcination at 500°C for 5 hours [8].

2.4.2 Furfural Production

The method described by Sokoto *et al.* (2018) was adopted for the synthesis of furfural. Dried samples (5.0g) of melon seed husk and sodium chloride (NaCl) (5.0g) were mixed in a clean beaker. The mixture was placed into a borosilicate glass tube reactor (250cm³) and dilute sulphuric acid (H₂SO₄) (50cm³ of 10%,) was added to the glass tube. The reactor was placed upright inside the furnace and connected to a water condenser. The distillation process was carried out according to the chosen variables of sulphuric acid concentration (10%), temperature (220°C), and time (55mins). The organic portion of the distillate was extracted with dichloromethane using a separating funnel and sodium sulphate (0.2g) was added to remove any trace water in the distillate. The solvent used was removed using a rotary evaporator at 40°C [11].

2.4.3 Aldol Condensation of Furfural with Acetone

A flat bottom flask with a volume of 250 cm³ and a magnetic stirrer was used to carry out the aldol condensation of furfural with acetone. Following that, 10 cm³ of the distillate furfural was combined with 5 cm³ of acetone in a 2:1 ratio, and the combination was then transported into the reactor where it was combined with 50 cm³ of water and 50 cm³ of ethanol (v/v). 20cm³ of a 4M NaOH solution was added to the mixture after the reactor had been heated to 85°C and stirred vigorously (at a rate of 500 rpm/min) for 30 minutes. To eliminate extra NaOH, the resultant liquid was filtered and three times rinsed with ethanol. Any generated crystalline products were dissolved with ethylacetate [2].

2.4.4 Hydrodeoxygenation of Furfural-Acetone adduct (FAA) to Hydrocarbon fuels

Hydrodeoxygenation of the Furfural-Acetone Adduct (FAA) Condensation product was carried out in the liquid phase using Stainless steel tubular reactor at 150°C over NiO/SiO₂ catalyst. 5g of the Aldol adduct (FAA) and 0.2g NiO/SiO₂ catalyst and 60cm³ of water were transferred into the reactor and the reactor was purged with nitrogen gas. The reactor was pressurized with hydrogen gas at up to 2bars and heated to

150°C for 8 hours. The liquid product obtained at the end of the reaction was then filtered and extracted using dichloromethane and analyzed by gas chromatography and mass spectrometry (GC-MS) [12].

III. RESULT AND DISCUSSION

3.1 Furfural and Aldol adduct Identification

The produced furfural and aldol adduct were analyzed using Carry630 Model FT-IR Spectroscopy.

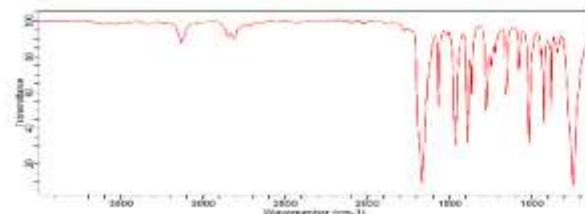


Figure 1 FT-IR Spectrum of Furfural Produced.

The FT-IR spectrum (Fig. 1) shows a very strong absorption at 1670 cm⁻¹. This absorption shows a very significant functional group that corresponds to the absorption of conjugated carbonyl (C=O). The C=O absorption wave number is slightly lower than usual (i.e 1740-1720 cm⁻¹) absorption of aldehyde due to internal hydrogen bonding which occurs in conjugated unsaturated aldehydes, and conjugation lower the vibrational frequency of carbonyl compounds. The absence of a peak at 1725 cm⁻¹ indicates strongly the presence of aldehydes not the ketone group [12]. Two weak absorptions at 2850 cm⁻¹ and 2800 cm⁻¹, which indicate moderately intense stretching of the aldehydic C-H and are frequently seen for the aldehyde group, were used to demonstrate the presence of the aldehyde group. These bands are caused by a Fermi resonance between the fundamental stretching of the aldehydic C-H and the first overtone of the bending vibration of the aldehydic C-H, which appears at 1,370 cm⁻¹. In the spectra, it appears at 1,370 cm⁻¹; these bands are typically seen for the aldehyde group. Furthermore, the strong peaks between 1570 cm⁻¹ and 1470 cm⁻¹ are inactive of stretching of C=C from the aromatic ring. Aromatic =C-H bending out of plane peaks was observed from 900 to 750. Two strong peaks at 1,160 cm⁻¹ and 1,200 cm⁻¹ indicated C-O stretching vibration. This IR spectrum was compared with the furfural IR spectrum published by Garba *et al.*, (2019), Ameh *et al.*, (2016), and Ong and Sashikala (2007) and it suits that spectrum.

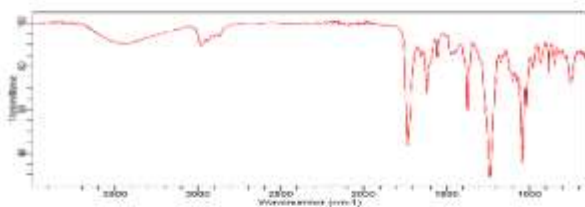


Figure 2: FT-IR Spectrum of Furfural-Acetone Adduct (FAA).

The FT-IR analysis of the Furfural-Acetone-Adduct (Fig. 2) obtained, shows the frequency of the main absorption bands illustrates the C-H vibrational frequency which appears at 3140 and 3120 cm^{-1} , corresponding to the sp^2 vibration in the furan ring. The stretching absorbance C=O observed at 1600 cm^{-1} infers the carbonyl group, and a sharp stretching absorbance band at 1010 cm^{-1} probably indicates C-O stretching for cyclic C-O-C linkages of furfural. The peaks at 1450 cm^{-1} and 1550 cm^{-1} may be a result of C=C stretching vibration in the furan unit. Similarly, the lower broad absorption at 3400 cm^{-1} could be due to the presence of O-H vibration, which could be attributed to the absorption of the solvent (ethylacetate) that remained in the product, similar to finding of Garba, *et al* (2019) and Gandini (2010).

3.2 NiO/SiO₂ Catalyst Characterization

The prepared NiO/SiO₂ catalyst was characterized using X-ray Fluorescence (XRF) ARL QUANT'X EDXRF ANALYSER SN9952120 Model and The Fourier transform infrared (FT-IR) M530 model Spectroscopy.

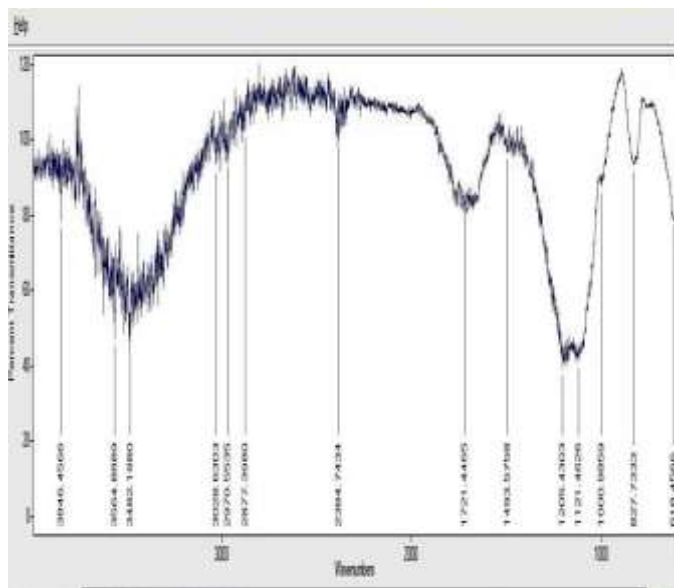


Figure 3: FT-IR Spectrum of NiO/SiO₂ catalyst.

The FT-IR spectra for NiO/SiO₂ registered in the range of 600-4000 cm^{-1} as presented in Figure 3 above. Absorption peaks with the FT-IR spectrum of NiO/SiO₂ show the vibrational peaks representing the characteristic metal-oxygen stretching frequencies associated with the vibrations of Ni-O-Si-O and Ni-O-Si bonds. The spectra show a broad band at 3411 cm^{-1} that is related to the silanols SiOH stretch vibration (O-H) present on the silica surface (Querem *et al.*, 2018). The bands centered at 1,121.46 and 827.73 cm^{-1} correspond to the asymmetrical and symmetrical stretch vibration mode associated with the Si-O-Si which is found at 1050 cm^{-1} for pure silica, and stretch Ni-O-Si respectively (Bonakin *et al.*, 2015), finally, The absorption peak at 618.45 cm^{-1} can be associated with the Ni-O. The characteristic absorption of NiO/SiO₂ observed corresponds to the absorption of NiO/SiO₂ reported by Zhang *et al.*, (2013) and Tarafdar *et al.*, (2005).

Table 1 XRF Results of NiO/SiO₂ Prepared using Impregnation method used for hydrodeoxygenation of FAA to Liquid hydrocarbons.

Element	Peak(cps/mA)	Relative Peak (%)
SiO ₂	125654	73.939
NiO	41875	24.641
Fe ₂ O ₃	24	0.014
Al ₂ O ₃	890	0.524
MgO	109	0.064
Na ₂ O	2	0.001
SO ₃	363	0.214
P ₂ O ₅	942	0.554
CaO	30	0.018
K ₂ O	2	0.001
TiO ₂	9	0.005
Cr ₂ O ₃	13	0.008
BaO	2	0.001
SrO	2	0.001
Sb ₂ O ₃	6	0.004
Cs ₂ O	5	0.003
ZrO ₂	14	0.008

The percentage of metal analysed by XRF (Table 1) presents a relative peak of 73.939% SiO₂ support and 24.641% NiO. The result also reveals the presence of some other elements which were also detected at low percent as presented in the table above.

Table 2: Compositions of Hydrodeoxygenated Products

Name of Hydrocarbon	Molecular Formula	Molecular Weight(g)
Nonane	C ₉ H ₂₀	128
Decane	C ₁₀ H ₂₂	142
Dodecane	C ₁₂ H ₂₆	170
2-propenylidenecyclobutene	C ₇ H ₈	92

3.3 GC-MS of Hydrodeoxygenated Product of Furfural Acetone Adduct (FAA)

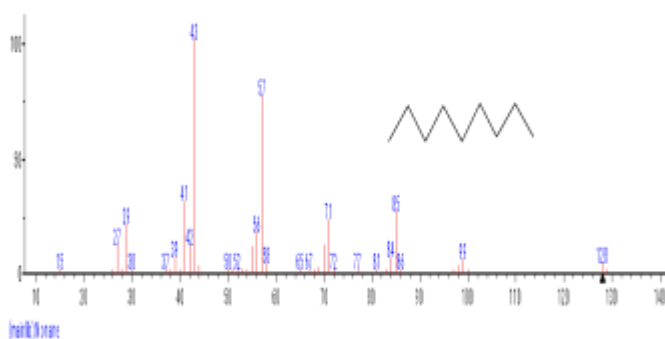
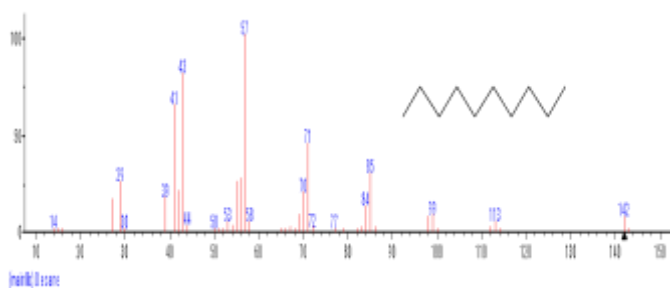
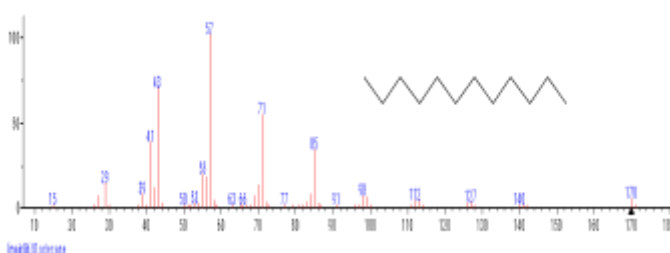
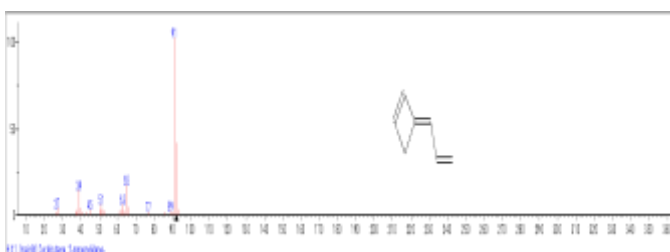


Figure 4a: GC-MS Chromatogram of Nonane (C₉H₂₀)

Figure 4b: GC-MS Chromatogram of Decane (C₁₀H₂₂)Figure 4c: GC-MS Chromatogram of Dodecane (C₁₂H₂₆)Figure 4d: GC-MS Chromatogram of 2-propenylidencyclobutene (C₇H₈)

The mixture of Furfural Acetone Adduct (FAA) was subjected to direct Hydrodeoxygenation (HDO) using NiO/SiO₂ as a catalyst. The reaction was carried out in a stainless-steel tubular reactor using water as solvent. After heated at 150°C for 8hrs and 2bar hydrogen, the product was analysed using GC-MS (GC 7890B, MSD5977A, Agilent Technology). The result in Table 2 above shows the distribution of the alkanes obtained from hydrodeoxygenation of aldol adducts. The Hydrodeoxygenation products using NiO/SiO₂ catalyst were detected as the mixture of alkane derivatives and oxygenated product. The products were mainly liquid hydrocarbons with a carbon range C₉-C₁₂. Hydrocarbons yields of the Alkanes and Cycloalkenes products obtained from hydrodeoxygenated product over NiO/SiO₂ were 86.61% and 1.46% respectively. similar work was reported by Han, *et al.*, (2015) on hydrodeoxygenation of pyrolysis oil for hydrocarbon production using nanospring-based catalysts. Analysis of GC-MS of the product (Fig. 4(a-d)) above showed the products obtained are Nonane, Decane, Dodecane, and 2-propenylidencyclobutene. There were some other organic oxygenates identified by the GS-MS data including 2-butoxy ethanol and 11-(2-cyclopenten-1-yl) undecanoic acid which are most likely by-products. The hydrogenation, ring opening, and deoxygenation reaction occurred giving the varied products. Wang *et al.*, (2014) obtained an experimental yield of more than 90% liquid alkanes (aviation fuels range C₈-

C₁₅) using Ni/ZrO₂-SiO₂ from raw concorb. Garba *et al.*, (2019) reported 77.50% of liquid hydrocarbons with a carbon range C₁₀-C₂₂ from hydrodeoxygenation of furfural-acetone adducts over NiO/Al₂O₃ obtained from hemicelluloses extract of millet husk.

IV. CONCLUSION

Liquid hydrocarbons were produced from Furfural obtained from Hemicellulose of melon seed husk by catalytic hydrodeoxygenation. The pathway involved the simultaneous steps of melon seed husks hydrolysis/dehydration to furfural, Aldol condensation of furfural and acetone to give Furfural-acetone adduct (FAA), and hydrodeoxygenation of the Furfural Acetone Adduct (FAA) to the final hydrocarbons (C₉-C₁₂ alkanes and cycloalkene). The NiO/SiO₂ catalyst was produced via the impregnation method. The FT-IR of NiO/SiO₂ revealed the presence of functional group Si-O-Si and a peak at 618.45 cm⁻¹ associated with the Ni-O. 73.939% Silica (SiO₂) and 24.641% NiO were obtained by the XRF analysis of NiO/SiO₂ Catalyst. More than 86% of liquid alkanes and 1.46% cycloalkenes yields were obtained by hydrodeoxygenation of Furfural Acetone adduct (FAA) over NiO/SiO₂. In the liquid alkanes, the main carbon chain was in the ranges of C₉-C₁₂, both of which are suitable for transportation fuels.

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