

Production of Diesel and Jet Fuel Range Hydrocarbon from Furfural via Aldol-Condensation and Hydrodeoxygenation Process

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Abstract

The exploitation of biomass for energy and biochemical production has been recognized as a viable option to overcome the challenges of fossil fuel posed to the environment. The study reviled the production of jet fuel range and diesel via aldol condensation and hydrodeoxygenation process. Furfural produced from millet husk was condensed with acetone using an aldol condensation reaction to obtain the furfural-acetone-furfural (F-Ac-F) dimers under mild condition 85°C, 20 cm³ of 4M NaOH and vigorous stirring (500 rpm/min) for 30 min. The Furfural-Acetone-Furfural dimer was subjected to hydrodeoxygenation to produce liquid hydrocarbons with the selectivity of 77.5% over NiO/Al₂O₃ at 220°C reaction temperature, 30 bar pressure, and reaction time of 1 h. The study revealed the potential of furfural in the generation of diesel and jet fuel range hydrocarbons as well as the efficacy of NiO/Al₂O₃ as a catalyst for hydrodeoxygenation reaction.

Keywords: Furfural; Aldol-condensation; Hydrodeoxygenation; Jet Fuel; Diesel.

1. Introduction

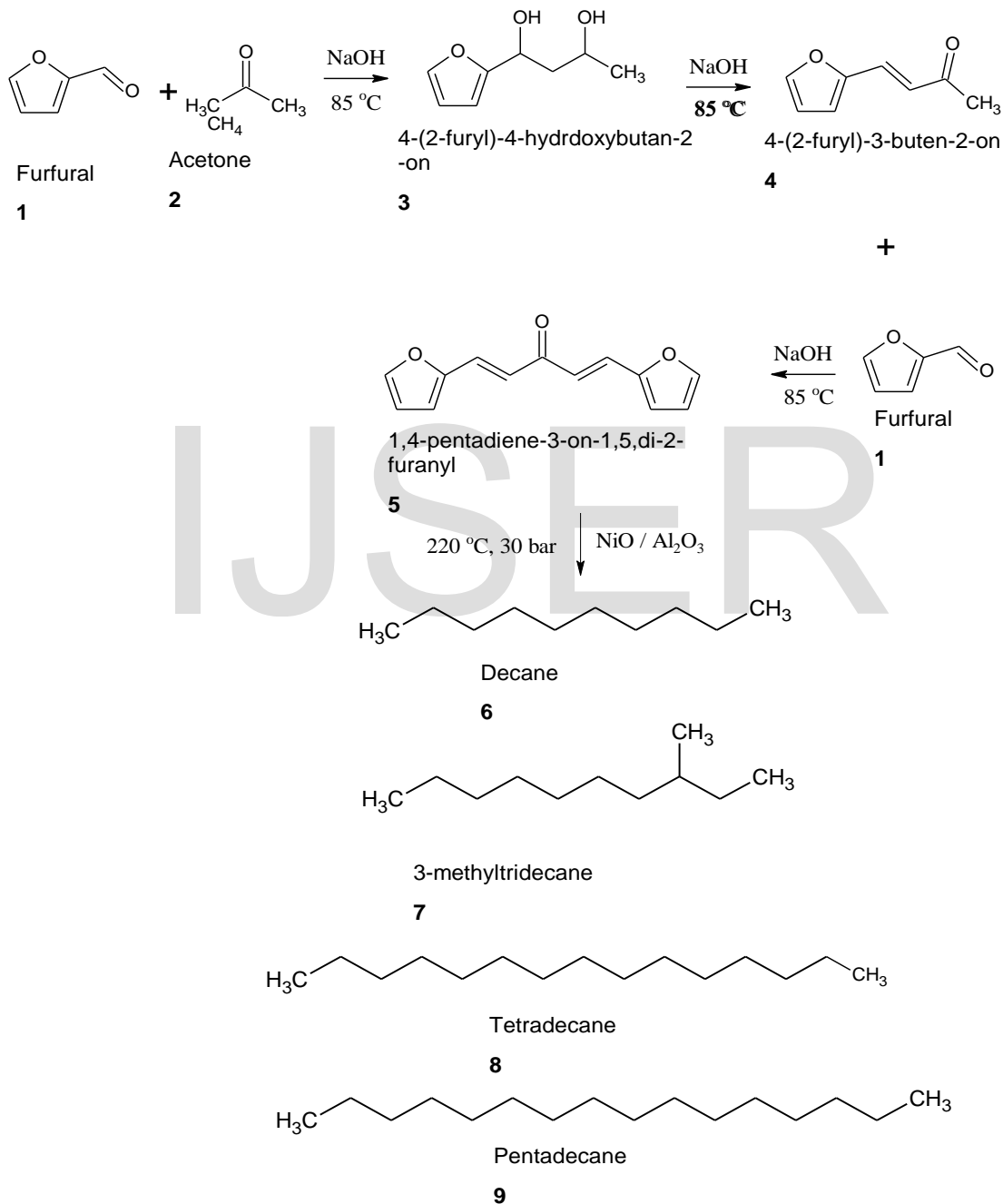
The challenges of fossil fuels and constant problems it posed to the environment has shifted the world in finding an alternative bio-based liquid fuels from a renewable source to counter the current global concern [1-3]. Hence, the utilization of renewable feedstocks [4] such as lignocellulosic materials for the production of valuable chemicals and fuels has been perceived as a viable option to solve the current environmental challenges.

Huber et al. [5] reported that jet fuels range alkanes could be obtained from lignocellulosic biomass by a novel route, wherein C₆ and C₅ sugars were firstly produced by hydrolysis of biomass and then converted into 5-hydroxymethylfurfural and furfural, respectively, by a dehydration step; 5-hydroxymethylfurfural and furfural were further reacted with acetone by an aldol condensation step to produce jet fuel intermediates. Aldol condensation was typically performed in the presence of base catalysts, usually by adding homogeneous catalysts such as NaOH [6-7], KOH, and NH₃·H₂O [8]. In a subsequent study, West et al. [9] conducted the condensation of furfural and hydroxymethylfurfural with acetone in an aqueous phase, using NaOH as a catalyst and the limited solubility of furfural in water made it necessary to use high amounts of a base to observe the substantial activity. Recently, Deepak and Ganapati, [10] used mixed oxide catalysts with various ratios for the condensation of furfural with acetone and achieved furfural conversion (96%) and high selectivity of FAc (98%). Similarly, Zdenek et al. [11] described aldol condensation of cyclohexanone and furfural using Mg/Al mixed oxides and rehydrated mixed oxides and the yield of condensation product was up to 68%.

Lesiak et al. [12] also described liquid phase hydrogenation of furfural in water at 90°C and 2.0MPa of hydrogen pressure over Pd–Cu/Al₂O₃ catalysts. After 2 h of reaction and using huge loading of monometallic 5% Cu/Al₂O₃ catalyst (about twice as the amount of furfural) 100%, selectivity to liquid hydrocarbon at 81% conversion was obtained.

A recent study by Peiying et al. [13] reported the hydrodeoxygenation of aldol adduct over NiCu/Nb₂O₅ catalyst to liquid alkanes and the result shown promising

performance with 86.5% yield of octane and 5.1% yield of heptane. In another study Isaac et al. [14] demonstrated the efficient tandem catalyst to selectively convert bio-oil to hydrocarbons with enhanced C₄₊ fuel yield in a fixed bed reactor of a small pilot plant.



Scheme 1: Scheme of possible routes for Aldol- Condensation and hydrodeoxygenation of Furfural with Acetone

2. Material and Methods

2.1 Catalyst Preparation

The catalyst was prepared by the incipient wetness method [15]. 100 cm³ of 0.6M solution of hydrated Nickel (II) nitrate was added drop-wise into the alumina powder (Al₂O₃) with continuous mixing using a magnetic stirrer. The prepared slurry was dried in an oven at 80°C for 8 hours and then calcined in the furnace at 600°C for 4 hours.

2.2 Aldol Condensation of Furfural with Acetone

Aldol condensation of furfural with acetone was performed in a stainless-steel reactor equipped with a magnetic stirrer. 10 cm³ of the distillate (furfural) was mixed with 5 cm³ of acetone in the ratio of 2:1 and then aqueous ethanol (50%) was added. The reactor was heated to 85°C, and then 20 cm³ of 4M NaOH was added into the mixture with vigorous stirring (500 rpm/min) for 30 min [6]. After reaction time elapsed, the resultant mixture was filtered and washed three times with ethanol to remove the excess NaOH. The crystals obtained from the reaction was dissolved in ethyl acetate and was analyzed using Fourier-transformed infrared spectroscopy (FT-IR) and ultraviolet-visible spectroscopy at a wavelength of 200 to 400 nm, respectively

2.3 Hydrodeoxygenation

The hydrodeoxygenation (HDO) of the aldol product was carried out at 220°C in a stainless steel tubular reactor. 30 cm³ of the aldol adduct and 1.8 g NiO/Al₂O₃ catalyst was heated in the reactor at 220°C for 1 hr under an inert atmosphere and at 30 bars of Hydrogen. The liquid product obtained at the end of the reaction was filtered and analyzed using Gas chromatography-mass spectrometry (GC-MS) [16].

3. Results and Discussion

3.1 Analysis of the Aldol Adducts

The result for the characterization of aldol adducts using FT-IR was shown in Table 3.1 and the peak for each absorption was assigned.

Table 3.1: FT-IR 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

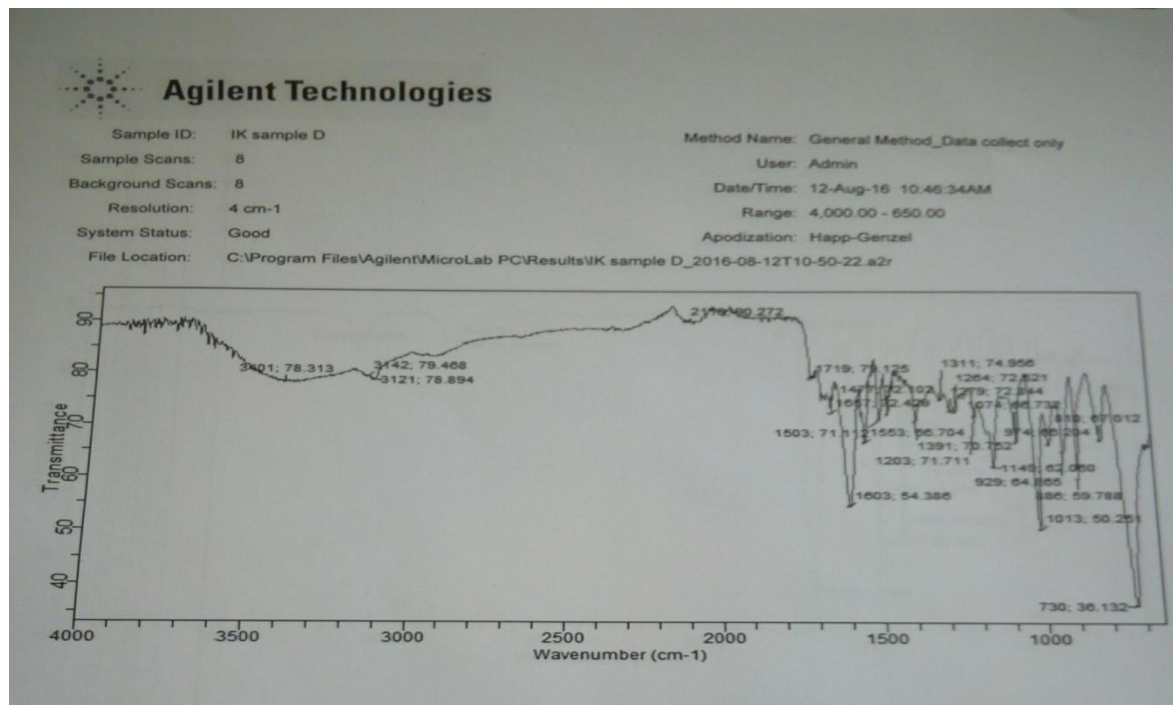


FIGURE 1: FT-IR Spectrum of the Aldol Adducts

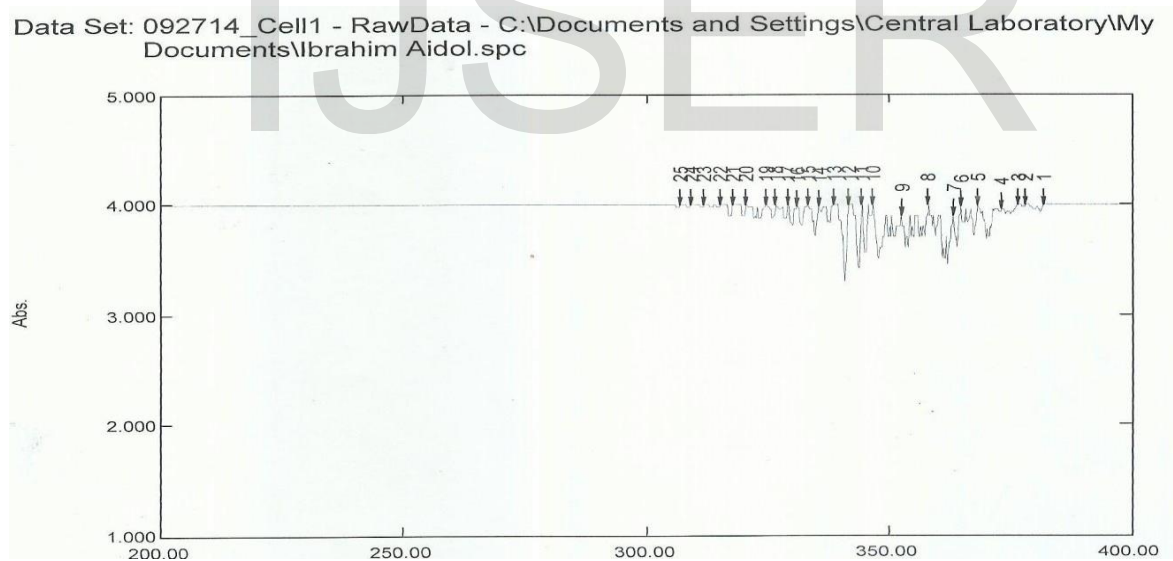


Figure 2: Ultraviolet-visible spectrum of the Aldol adduct (Source: This work)

The IR spectrum of Furfural-Acetone dimer obtained was recorded (Table 3 and figure 1). The frequency of the main absorption bands illustrated that the (C–H) vibrational frequency appears at 3142 cm^{-1} and 3121 cm^{-1} correspond to the sp^2 vibration in the

furan ring. The stretching absorbance ($C=O$) was observed at 1603 cm^{-1} infers the carbonyl group and a sharp stretching absorbance band at 1013 cm^{-1} indicates C-O stretching for cyclic C-O-C linkage of furfural. The peak at 1553 cm^{-1} and an overtone at 2116 cm^{-1} as a result of $C=C$ stretching vibration in the furan unit. Also, there is 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 remains in the product. The spectrum observed was similar to those reported by [17-18].

The product was also analyzed using the Ultraviolet-visible spectroscopic method (Figure 2). Absorption maximum in the region of 200–400 nm could be assigned to the conjugated system of the substituted furan molecule. The UV/Vis spectrum shows a strong absorption maximum at 341nm and 363 nm that correspond to Furfural-Acetone and Furfural-Acetone-Furfural respectively as observed [19]. This indicated that substituting the hydrogen atom by the furyl chain in position 5 causes significant bathochromic shift (by 52 nm) of the absorption maximum of hemicellulose hydrolysates (284-320nm), which can be assigned to the prolongation of the conjugated system of the molecule [20].

3.2 Analysis of the Hydrodeoxygenated Products

The chemical compositions of hydrodeoxygenation products over NiO/Al_2O_3 catalyst analyzed using GC-MS are presented in Table 3.2 below:

Table 3.2: Compositions of Hydrodeoxygenated Products

Name of Hydrocarbon	Molecular Formula	% Relative Peak
Decane	C ₁₀ H ₂₂	13.59
3-Methyltridecane	C ₁₄ H ₃₀	12.01
Tetradecane	C ₁₄ H ₃₀	5.36
Pentadecane	C ₁₅ H ₃₂	6.13
Hexadecane	C ₁₆ H ₃₄	17.48
Eicosane	C ₂₀ H ₄₂	12.52
Docosane	C ₂₂ H ₄₆	10.41

Results in Table 3.2 shows the distribution of the alkanes obtained from hydrodeoxygenation of aldol adducts. The products were mainly liquid hydrocarbons with a carbon range of C₁₀ – C₂₂. 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 C₁₆ viz., eicosane, and docosane, which could be formed due to decomposition and polymerization reaction. In the liquid phase, other than alkanes, there were some other organic oxygenates identified by GC– MS, including ethanol, 2-oxepanone, and acetic acid which are most likely byproducts. Rong *et al.* [7], obtained an overall experimental yield of 76% liquid alkanes (jet fuel range) corresponds to a weight-percent yield of 0.46 kg of alkanes per kg of xylose (monomer and oligomers) in the hemicelluloses extract. Faba *et al.* [16]

reported 21.5% of tridecane from 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 problems associated with fossil fuels and the demand for sustainable and ecofriendly fuel over the past decade was one of the driving forces for the researchers and industries to quest for an alternative source of liquid fuels and chemicals from renewable sources. The study showed that the production of liquid diesel and jet fuel range from the aqueous phase aldol condensation of furfural with acetone followed by subsequent hydrodeoxygenation was successfully performed using a catalytic conversion. A high temperature of 220°C was found to be most suitable for catalysts to perform the hydrodeoxygenation activity. However, the use of NiO/Al₂O₃ at 220 °C was discovered to be highly active and stable for the hydrodeoxygenation of aldol condensation product. 77.5% carbon yield of diesel and jet fuel range was achieved and no significant catalyst deactivation was observed during the reaction time. The study revealed the potentials of producing bio-based fuels from renewable biomass.

5. Compliance with ethics requirements

This paper does not contain studies with human/animal subjects

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

Authors acknowledge Petroleum Technology Development Trust Fund for financial support.

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