

Aqueous-Phase Synthesis of Hydrocarbons from Furfural Reactions with Low-Molecular-Weight Biomass Oxygenates

Foster A. Agblevor* and Hossein Jahromi

USTAR Bioenergy Center, Biological Engineering Department, Utah State University, Logan, Utah 84322, United States

ABSTRACT: Catalytic pyrolysis of lignocellulosic biomass generates water-soluble low-molecular-weight oxygenates such as acetic acid, acetone, furfural, butanone, guaiacol, phenol, etc. These compounds are usually not suitable for conventional hydrocarbon fuel applications. A new heterogeneous catalyst has been developed that simultaneously catalyzes alkylation, hydrodeoxygenation, and hydrogenation of these small oxygenate molecules in aqueous media to produce C₆ to C₁₄ hydrocarbons in a one-pot synthesis. In these syntheses, acetic acid, propionic acid, furfural, butanone, pentanone, heptanone, and 2,6-dimethyl-4-heptanone reacted to produce straight- and branched-chain alkanes. The aldehydes reacted with furan to form straight-chain liquid hydrocarbons, while the ketones reacted with 2-methylfuran to produce branched-chain liquid hydrocarbons. All the reactions occurred in aqueous media at 350 °C. The gaseous products included low-molecular-weight hydrocarbons such as methane, propane, butane, and pentane.

1. INTRODUCTION

The production of hydrocarbon fuels from renewable biomass sources remains a major challenge to the research community.^{1–4} Although progress has been made in the pyrolysis of biomass to liquid fuels,^{5,6} there are still major challenges in the quality of the fuel, especially in its application as a transportation fuel.^{7,8} The pyrolysis oils are unstable, acidic, viscous, and reactive, and they have low energy density and high oxygen content; therefore, they cannot be directly used as transportation fuels.⁹ Furthermore, there are only a few companies that are producing the raw pyrolysis oils as heating fuels on a commercial basis.^{10,11} Current research efforts are focused on stabilizing the pyrolysis oils to enable them to be co-processed with petroleum feeds, processed on standard unit operations, and potentially processed in stand-alone biorefinery plants.¹² The stability improvement studies include esterification, low-severity hydrotreatment, and catalytic pyrolysis.¹³ The focus of this paper is on the catalytic pyrolysis oils of lignocellulosic biomass. Although catalytic pyrolysis (*in situ* and *ex situ*) produces a much more stable pyrolysis oil with lower oxygen content and higher energy density, it suffers from major deficiencies: it produces large quantities of non-condensable gases and large quantities of low-molecular-weight water-soluble oxygenates.^{12,14–17} The water-soluble oxygenates pose several challenges, including wastewater treatment, loss of carbon, and overall decrease in product yield.^{18,19} The aqueous-phase pyrolysis products, which constitute 10–30 wt% of the products, are dissolved in water in concentrations of 10–20 wt%.^{12,17,18} Recovery of these water-soluble products from the aqueous phase to improve the overall efficiency of the biofuel production has also been a challenge.^{20,21} Several methods have been investigated using both model compounds, fractionated pyrolysis oils, and raw aqueous-phase oils.^{17,22–25} In the upgrading studies reported in literature, the model compounds and syntheses processes required the application of multiple steps, multiple catalysts, and different reaction conditions to produce hydrocarbon compounds.^{22,26–31} Usually one type of catalyst was used for ketonization, another for aldol condensation, and a third for hydrodeoxygenation.

Barrett et al.²⁷ reported a single-reactor process for aldol condensation and hydrogenation, but even that process required 24–26 h for the aldol condensation, followed by 4–6 h for hydrogenation, which produced C₆–C₁₃ oxygenated compounds. As far as the authors know, there are no reported catalysts for simultaneous ketonization, alkylation, hydrodeoxygenation, and hydrocarbon formation in a one-pot system in a few minutes.

In this paper we report aqueous-phase hydrotreatment of low-molecular-weight water-soluble products into a wide range of hydrocarbons using a novel catalyst in a one-pot synthesis process. The results show interactions between various aqueous-phase compounds to form hydrocarbons of various chain lengths. Although model compounds are reported in this paper, when the method was applied to real biomass aqueous-phase pyrolysis oil, the results were very similar.³⁵ The ultimate goal of this research is to produce hydrocarbon fuels and chemicals from biomass.

2. EXPERIMENTAL METHODS AND MATERIALS

2.1. Materials. The selection of model compounds for this research was based on the analysis of the aqueous-phase red mud catalytic pyrolysis liquids. The major compounds detected in this liquid were used for the model compounds studies to elucidate the reactions that occur during the hydrotreating of the aqueous-phase liquids and catalytic pyrolysis oils reported elsewhere.^{14,16,31,35} The liquid was obtained from the red mud catalytic pyrolysis of pinyon juniper wood using a pyrolysis pilot plant (Figure 1) details of which are explained elsewhere.¹⁴ The model compounds used for these studies were obtained from various chemical vendors and were used as received without any further purification. The compounds included acetic acid (EMD Millipore Billerica, MD, USA), guaiacol, anisole, 2,3-butanedione, 3-hydroxy-2-butanone (Alfa Aesar, Haverhill, MA, USA), acetaldehyde, phenol, benzene, furfural, furan, 2-methylfuran (Sigma-Aldrich, St. Louis, MO, USA), acetone, ethanol, toluene, methanol (Pharmaco-AAPE9R, Orange County, CA, USA). Various standards were also obtained from these companies for product identification and quantification.

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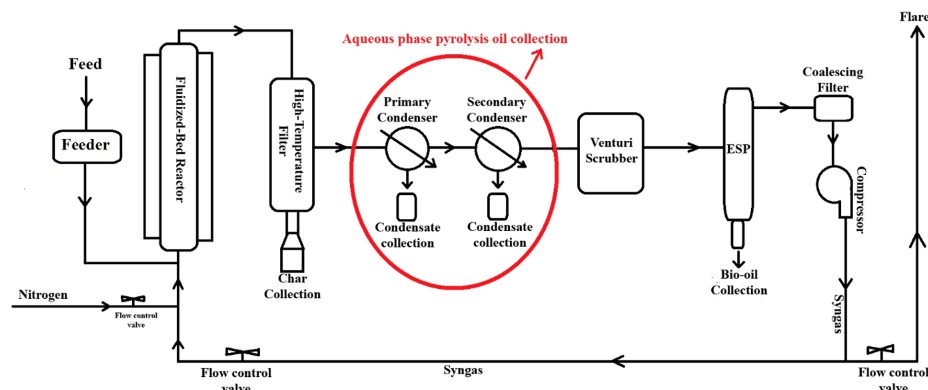


Figure 1. Pyrolysis pilot plant used for production of pinyon-juniper bio-oil.¹⁴

2.2. Catalyst Preparation and Characterization. Nickel/red mud (Ni/RM) catalyst was prepared in-house using the procedure described by Jahromi and Agblevor.^{34,35}

Ni/RM catalysts were prepared at 40 wt% nickel metal loading using wet impregnation method.^{34–38} At room temperature the calculated amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL of deionized water and then mixed with red mud (particle size $<90 \mu\text{m}$). The mixture was heated to 70°C and continuously stirred for 5 h to prepare the catalyst precursor. The catalyst precursor was dried at 105°C for 10 h and then calcined in a muffle furnace (Thermo Scientific, Inc., Waltham, MA, USA) at 620°C for 5 h. The calcined material was reduced for 6 h at 450°C with a reducing gas mixture of 10% H_2 and 90% N_2 at flow rate of 20 mL/min to obtain the final catalyst, which was labeled Ni/RM.³⁹

The preparation of the reduced red mud catalyst (RRM) was similar to that of the Ni/RM except that the Ni addition step was eliminated. The red mud catalyst precursor was dried at 105°C , for 10 h and calcined in a muffle furnace at 620°C for 5 h. The precursor was then reduced with 10% H_2 and 90% N_2 at a flow rate of 20 mL/min to obtain the final catalyst, which was labeled RRM.

The catalysts were characterized using thermogravimetric temperature-programmed reduction (TG-TPR), Brunauer–Emmett–Teller (BET) surface area analyzer, X-ray diffraction (XRD), inductively coupling plasma (ICP), and scanning electron microscopy (SEM) as reported previously.^{34,35}

2.3. Aqueous-Phase Hydrodeoxygenation Experiments. All aqueous-phase hydrodeoxygenation (AQHDO) experiments were conducted in a Parr Series 4560 300 mL autoclave reactor (Parr Instruments, Moline, IL, USA). This reactor had a variable speed magnetic drive and turbine agitator. A pressure gauge was used to measure the total pressure inside the reactor. A K-thermocouple immersed in the reactor was used to measure the reactant temperature. The reaction temperature was maintained at its desired value with an accuracy of $\pm 1^\circ\text{C}$. The setup had an electrically heated jacket to ensure isothermal conditions. The temperature and speed of agitation were controlled by a Parr 4848 controller.

In each experiment, the reactor was charged with reactant (100 g) and Ni/RM catalyst (3 g). The reactant consisted of 15 wt% organic compound. Thus, for a single compound 15 g of material was added to 85 g of water, and 3 g of catalyst was added. It was assumed that the water was only a reaction medium. If two compounds were under investigation, then 7.5 g of each compound was dissolved in the water. The combination of various compounds investigated are shown in section 3.5. The reactor was purged with N_2 to ensure an inert atmosphere. The reactor was then charged with high purity hydrogen supplied from a reservoir tank to the desired pressures of 6.21 MPa (900 psi). A gas sample was taken from a gas release valve from the gas sampling port for gas analysis when the reactor was at room temperature. The reactor

was then heated to reaction temperature (350°C) at heating rate of $15^\circ\text{C}/\text{min}$. The reaction time was recorded when the set temperature was reached. After the desired reaction time (30 min), the reactor was cooled to room temperature using the internal cooling coil. A gas sample was collected in a Tedlar bag for gas analysis when the reactor was cooled to room temperature. The reproducibility of experiments was checked and the error in all experimental measurements was found to be less than 3%.

Another set of experiments was carried out on the RRM (catalyst support), which did not contain any nickel to determine the effect of the support on the reactions. The reaction conditions were identical to those for the Ni/RM.

In blank experiments (without catalyst) 100 g of reaction mixture was charged into the reactor and the reactor was pressurized to 6.2 MPa (900 psi) with hydrogen and allowed to react for 30 min at 350°C to determine if the reactor walls played any role in the observed reactions. All experiments were conducted in triplicate. The blank experiments showed no reactivity of the reactor walls. All results reported are therefore assumed to have no reactor wall influence.

2.4. Analysis of AQHDO Products. Hydrogen consumption was measured according to the procedure reported previously.³³ Gas analysis was performed using an Agilent 490 micro-gas chromatograph. The micro-GC was equipped with 5-Å molecular sieves and porous polymer (PP) columns and two TCD detectors for each column.³³ The liquid products of AQHDO experiments were analyzed by HPLC (Shimadzu Scientific, Columbia, MD, USA) using a RID-10A detector and a Kromasil 100-5-C18 column (AkzoNobel, Amsterdam, The Netherlands). The HPLC instrument was equipped with an LC-10AT pump, SCL-10Avp controller, and SIL-10A autosampler. CLASS-VP 7.3 SP1 software was used to analyze HPLC chromatograms. A CTO-10A column oven was used to maintain the column temperature at 55°C during the analysis. The injection volume was $0.25 \mu\text{L}$, and acetonitrile at flow rate of 0.6 mL/min was used as the mobile phase. Data acquisition time was 80 min for all analyses.

The liquid samples were analyzed for furfural, furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFA), furan, 2-methylfuran (2-MF), tetrahydrofuran (THF), 2-methyltetrahydro furan (2-MTHF), butanone, 2-butanol, 2-butanone, 2-pentanone, 3-pentanone, 3-pentanol, 2-heptanone, ethanol, ethyl acetate, acetaldehyde, propionaldehyde, propanol, acetone, hexane, heptane, 3-methyloctane, 3-ethyloctane, 2-methylheptane, and 4-methylnonane. The identity of the synthesized compounds were confirmed by gas chromatography/mass spectrometry (Shimadzu GC/MS-QP5000, Shimadzu Scientific, Columbia, MD, USA) and NMR (^1H and ^{13}C) using a Bruker 500 MHz instrument (Bruker Corporation, Japan).

The elemental composition of AQHDO products was determined using a ThermoFischer Scientific Flash 2000 organic elemental analyzer

Table 1. AQHDO of Individual Compounds Using Ni/RM Catalyst

parameter	reactant			
	acetic acid	propionic acid	furfural	2,3-butanedione
conversion (%)	78.5	85.3	100	100
H ₂ consumption (mol H ₂)	1.17	1.04	0.89	0.67
product distribution (wt%) (H ₂ O-free basis)	acetaldehyde, 6.7 ethanol, 17.3 acetone, 30.7 ethyl acetate, 29.5 isopropyl alcohol, 15.8	propionaldehyde, 56.2 propanol, 31.5 3-pentanone, 6.6 3-pentanol, 5.7	furan, 36.1 2-MF, 31.9 THF, 14.8 2-MTHF, 17.2	2-butanone, 63.7 2-butanol, 36.3
gas analysis (mol%) (H ₂ -free basis)	CO CO ₂ CH ₄ C ₂ H ₆ C ₃ H ₈ C ₄ H ₁₀ C ₅ H ₁₂	5.9 9.0 46.6 25.2 13.4 — — 14.4	6.9 13.4 24.1 6.5 34.7 34.4 37.4	3.6 6.2 18.5 — — 100 —

Table 2. Catalytic Processing of Carboxylic Acids Using RRM Catalyst Support

parameter	reactant (under N ₂)		reactant (under H ₂)	
	acetic acid	propionic acid	acetic acid	propionic acid
conversion (%)	67.6	73.4	69.3	74.7
product distribution (wt%) (H ₂ O-free basis)	acetone, 100	3-pentanone, 100	acetone, 100	3-pentanone, 100
elemental composition (wt%)	C H O	62.06 ± 0.03 10.35 ± 0.04 27.59 ± 0.02	69.74 ± 0.05 11.64 ± 0.02 18.62 ± 0.04	62.04 ± 0.02 10.36 ± 0.05 27.60 ± 0.01
gas analysis (mol%) (N ₂ - and H ₂ -free basis)	CO ₂	100	100	100
¹³ C NMR chemical shifts (ppm)	30.06, 205.69	7.37, 34.95, 211.23	30.09, 205.63	7.39, 34.91, 211.26

(ThermoFisher Scientific, Waltham, MA, USA; CHNS configuration), and the oxygen content was calculated by difference according to ASTM D5291.

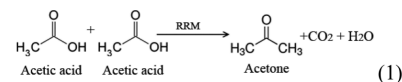
3. RESULTS

The characterization of the Ni/RM catalyst has been reported elsewhere and will not be repeated here.^{24,35} The AQHDO results were grouped according to the main substrates investigated. AQHDO of individual compounds on red mud-supported nickel (Ni/RM) and reduced red mud (RRM) are reported below.

3.1. Aqueous-Phase Acetic Acid HDO on Ni/RM and RRM. The 15 wt% acetic acid water solution was hydrotreated on Ni/RM without any other compound as a baseline for comparison. The liquid products were ethanol, propanol, acetaldehyde, ethyl acetate, and acetone (Table 1). These hydrogenation reactions were catalyzed by Ni as reported by other researchers.⁴⁰ The ethyl acetate derived from the reaction of acetic acid with ethanol, and the propanol from the hydrogenation of acetone.^{40,41} The acetic acid reduction products such as acetaldehyde and ethanol were also catalyzed by elemental Ni as reported in the literature.^{33,40,42}

The most interesting aspect of the aqueous-phase hydrodeoxygenation (AQHDO) of acetic acid was the formation of acetone, which was not reported by other researchers using

nickel catalyst.^{40,42} The acetone was formed from the ketonization reaction of acetic acid as shown in eq 1 below.^{40,42}

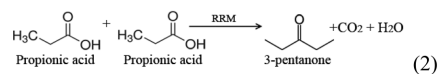


It was hypothesized that the ketonization reaction occurred on the RRM and therefore aqueous acetic acid was treated under similar conditions using RRM, and only acetone was detected in the liquid products (Table 2). This clearly showed that RRM catalyzed the ketonization reaction, which is in agreement with Yathavan and Agblevor who observed production of high levels of ketones in the biomass pyrolysis products.¹⁶ Ketonization of acetic acid to acetone has been extensively studied by several researchers including Glinsk et al.⁴³ who investigated ketonization of carboxylic acids using 20 metal oxides. They reported that CeO₂/Al₂O₃ and MnO₂/Al₂O₃ were the most active catalyst systems and individual oxides were less active than supported oxides. Since the RRM contain a large number of oxides, this explains the ketonization of the acetic acid to acetone. Furthermore, since both ketonization and hydrogenation reactions were observed on Ni/RM catalyst, this suggested that the surface of the catalyst support was not totally covered by the Ni. Scanning electron microscopy (SEM) analysis of the catalyst confirmed

that Ni was distributed as nanoparticles on the RRM support and therefore ketonization reactions could occur on the exposed areas of the support.³⁴

The gaseous products analyzed using micro GC were dominated by methane, ethane, and propane (Table 1), which were due to methanation of CO₂ and CO as well as cracking of other low-molecular-weight hydrocarbon components (Table 1).

3.2. Aqueous-Phase HDO of Propionic Acid on Ni/RM and RRM. The AQHDO reaction of the propionic acid on Ni/RM followed a similar pathway as the acetic acid. In this case, there were two major pathways, reduction of propionic acid to propanal (propionaldehyde) and propanol^{44,45} and ketonization of propionic acid to pentanone.³² In addition to these two major compounds, other compounds such as 3-pentanol (as a result of partial hydrogenation of 3-pentanone), and gases were produced (Table 1).⁴⁶ When RRM was used as the catalyst, only pentanone was produced, which corroborated the acetic acid ketonization reaction. The reaction for this process is shown below (reaction 2):



Although the conversion of the propionic acid was higher than the acetic acid (Table 1), the 3-pentanone produced was 5 times lower than acetone production from acetic acid ketonization. The dominant products from AQHDO of propionic acid were propanal and propanol. These differences in ketonization rates between the acids were also observed by Glinski et al.⁴³ who reported that at temperature below 325 °C, acetic acid ketonization was faster than that of propionic acid, but at higher temperatures, the ketone productions were similar. Selective hydrogenation of propionic acid to propanal was therefore faster than the ketonization.

The ketonization reactions of both acetic and propionic acids on RRM were independent of the gaseous atmosphere. Under H₂ and N₂ atmospheres the conversions of both acids were similar (Table 2), but both pressure and reaction temperatures influenced the reactions. At higher temperatures and pressures the reactions proceeded faster.

3.3. Aqueous-Phase Furfural HDO on Ni/RM and RRM.

The AQHDO of furfural was conducted in a similar manner as the acetic acid using Ni/RM. The compounds detected in the liquid products were THF, 2-MTHF, furan, and 2-MF. These products clearly derived from partial hydrogenation and hydrodeoxygenation of furfural (Table 1).^{47–50} In addition to these products, there were gaseous products dominated by methane, butane, and pentane (Table 1). When aqueous furfural was run on the RRM, there was no reaction, which was in contrast to the acetic and propionic acids reactions; but it clearly confirmed that the products detected were due to the nickel hydrodeoxygenation of furfural.

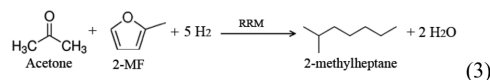
3.4. Aqueous-Phase HDO of 2,3-Butanedione on Ni/RM and RRM. The AQHDO of the 2,3-butanedione was similar to those for the other compounds. In this case, the main products were butanol, butanone, and butane (Table 1). Butanol and butanone formation were all attributed to the AQHDO on the Ni catalyst because when the 2,3-butanedione was run on RRM, no products were formed, which again confirmed that RRM did not participate in the hydrodeoxygenation of the ketones. The AQHDO of the acetic and propionic acids, furfural, and 2,6-butanedione clearly showed that the catalyst support in Ni/RM catalyzed the ketonization of the carboxylic acids, but did not

have any influence on the reactivity of furfural, ketones, and aldehydes when single substrates were used.

3.5. Aqueous-Phase HDO of Dual Compounds on Ni/RM and RRM. In these series of studies, dual reactants were investigated to assess the interactions between them. The reactions of these dual mixtures are discussed below.

3.5.1. Aqueous-Phase HDO of Acetone/Furfural on Ni/RM and RRM. Acetone is one of the soluble oxygenates found in the biomass pyrolysis aqueous-phase products, and it is also an intermediate in the AQHDO of acetic acid. The reactions of acetone with furfural were investigated under similar AQHDO conditions as those described above to support the proposed pathways for the acetic acid reactions with furfural.

In the case of acetone/furfural AQHDO on Ni/RM the only liquid hydrocarbon produced was 2-methylheptane (octane) which was immiscible with water. The other liquid products were THF, 2-MTHF, and furan (Table 3) that dissolved in the aqueous phase. When the reaction was conducted on RRM, there were no products either in the liquid or gas phases. Since no 2-MF was detected in the acetone/furfural AQHDO, it was hypothesized that the octane was produced from the reaction of 2-MF with acetone. This hypothesis was confirmed by conducting AQHDO on RRM using 2-MF and acetone. The only organic product of this reaction was octane, which was identified with HPLC, ¹³C NMR, and CHNOS analyses (Table 4). The reaction was stoichiometric with 100% conversion and stoichiometric yield of octane (reaction 3).



The 2-methylheptane formation was attributed to the reaction of acetone with a cyclic ether (2-MF) through alkylation reaction, which occurred on the RRM. It is interesting to note that the reaction of the acetone with the 2-MF resulted in ring opening and saturation catalyzed by the RRM to produce 2-methylheptane, which is in contrast to Li et al.²⁴ who did not report the formation of 2-methylheptane, but instead reported an oxygenated compound derived from the coupling of 2-MF dimer with acetone. This compound was further hydrotreated on various Pt catalysts to produce hydrocarbon compounds. Barrett et al.²⁷ reported a single-reactor process for sequential aldol-condensation and hydrogenation of biomass-derived compounds in water in which an oxide catalyst was used to catalyze the reaction between furfural and acetone and subsequently followed by hydrogenation with Pd/MgO-ZrO₂ catalyst. The condensation process alone required 24–26 h reaction time and under pressure and the hydrogenation step which followed immediately after flushing the reactor with hydrogen also required 4–6 h reaction time under starting pressure of 55 bar. The final product consisted of oxygenated C₅, C₈, and C₁₃ products. The Barrett et al.²⁷ and Li et al.²⁴ methods were clearly multiple-step processes and could not produce hydrocarbons through alkylation of the 2-MF in a single step as shown in the current work. These reported processes also required very long reaction times compared to 30 min or less required for the current method of hydrocarbon production. The current process did not involve aldol condensation of the furfural or furans with acetone because only one 2-MF molecule reacted with the acetone and no other organic compounds were produced on the RRM.

The formation of the 2-methylheptane occurred through an attack on the furan ring by the carbonyl oxygen and therefore the

Table 3. AQHDO of Dual Compounds Using Ni/RM Catalyst

parameter	reactant							
	acetone /furfural	acetic acid/furfural	propionic acid/furfural	2,3-butanedione/ furfural	2-pentanone/furfural	2-heptanone/furfural	2,6-dimethyl-4-heptanone/furfural	
conversion (%)	93.2	100	100	100	95.6	91.5	88.4	
H ₂ consumption (mol H ₂)	1.24	1.48	1.32	1.39	1.34	1.27	1.21	
product distribution (wt%) (H ₂ O- free basis)	2-methylheptane, 54.7	acetone, 11.5	3-pentanone, 9.4	3-methyloctane, 54.2	4-methylnonane, 56.2	6-methylundecane, 55.7	2-methyl-4-(2-methylpropane) nonane, 50.8	
	furan, 20.6	hexane, 36.9	heptane, 38.1	furan, 11.9	furan, 17.3	furan, 21.8	furan, 32.2	
	THF, 18.4	2-methylheptane, 28.7	3-ethyloctane, 34.7	2-butanone, 6.0	THF, 18.6	THF, 15.7	THF, 11.4	
	2-MTHF, 6.3	THF, 13.3	THF, 8.5	THF, 17.5	2-MTHF, 7.9	2-MTHF, 6.8	2-MTHF, 5.6	
gas analysis (mol%) (H ₂ -free basis)		2-MTHF, 9.6	2-MTHF, 9.3	2-MTHF, 10.4				
	CO	4.1	6.7	6.2	6.2	5.9	4.7	5.6
	CO ₂	10.9	13.3	13.5	14.4	15.1	14.4	15.3
	CH ₄	24.4	30.3	22.9	16.6	15.3	21.3	22.1
	C ₂ H ₆	—	21.9	12.7	—	—	—	—
	C ₃ H ₈	22.7	10.8	21.3	—	—	—	—
	C ₄ H ₁₀	32.3	9.7	13.1	43.9	22.1	26.6	30.5
	C ₃ H ₁₂	5.6	7.3	10.3	18.8	41.6	26.5	

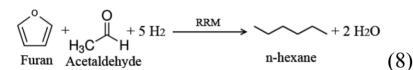
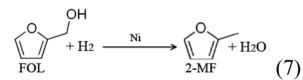
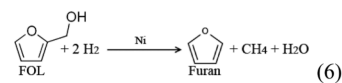
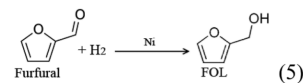
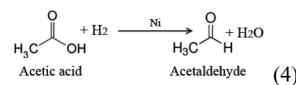
Table 4. AQHDO of Dual Compounds Using RRM Catalyst Support

parameter	reactant				
	acetaldehyde/ furan	acetone/2-MF	butanone/2-MF	2-pentanone/2-MF	2-heptanone/2-MF
conversion (%)	100	100	100	100	100
H ₂ consumption (mol H ₂)	0.55	0.44	0.46	0.44	0.26
product distribution (wt%) (H ₂ O-free basis)	n-hexane, 100	2-methylheptane, 100	3-methyloctane, 100	4-methylnonane, 100	6-methylundecane, 100
elemental composition (wt%)	C 83.70 ± 0.03 H 16.30 ± 0.04	84.19 ± 0.02 15.81 ± 0.04	84.37 ± 0.03 15.63 ± 0.02	84.51 ± 0.04 15.49 ± 0.01	84.72 ± 0.02 15.28 ± 0.02
¹³ C NMR chemical shifts (ppm)	14.16, 22.89, 31.87	14.15, 22.04, 22.71, 27.23, 28.09, 32.30, 39.17	14.17, 22.05, 22.87, 23.56, 24.67, 27.45, 28.31, 32.89, 39.43	14.22, 14.84, 19.78, 20.34, 23.24, 24.12, 29.57, 32.69, 37.01, 39.67,	14.21, 14.78, 22.25, 22.84, 23.19, 24.56, 27.39, 28.36, 29.36, 32.14, 37.55, 39.37

resulting hydrocarbon compound was branched. This hydrocarbon formation reaction occurred on one catalyst and did not require multiple steps and reactors as reported by other researchers.^{24,27}

The production of THF, 2-MTHF, and furan were attributed to HDO of the furfural on elemental nickel.^{47,48} The furan was converted to THF through ring saturation and the 2-MTHF was produced from the saturation of the 2-MF ring. It appears that the reaction of 2-MF with acetone was slower than the ring saturation reaction and thus some of the 2-MF formed initially was converted to 2-MTHF. Significant amounts of butane was also detected in the gaseous products because of the ring opening and further hydrogenation of THF on the nickel (Table 3). Further investigation of the reactions showed that acetone and other ketones did not react with 2-MTHF despite the fact that it is also a cyclic ether.

3.5.2. Neat and Aqueous-Phase HDO of Acetic Acid/Furfural on Ni/RM and RRM. The AQHDO of the acetic acid/furfural mixture on the Ni/RM catalyst showed very interesting results. The products consisted of *n*-hexane, 2-methylheptane, THF, 2-MTHF, and acetone (Table 3). The THF and 2-MTHF were typical furfural hydrodeoxygenation products as shown in the AQHDO of furfural on Ni/RM. However, what was significant was the near absence of the acetic acid AQHDO products observed when it was run alone and the absence of some of the furfural AQHDO products (furan and 2-MF). In place of the acetic acid AQHDO products, hexane and octane were the major compounds detected in the liquid products, which were immiscible with the water. The formation of these two products was explained in terms of the reaction network shown below:



Products of reactions 4–7 were intermediate compounds formed on the nickel surface, but reactions 8 and 9 occurred on the RRM surface. To verify this hypothesis, pure reactants for reaction 8 (furan and acetaldehyde) were obtained from vendors and reacted on the RRM. The only organic product detected was *n*-hexane (C₆H₁₄) (Table 4), which was immiscible with water

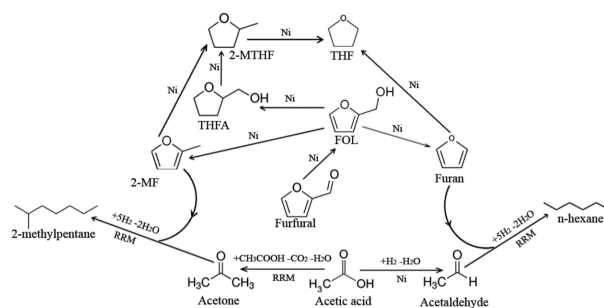


Figure 2. Overall reaction network of acetic acid/furfural AQHDO using Ni/RM catalyst.

and was easily separated as a very pure product. The structure of C_6H_{14} was verified by GC/MS and ^{13}C NMR of the sample (Table 4) and comparing it to those of authentic standards.

Similarly, pure reactants of reaction 9 (2-MF and acetone) were obtained from vendors and reacted on the RRM and this produced only 2-methylheptane with stoichiometric amount of hydrogen consumption (Table 4). The ^{13}C NMR of the synthesized 2-methylheptane was in agreement with the published ^{13}C NMR of 2-methylheptane.⁵¹ Thus, it is clear that the RRM was responsible for the alkylation and hydrodeoxygenation reactions of the intermediate products. The nickel produced the intermediate reactants, which then reacted on the RRM. The THF and 2-MTHF did not participate in these reactions and were detected in the aqueous-phase products (Table 3). The reaction rate of the AQHDO was probably slower than the formation of THF and 2-MTHF reactions and therefore some of the furan and 2-MF were saturated to form these compounds. The acetone for reaction 9 was attributed to the ketonization reaction shown in reaction 1 and discussed in section 3.5.1. The overall reaction network of acetic acid AQHDO is shown in Figure 2.

The formation of hexane from reaction 8 appears to be an alkylation reaction where carbonyl compound reacted with the furan and the oxygen from both the furan and the aldehyde were eliminated as water. In addition to elimination of the oxygen atoms, there was also ring opening and ring saturation on the RRM support. These reactions have not been reported in published literature. Although, several authors have reported hexane production from biomass, this derived from the ring opening and saturation of the benzene ring usually catalyzed by supported noble metals such as Pd, Pt, Re, Rh, and Ru or base metal catalysts such as Cu, Fe, and Ni. Barrett et al.²⁷ reported a C_6 product from biomass-derived compounds, but that was obtained from the hydrogenation of 5-hydroxymethylfurfural and not reaction of acetaldehyde with furan. Condensation reaction of acetaldehyde with furan catalyzed by hydrochloric acid for over 17 h resulted in the production of two oxygenated condensation products ($C_{10}H_{10}O_2$ and $C_{22}H_{22}O_4$).⁵² It is obvious that in order to obtain an alkane product, this condensation product will need to be hydrogenated.

When the acetic acid/furfural HDO was run in the neat form, there was rapid deactivation of the catalyst and large amounts of coke and gases were produced. The liquid products yield was very low but the composition of the liquid products was similar to that of the aqueous acetic acid/furfural HDO.

The cokes formed on the catalyst surface from both aqueous acetic acid/furfural and neat acetic acid/furfural HDO were

examined with thermogravimetric analyzer (TGA) in nitrogen and air atmospheres. When nitrogen was used for the TGA, no weight loss was detected, showing that no volatile compounds were left on the catalyst and only coke was present. However, when air was used on the recovered catalyst, the aqueous acetic acid/furfural HDO coke produced only one weight loss peak at 289 °C. The neat acetic acid/furfural HDO coke had four weight loss peaks (Figure 3). The first peak corresponded to the peak

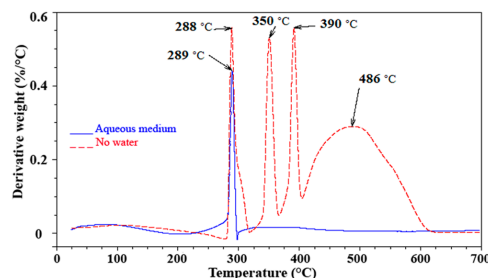
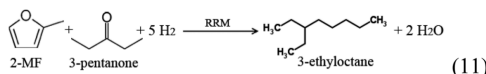


Figure 3. TGA of the used catalyst in aqueous medium (blue solid line) and in absence of water (red dashed line).

produced in aqueous acetic acid, but the three other weight loss peaks occurred at higher temperatures of 350, 390, and 486 °C. The occurrence of the three extra peaks at higher temperature suggested that there was further deoxygenation of the initial coke formed resulting in a coke with less H_2 and O_2 contents.

3.5.3. AQHDO of Propionic Acid/Furfural on Ni/RM and RRM. The AQHDO of the propionic acid/furfural mixture on the Ni/RM catalyst showed interesting results with similar pathway to that of acetic acid/furfural. The products consisted of 3-pentanone, heptane, 3-ethyloctane, THF, and 2-MTHF (Table 3). The THF and 2-MTHF were typical furfural hydrodeoxygenation products as shown in the AQHDO of furfural on Ni/RM. However, what was significant was the absence of the propionic acid AQHDO products observed when it was run alone and the absence of furan and 2-MF. Instead of the propionic acid AQHDO products, heptane and 3-ethyloctane were the major compounds detected in the liquid products, which were immiscible with the water. The formation of these two products was explained in terms of the reactions 10 and 11.



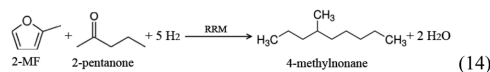
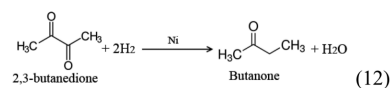
Reactions 10 and (11) occurred on the RRM in a similar manner as those explained for acetaldehyde and acetone in the case of the acetic acid/furfural AQHDO. The propanal (propionaldehyde) for reaction 10 was produced from the selective hydrogenation of the propionic acid on the elemental Ni, while the 3-pentanone for reaction 11 was produced from the ketonization of propionic acid on RRM (reaction 2).

3.5.4. Aqueous-Phase HDO of 2,3-Butanedione/Furfural on Ni/RM and RRM. 2,3-Butanedione is one of the compounds found in the catalytic pyrolysis products of lignocellulosic biomass and so it was also investigated to ascertain if it produced any hydrocarbons. The 2,3-butanedione/furfural AQHDO on Ni/RM produced 3-methyloctane (C_9H_{20}), furan, butanone, THF, and MTHF liquid products as well as gases (Table 3). The AQHDO converted the furfural to furan and 2-MF on the nickel (reactions 5–7), while the 2,3-butanedione was converted to butanone (reaction 12). The butanone, which behaves like other ketones such as acetone and propanone, reacted only with 2-MF and not with furan (reaction 13). Thus, in this process, the butanone reacted with the 2-MF to produce 3-methyloctane (C_9H_{20}) while the furan, THF, and 2-MTHF did not react and were part of the final liquid product (Table 3). Also a small quantity of butanone (~6 wt%) remained unreacted in the final product probably because there was insufficient amount of 2-MF.

When the 2,3-butanedione/furfural was taken through AQHDO on RRM, there was no reaction, but when butanone/2-MF was reacted on the RRM, 3-methyloctane (C_9H_{20}) was the only organic product and no gases were produced (Table 4). Because the C_9H_{20} was immiscible with water, this product was easily separated and its identity confirmed by ^{13}C NMR, GC/MS, and CHNOS analyses (Table 4). It is therefore clear that the active reactant was the 2-MF and not the furfural itself. Thus, if the furfural cannot be reduced to 2-MF, the production of the hydrocarbon will not occur because the alkylation reaction occurred on the RRM surface and RRM could not reduce the furfural to 2-MF. The presence of nickel in the catalyst was therefore very crucial for the effectiveness of this process.

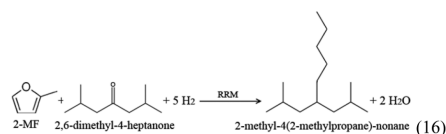
Li et al.²⁴ reported the condensation reaction of butanal and acetone with 2-MF using various Nafion catalysts to produce condensation products which were hydrogenated with Ni-WxC/C to produce various hydrocarbon compounds. Corma et al.²⁹ also reported the condensation of 2-MF with ketones catalyzed by sulfuric acid and *p*-toluenesulfonic acid; the oxygenated condensation products were hydrotreated to produce long-chain alkanes. Although these researchers produced hydrocarbons, their reaction pathways were quite different from the current method.

3.5.5. Aqueous-Phase HDO of 2-Pentanone/Furfural on Ni/RM and RRM. The AQHDO of furfural and 2-pentanone was similar to those of acetone and butanone, in that the reaction occurred between the 2-MF and 2-pentanone to produce 4-methylnonane ($\text{C}_{10}\text{H}_{22}$), a branched hydrocarbon as shown in the equation below (reaction 14):



In addition to the $\text{C}_{10}\text{H}_{22}$ hydrocarbon, other compounds produced were furan and THF, which were the reduction products of furfural (Table 3). The AQHDO of 2-MF and 2-pentanone on RRM produced only $\text{C}_{10}\text{H}_{22}$, which was confirmed by ^{13}C NMR, GC/MS, and CHNOS analyses (Table 4).

3.5.6. Aqueous-Phase HDO of 3-Heptanone/Furfural and 2,6-Dimethyl-4-heptanone/Furfural on Ni/RM and RRM. The reactions of these ketones were similar to the other ketones described above. They were two-step reactions where the furfural was first reduced to furan and 2-MF on the nickel and subsequently the alkylation reaction occurred on the RRM support. The only major difference was longer chain hydrocarbons were produced in addition to the furan, THF, and gases (Table 3). For the 2-heptanone/furfural AQHDO reaction, 6-methylundecane ($\text{C}_{12}\text{H}_{26}$) was produced, while for the 2,6-dimethyl-4-heptanone, 2-methyl-4-(2-methylpropane)nonane ($\text{C}_{14}\text{H}_{30}$) was produced. When 2-MF was reacted with these two ketones on RRM only one organic compound was produced for each of them (Table 4). For 3-heptanone/2-MF the only product was $\text{C}_{12}\text{H}_{26}$ (reaction 15) while for 2,6-dimethyl-4-heptanone/2-MF the only product was $\text{C}_{14}\text{H}_{30}$ (reaction 16). The identities of these compounds were confirmed by ^{13}C NMR, and GC/MS analyses because they were immiscible with water and were therefore separated in very pure forms (Table 4).



4. DISCUSSIONS

The results of the AQHDO of the various compounds clearly showed that low-molecular-weight oxygenates from biomass could be hydrotreated in aqueous phase to produce a wide range of long-chain hydrocarbon compounds. These products were readily separated because of immiscibility with water. In principle, these were catalytic reactions between unsaturated cyclic ethers (e.g., furan and 2-MF) with linear and branched ketones, and linear aldehydes in water reaction medium. The driving factor appeared to be the partial reduction products of a few small molecules such as acetic and propionic acids, furfural, and 2,3-butanedione to active reactants that underwent several alkylation and hydrodeoxygenation reactions to produce hydrocarbons of various

carbon chain lengths. In contrast, ketones such as acetone, pentanone, heptanone, and 2,6-dimethyl-4-heptanone did not require activation to be converted into long-chain hydrocarbons. These reactions were called “carbonyl alkylations”, because as can be seen from the above reactions, the carbonyl alkyl group was directly added to the furan nucleus, followed by ring opening and ring saturation.

The reduction of furfural to furan and 2-MF was crucial for these reactions. The double bonds in furan and 2-MF appeared to be also very important for these reactions because when the furan ring was saturated to THF or the 2-MF saturated to 2-MTHF, they did not react with any of the ketones and aldehydes under the current reaction conditions. A very important role of nickel in this process was the production of partially reduced intermediate compounds that underwent further reactions with other reduced compounds. If the nickel was too active and produced unsaturated furans, there were no alkylation reactions and no subsequent increase in carbon chain lengths.

Similarly, acetic and propionic acids did not react with any of the furan compounds unless they were either reduced to aldehydes (e.g., acetaldehyde and propanal) or ketonized to ketones (e.g., acetone and pentanone) before they underwent any of the carbonyl alkylation reactions. In contrast it was shown by Ackman et al.⁵³ that acetone can undergo condensation reactions with furan catalyzed by hydrochloric acid to form 2,2-difurylpropane, while under our reaction conditions furan did not react with acetone, clearly showing the reactions were not due to condensation, but carbonyl alkylation. When acetone was reduced to propanol, it did not partake in any of the reactions, which showed that there was no alcohol alkylation.⁵⁴ The 2,3-butanedione and hydroxyl butanone also did not react until they were converted to butanone. It appeared that the presence of the hydroxyl and dione groups deactivated the reactants, while the presence of methyl groups activated the reactants.

The RRM appeared to play a very important role in these reactions. When the RRM support was replaced with silica–alumina, none of these reactions was observed, and the major products were gases (data not reported). The RRM therefore served as the active site for carbonyl alkylation reactions. In the case of acetic and propionic acids, the RRM also catalyzed the ketonization reactions with the loss of H₂O and CO₂, but more importantly, it did not produce alcohols which were inactive. The RRM also catalyzed ketonization of acid mixtures to produce ketone mixtures. For example a mixture of propionic and acetic acid produced acetone, butanone, and pentanone, which then reacted with the 2-methylfuran.

It is also interesting to note that RRM produced only one alkylation compound for each pair of cyclic ether and pure ketones or aldehydes investigated. When mixtures of several pairs of compounds were investigated, they appeared to react independently and produced the sum of compounds produced from the individual pairs.

In the reactions of the aldehydes (acetaldehyde, propanal) with the cyclic ether (furan), the presence of H₂ and H₂O was important. These reactions involved the nucleophilic addition to the carbon–oxygen double bond (carbonyl carbon) catalyzed by the RRM. The addition compound was then hydrodeoxygenated to the subsequent longer chain alkanes. The exact sequence of the reactions is not well understood at this time. However, in all cases investigated, no alkene compounds were detected in any of the products, which is in contrast to Baylon et al., who reported the production of olefins using

balanced Lewis acid–base pairs as catalysts.³² Furthermore, aromatic aldehydes did not undergo these reactions under our current conditions. The production of hydrocarbon molecules from the reaction of aldehydes with furan is quite different from those reported in literature by several authors^{26–30,55–57} because those reactions involved aldol condensation followed by hydrodeoxygenation. The aldol condensation reactions used furfural, furan, 5-hydroxymethylfurfural, and ketones as reactants, which were then hydrodeoxygenated to form long-chain hydrocarbons. These reported reactions required several steps using different catalysts and some of these processes taking several hours (28–32 h) to complete and some requiring very corrosive and toxic catalysts such *p*-toluenesulfonic acid and sulfuric acids.^{29,30} In contrast, the current reported reactions involved simultaneous partial hydrogenation of furfural to furan, and carboxylic acids to aldehydes, which then underwent direct alkylation of furan ring, opening of the ring, and deoxygenation reactions all occurring on one catalyst. This type of simultaneous reaction has no equivalent in published and patent literature.

The ketones such as acetone, butanone, pentanone, heptanone, and 2,6-dimethyl-4-heptanone reacted with 2-MF but not with the furan or any of the saturated furans. Similarly, substituted butanones such as 2,3-butanedione and 2-hydroxybutanone did not react with 2-methylfuran unless they were converted to butanone before they underwent the reaction. Alcohols did not undergo any of these reactions and neither did aromatic ketones. In the case of ketones, the nucleophilic addition was also on the carbon–oxygen double bond (carbonyl carbon) and therefore branched hydrocarbons were produced in all cases studied. Although Li et al.^{24,55} reported 2-MF and furfural reactions with butanal and acetone, their reaction pathways were different and required aldol condensation using several catalysts and then finally hydrodeoxygenation. Sutton et al.³⁰ also reported the reaction of acetone with 2-MF using a condensation scheme which involved use of several catalysts and finally hydrodeoxygenation using Pd catalysts. Similarly, Ulfa et al.⁵⁷ reported hydrodeoxygenation of furfural–acetone condensation products to produce alkane compounds. None of these processes used a one-step reaction where the 2-MF was alkylated and deoxygenated simultaneously. The current results show that ketonization of carboxylic acids, selective hydrogenation of furfural to 2-MF, alkylation and hydrodeoxygenation can occur simultaneously on one catalyst, which makes the production of hydrocarbons from oxygenated products very simple.

The aqueous medium was very critical for the reactions; in the absence of water, there was rapid coking and deactivation of the catalyst especially when the medium was acidic. The coke properties for neat acids were different from those produced under aqueous conditions. This observation is similar to the effect of steam on FCC reactions in the hydrocracking processes in the petroleum industry. Clearly, these are unique reactions that we called “carbonyl alkylation” because in all cases, it appeared the linear or branched chain ketone or aldehyde was added to the unsaturated cyclic ether ring then followed by ring opening and saturation to form the aliphatic hydrocarbons. The use of aqueous medium for the synthesis of the hydrocarbons also made the separation of the products very easy because of immiscibility of products with the synthesis medium.

In the reactions of the furans (furan or 2-MF), the number of carbon atoms was conserved and therefore the length of the aliphatic carbon chain produced was always the sum of the carbons in the two reactants and could be represented by the formula C_{n+4} for aldehyde reactions and C_{n+5} for ketone

reactions (n = number of carbon atoms in carbonyl compound; 4 = number of carbon atoms in furfural and 5 = number of carbon atoms in methylfurfural). Thus, 2-MF which has five carbons when reacted with butanone will produce alkane with nine carbons and similarly 2,6-dimethyl-4-heptanone (9 carbons) reacted with 2-MF to produce 14-carbon aliphatic hydrocarbon ($C_{14}H_{30}$). The structure of these compounds were quite different from those reported in published literature. It is important to emphasize that all the compounds investigated in this work were identified in the aqueous-phase catalytic pyrolysis products of pinyon juniper wood. The catalyst was also very effective in the HDO of pinyon juniper catalytic pyrolysis oils published elsewhere;³⁵ thus, the catalyst is not only effective for the model compounds but also effective for the pyrolysis products, which therefore makes it easier to interpret the data for the HDO of catalytic pyrolysis oils.

5. CONCLUSIONS

It has been demonstrated that through unique catalyst activity, low-molecular-weight water-soluble oxygenates found in biomass pyrolysis products can be hydrotreated in aqueous phase to form long-chain aliphatic hydrocarbons. Aliphatic hydrocarbons containing 6–14 or more carbon chains can be produced from these carbonyl alkylation reactions in a one-pot synthesis. This method can also be used to synthesize pure compounds with almost 100% conversion, high selectivity, and excellent yields on RRM. The reactions occurred in water, which reduced coke formation on the catalyst and made separation of products very easy. These syntheses provide elegant and efficient methods of producing hydrocarbon fuels and chemicals from renewable biomass resources.

AUTHOR INFORMATION

Corresponding Author

*E-mail: foaster.agblevor@usu.edu.

ORCID

Foster A. Agblevor: 0000-0001-8177-3977

Notes

The authors declare no competing financial interest.

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