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ARTICLE *in* ACS SUSTAINABLE CHEMISTRY & ENGINEERING · OCTOBER 2015

Impact Factor: 4.64 · DOI: 10.1021/acssuschemeng.5b00730

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Aqueous Extractive Upgrading of Bio-Oils Created by Tail-Gas Reactive Pyrolysis To Produce Pure Hydrocarbons and Phenols

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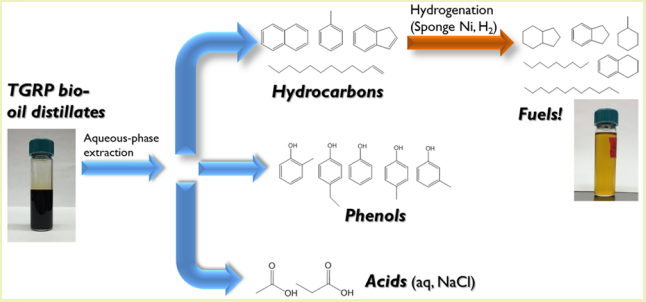
Supporting Information

ABSTRACT: Tail-gas reactive pyrolysis (TGRP) of biomass produces bio-oil that is lower in oxygen (~15 wt % total) and significantly more hydrocarbon-rich than traditional bio-oils or even catalytic fast pyrolysis bio-oils. TGRP bio-oils lend themselves toward mild and inexpensive upgrading procedures. We isolated oxygen-free hydrocarbons by extraction of TGRP bio-oil distillates. Extraction proceeded by adding aqueous sodium hydroxide to distillates, resulting in a hydrocarbon layer and a phenolic salts layer. The hydrocarbons consist primarily of mono- and bicyclic aromatics, are essentially free of oxygen (<1.0 wt %), and possess low moisture (<1.0 wt %) and low acidity (TAN < 5.0 mg KOH/g). The phenolic salts can be reacidified to produce phenols with low moisture (~2.5 wt %) and with narrow product distribution. The aqueous phase byproduct contains organic acids and precipitated sodium chloride. The hydrocarbon layer can be upgraded via mild hydrogenation with a sponge nickel base metal catalyst in water, producing naphtha compounds appropriate for direct use as drop-in fuel and/or refinery blendstock. Furthermore, using only hydrogenation eliminates CO and CO_2 production that normally accompanies hydrodeoxygenation.



KEYWORDS: *Fast pyrolysis, bio-oil, distillation, extraction, hydrogenation*

INTRODUCTION

Separations processes are critical for oil refineries, as they are a means for effective hydrotreatment[1] and elimination of highly viscous residues.[2] Bio-oils produced by traditional fast pyrolysis processes[3] are nonconducive toward many separation processes, outside of simple extractive processes. As a result of the very wide diversity of compounds in bio-oil, extractions for fuel purposes are primarily classified based on solubilities in extraction solvents[4−7] (dichloromethane, ethyl acetate, etc.), frequently requiring multiple steps in series.[8,9] A large body of work focuses on the extraction of phenolic compounds from both bio-oils[5,10,11] and biomass[12−14] for various nonfuel applications. Since traditional bio-oil is almost entirely comprised of many different oxygenated compounds, separation of pure hydrocarbons is futile, due to the extremely low yields.

An important advancement toward fungible pyrolysis-based fuels has been the tail-gas reactive pyrolysis (TGRP)[15,16] process for bio-oil production. TGRP is a (patent-pending) USDA-ARS process that relies on performing fluidized bed pyrolysis at carefully controlled reaction conditions under a noninert atmosphere, partially comprised of gas recycled from the tail stream. Under optimized conditions, TGRP yields a bio-oil with oxygen content comparable to or less than that of catalytic fast pyrolysis (via production of aromatic hydrocarbons), without the use of an externally added catalyst. Highly reactive compounds like acids and furfurals are eliminated, resulting in a bio-oil with enhanced thermal stability and high concentrations of valuable compounds. As a result, the thermal stability is one such quality of TGRP oil which can be exploited for effective separations based on volatility via fractional distillation.[17]

Due to the reductive and deoxygenative nature of the TGRP process, higher concentrations of deoxygenated hydrocarbons are readily available. On top of this, the oxygenated compounds within TGRP oils are nearly entirely phenols. Ketones, furfurals, acetic acid, acetol, and levoglucosan exist only in trace amounts, if at all. While high concentrations of phenolics do exist, methoxyphenols like syringol and guaiacol are barely detectable, as the TGRP process effectively removes methoxy groups in a similar fashion to catalytic pyrolysis. Hence, the product distributions of TGRP bio-oils are very narrow compared with traditional bio-oils. This narrow product distribution represents a second characteristic that biorefineries can and should exploit for effective separations.

If applied to TGRP bio-oils, separation of phenolics can follow straightforward established protocols, leaving behind deoxygenated hydrocarbons. The hydrocarbons could then undergo simple hydrogenation with base metal catalysts under relatively mild conditions. Past attempts[18−21] to incorporate

Received: July 22, 2015
Revised: September 1, 2015
Published: October 8, 2015

DOI: 10.1021/acssuschemeng.5b00730
ACS Sustainable Chem. Eng. 2015, 3, 2809−2816

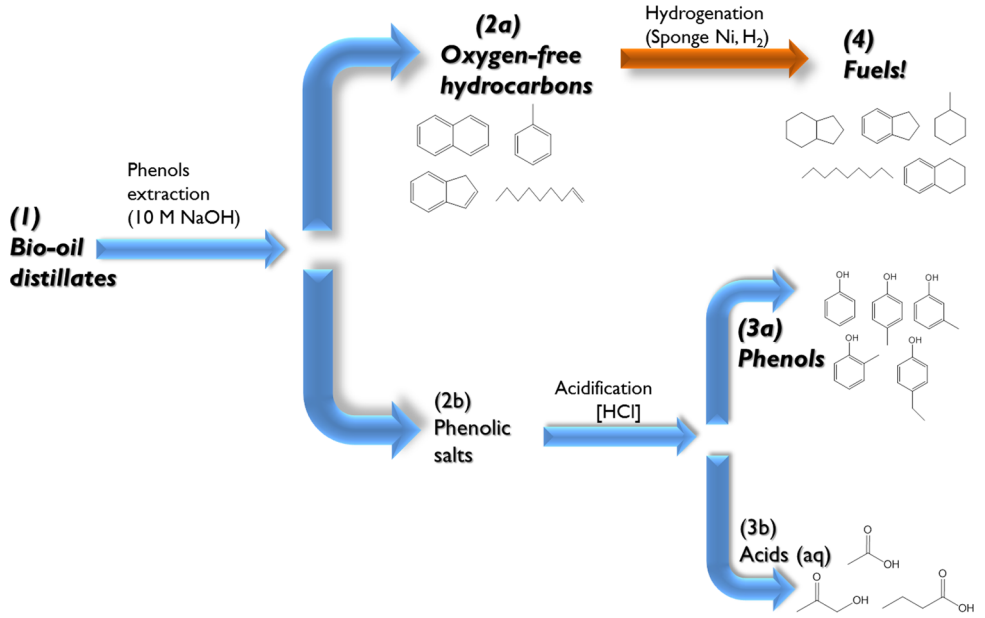


Figure 1. Process flow diagram for obtaining hydrocarbon blendstock by simple extraction from TGRP bio-oil distillates, followed by hydrogenation. Phenolics are obtained as a relatively pure side product.

base metal catalysts have mainly investigated their effects on model compounds and/or their limited hydrodeoxygenation (HDO) feasibility, oftentimes in environmentally harmful solvents. The potential elimination of precious metals afforded by TGRP hydrocarbon hydrogenation in aqueous neutral media would not only significantly reduce process costs but would also eliminate gas production. Hence, a more environmentally benign approach would be realized. Either way, the oxygen-free hydrocarbons could easily enter a refinery (whether upstream or downstream from a catalytic hydrotreater), while separated phenolics provide valuable commodity chemicals. This paper details a methodology for extractive upgrading of TGRP bio-oils, in combination with base metal hydrogenation.

EXPERIMENTAL SECTION

Fast Pyrolysis of Biomass. Prior to fast-pyrolysis experiments, all feedstocks were ground and dried to less than 5 wt % moisture. Both horse manure (pure horse droppings) and horse litter (manure mixed with stall bedding) were provided by Morrisville State College Equine Rehabilitation Center (Morrisville, PA, USA). Guayule bagasse was provided by Yulex (Chandler, AZ, USA) and switchgrass by McDonnell Farm (East Greenville, PA, USA). Fast pyrolysis was carried out using the ERRC fluidized bed fast pyrolysis system, as described previously.[15] All experiments used the oil obtained from the electrostatic precipitators (ESPs), which constituted >95 wt % of the total organics produced (condenser fractions comprised of >90 wt % water). For TGRP experiments, a fraction of the noncondensable gas stream was mixed with the N_2 stream and recycled into the fluidized bed, using a preheater and gas blower. The pyrolysis system recycled the tail gas in the range of 50−70%, and biomass was fed at 2−3 kg/h.

Bio-oil Distillation. Bio-oils were distilled in a batch short-path distillation apparatus, equipped with a water-coolant condenser and vacuum adapter outlet. A total of 50 to 100 g of bio-oil was placed in an appropriately sized round-bottom flask and clamped to the distillation adapter. A heating mantle heated the flask throughout the experiment, and quartz wool insulated the flask. The flask was heated quickly at ∼10−20 °C/min. Both the overhead and bottoms temperatures were recorded at the overhead vapor and bottoms flask, respectively. Individual distillate fractions were collected for the sake of facilitating separation of aqueous phases. When overhead temperatures exceeded 150 °C, the condenser water was shut off, and heating tape applied to the condenser was turned on. When the bottoms temperature reached 350 °C and distillate collection ceased, the heat supply was shut off. When the bottoms temperature cooled down to 320 °C, a vacuum was applied to collect the remaining fraction. After returning back to room temperature and pressure, the bottoms product remaining in the flask was collected and pulverized with a mortar and pestle. All analyses of distillates were performed after removing any phase-separated aqueous layers.

Bio-oil Extractions. TGRP bio-oil distillates were used for extraction experiments performed in a separatory funnel. The sequence of extractions (Figure 1) consisted of two general steps: (1) extraction of phenolics into salts using sodium hydroxide and (2) reacidification and isolation of phenolics. First, 5−8 mL of 10 M NaOH was added to 15 g of bio-oil distillates. The mixture was vigorously shaken, and the organic/aqueous phases were allowed to separate again. The top hydrocarbon organic layer (**2a**) was isolated for further analysis, while the bottom layer (**2b**) underwent reacidification. The reacidification step used concentrated HCl, added in a dropwise manner with vigorous stirring, until a clear and persistent phase separation occurred with two distinctly colored phases. This step produced the isolated phenolics (**3a**) and an aqueous layer with miscellaneous oxygenated organics (**3b**). The **3a** fraction was desalted via acetone dilution and filtration, followed by rotary evaporation to remove the acetone. The organics in the **3b** fraction were isolated from the aqueous phase via extraction with ethyl acetate.

Characterization and Analysis. Elemental analysis (CHNS) was conducted via a Thermo EA1112 CHNS analyzer. Oxygen content was calculated by difference, and water content was subtracted. For all samples, elemental results were verified by an outside party (Robertson Microlit Laboratories). Moisture content was measured with Karl Fischer titration in methanol with Hydranal Karl Fischer Composite 5 (Fluka) as the titrant. Total acid number (TAN) was measured using a Mettler T70 autotitrator using 0.1 M KOH in isopropanol as the titrant and wet ethanol as the titration solvent. Gas chromatography with mass spectroscopy (GC-MS) analysis of liquid products was performed on a Shimadzu GCMS QC-2010. The column used was a DB-1701, 60 m × 0.25 mm and of 0.25 μm film thickness. The oven temperature was programmed to hold at 45 °C for 4 min, ramp at 3 °C/min to 280 °C, and hold at 280 °C for 20 min. The injector temperature was 250 °C and the injector split ratio set to 30:1. Helium carrier gas flowed at 1 mL/min. All measured compounds were calibrated for wt % concentration with a three-level standard curve using fluoranthene as an internal standard. A complete list of

DOI: 10.1021/acssuschemeng.5b00730
ACS Sustainable Chem. Eng. 2015, 3, 2809−2816

Table 1. Characterization of Horse Litter and Horse Manure TGRP Bio-oils, before and after Extractive Upgrading into Hydrocarbons (2a) and Phenols (3a)

		horse litter				horse manure			
		bio-oil	distillates	HCs	phenols	bio-oil	distillates	HCs	phenols
wt % (db)	N	1.64	1.97	1.01	1.82	3.96	3.02	2.15	4.12
	C	72.25	80.03	92.20	74.33	79.26	78.72	90.13	74.73
	H	5.32	7.00	6.23	6.79	5.47	6.96	7.23	6.96
	O	20.79	10.99	0.57	17.06	11.30	11.31	0.49	14.19
wt % yield f/distillates				43	49			55	35
wt % yield f/bio-oil			66	28	33		62	34	22
wt % moisture		4.2	2.6	0.9	2.8	2.1	1.4	0.5	2.6
TAN (mg KOH/g)		12.8	23.7	8.2		18	26	3.4	
theoretical HHV (MJ/kg)		29.0	35.0	39.5	32.1	32.4	34.3	40.0	32.5

compounds quantified by GC-MS, along with their grouped categories, can be found in the Supporting Information. Higher heating values of combustion were calculated using the IGT empirical method.[22]

Hydrogenation. Extracted hydrocarbon product, **2a**, underwent a two-stage batch hydrogenation process in a 100 mL Parr reactor. A total of 6 to 10 g of the **2a** fraction was combined with sponge nickel catalyst (A-5000, Alfa Aesar) and water in the reactor vessel at a 1:1:0.38 oil/water/catalyst weight ratio. Catalyst was weighed and loaded into the reactor while immersed in water, to prevent possible reaction with atmospheric oxygen. After purging the reactor of air using hydrogen, 600 psi of hydrogen was introduced into the reactor, and the temperature was raised to 80 °C. After further increasing the pressure to 730 psi, the impeller speed was increased to 900 rpm to begin the reaction, which continued for 60 min. Then, the impeller speed decreased again to 200 rpm, and the reactor temperature increased to 200 °C. Subsequently, more hydrogen was introduced until a final system pressure of 1150 psi was attained. Hydrogen consumption was monitored by continually feeding the hydrogen from a fixed-volume buret while recording the buret pressure. Reaction time was considered to have started when the impeller speed was increased from 200 to 600 rpm, and the reaction proceeded for 3 h. The impeller then returned back to 200 rpm, the hydrogen closed off, and the reactor cooled down to room temperature before venting and collection of products. The entire catalyst/liquid slurry was filtered through a 0.45 μm PTFE membrane, and the organic layer was gravity-separated and pipetted to a different vial.

RESULTS AND DISCUSSION

Extraction of Distillates. Four biomasses were used as feedstock for the TGRP process; these include horse litter, horse manure, guayule bagasse, and switchgrass. Some effects of feedstock on bio-oil composition are discussed in detail in our previous work.[17,15] In short, most TGRP bio-oils contain significant amounts of napthalenes and one-ring phenolic compounds, with horse manure TGRP oil containing the most naphthalenes of any other bio-oil. Guayule bagasse TGRP oil contains predominantly BTEX (benzene−toluene−ethylbenzene−xylenes) and straight-chain paraffins, while switchgrass TGRP bio-oil contains predominantly phenolics. Hence, our choice of feedstocks represents the diversity of biomass available for thermochemical conversion to biofuels as well as possible biomass categories (grasses, woody biomass, and animal waste). While we used short path distillation to collect liquid volatiles, roughly three to four fractions were cut at specified temperatures: 120, 155, and 230 °C. Collecting fractions allowed for phase separation and discarding of water recovered from distillation. Without fraction collection, phenolic fractions with comparable density would emulsify the water phase. Distillate yields ranged from 50−65 wt % of the starting bio-oil; such yields are possible due to the absence of highly reactive aldehyde and acid groups, which would normally repolymerize under a high temperature.

Our strategy for extraction (Figure 1) utilizes a one-step addition of concentrated sodium hydroxide in aqueous solution. The sodium hydroxide deprotonates all phenolics, as well as any trace acids, into their corresponding sodium salts. A high concentration of sodium hydroxide (10 M) was used to ensure a high concentration of ionic salts without unnecessary water dilution. Due to the ionic nature of the salts, pure nonpolar hydrocarbons remain as a separated organic layer, while the ionic salts precipitate into a second layer. Both layers are black and nearly opaque, but only the hydrocarbon layer exhibits some degree of transparency when a light shines through the layers. Gravity separation with a separatory funnel allowed collection of the individual layers. To protonate the phenoxides back to the free phenolics, we then added concentrated hydrochloric acid to the ionic salts layer. Alongside the phenolics layer, a separate aqueous phase forms which retains both any trace organic acids from the oil as well as sodium chloride salt formed. One advantage of this procedure comes with the nontoxic side products formed (organic acid and salt), which could be used for other commodity purposes. We determined optimal amounts of sodium hydroxide by way of the disappearance of phenols from the hydrocarbon layer. While a lesser amount of hydroxide prevented full collection of phenolics, excess hydroxide did not adversely affect the yield or quality of hydrocarbons isolated.

Table 1 displays the characterization of layers before and after we carried out extraction on horse litter and horse manure bio-oil distillates. Although slight variations in hydrocarbon and phenolics yields exist, the mass balance of the extraction step exceeded 90%. The hydrocarbon layers are marked by low oxygen concentrations below 1 wt %. The high carbon percentages (>90 wt %) result from the high concentration of aromatic compounds present. On the whole, horse manure possesses greater nitrogen concentrations because the horse litter is diluted with woody biomass. With horse manure bio-oil distillates, the phenolics layer contained the majority of the nitrogen from the original distillates, suggesting two possibilities: (1) most of the nitrogen is chemically bound to the phenolics or (2) some nitrogenated compounds (e.g., amides) are transferred to the phenolics layer via the sodium hydroxide reaction. Overall, the phenolics fractions possessed elemental compositions similar to that of phenol. For guayule bagasse and switchgrass-based bio-oils, some characterization differences between their extracts were more significant than other characteristics. For guayule bagasse, all fractions contain significantly higher hydrogen content, resulting from the

DOI: 10.1021/acssuschemeng.5b00730
ACS Sustainable Chem. Eng. 2015, 3, 2809−2816

Table 2. Characterization of Guayule Bagasse and Switchgrass TGRP Bio-oils, Before and After Extractive Upgrading into Hydrocarbons (2a) and Phenols (3a)[a]

		guayule bagasse				switchgrass			
		bio-oil	distillates	HCs	phenols	bio-oil	distillates	HCs	phenols
wt % (db)	N	1.65	0.73	1.26	2.90	1.27	0.85	0.72	0.78
	C	76.33	79.74	86.63	69.14	74.03	71.92	88.41	71.76
	H	9.46	9.1	9.68	7.47	5.86	7.21	7.44	7.53
	O	12.56	10.42	2.43	20.50	18.84	20.02	3.43	19.94
wt % yield f/distillates				45	21			16	71
wt % yield f/bio-oil			50	22	11		58	10	41
wt % moisture		11.3	1.1	0.4	4.7	10.6	8.2	1.7	5.9
TAN (mg KOH/g)		30	31.6	7.6		80.3	99	5.2[a]	
theoretical HHV (MJ/kg)		36.8	37.9	41.9	30.6	30.6	31.6	39.5	31.9

[a]R2 titration end point used in absence of R1.

Table 3. GC-MS Concentrations of Selected Compounds Found in Bio-oil Distillate Extraction Layers

	horse litter		horse manure		guayule bagasse		switchgrass	
wt %	HCs	phenols	HCs	phenols	HCs	phenols	HCs	phenols
pyridine	0	0.02	0	0.03	0.01	0	0.01	0.02
indene	0.04	0	0.02	0.2	1.5	0.28	2.92	0.42
styrene	1.16	0.07	0.87	0.04	2.12	0.21	1.55	0.18
phenolics	0.03	17.92	0.05	15.43	0.59	13.01	0.04	22.63
naphthalenes	10.38	1	13.34	1.21	1.35	0.24	8.63	1.29
BTEX	2.34	0.06	0.96	0.01	12.7	0.56	2.76	0.07
PAHs	1.85	0.4	5.75	0.36	0.12	0.03	3.18	0.33

elevated paraffins content of the guayule biomass. The remaining oxygen content in the hydrocarbon fractions likely results from residual, unisolated phenols. Simply increasing the hydroxide used in extraction can further decrease the oxygen content to below 1%. Switchgrass hydrocarbons exhibit lower yields due to the increased content of phenolics, which were recovered in high yields. Nevertheless, the production of deoxygenated hydrocarbons remains effective.

Moisture and acidity correlated well with the fractional compositions. TAN was only measured for the hydrocarbon fractions since the TAN, as currently defined, is only meaningful for hydrocarbons and fuels. However, like the horse manure or litter, these HC fractions exhibited remarkably low TAN values (<5.0 mg KOH/g) and low moisture (0.5−1.5 wt %), indicative of functional group elimination—phenolics cause positive readings in TAN titration. For switchgrass-based hydrocarbons, an end point value of 5.2 was reported due to the absence of an inflection point in the titration curve (Table 2). For all feedstocks, the aqueous phase resulting from reacidfication (**3b**) contained at least 60−70% water, with the balance being salt and organic acids. Figure S1 of the Supporting Information displays a typical GC-MS chromatogram of extracted compounds. Hence, the total side products produced are environmentally benign, though recycling and reutilization of the aqueous salt could be more cost-effective. Based on total biomass used, about 1.5−2.0 g/100 g of biomass each of NaOH and HCl would be required for phenolics isolation (Table S2). A simple evaporation of the aqueous phase would leave behind the salt. Ethyl acetate could efficiently extract the organic portion without miscibility of the phases, but a technoeconomic analysis would determine whether extraction is practical on a large scale. Regardless of feedstock, the results illustrate how TGRP bio-oil hydrocarbon extraction can efficiently separate bio-oil constituents into fractions based on chemical identity.

Structural Characterization. Characterization of extracts via GC-MS proved to be critical for assessing extraction efficiency. Quantitative measurements of specific chemical groups are displayed in Table 3. The phenolics layer was concentrated with phenols and cresols, with negligible amounts of hydorcarbon impurities. Likewise, the hydrocarbon layer contained negligible amounts of phenols. Horse litter, horse manure, and switchgrass-based hydrocarbons contained naphthalenes as the primary hydrocarbon component,[17] while the primary component in guayule bagasse hydrocarbons is BTEX (benzene, toluene, ethylbenzene, xylenes). The organic portion of the aqueous salt layers (**3b**) postacidification, after extraction with ethyl acetate, contained as much as 15−20 wt % acetic acid, with the balance comprised of other organic acids, lost phenol, and catechols.

NMR of the extract layers further demonstrates the relative purity of hydrocarbons from any phenolics (Figures 2 and S2−S9 of the Supporting Information). The high concentration of naphthalene in **2a** of the horse manure bio-oil is evident by the prominent characteristic peaks in both the proton (7.45 and 7.85 ppm) and ^{13}C NMR (127, 128, and 134 ppm). The remainder of each spectrum demonstrates the highly aromatic nature of the hydrocarbon layer. For the phenolics layer (**3a**) of the horse manure bio-oil, the high concentration of phenol is verified by its characteristic peaks in each spectrum (~6.75, 6.80, and 7.15 ppm in ^{1}H and 116, 119, 130, 158 in ^{13}C). Overall, the spectra indicate that the material is nearly all phenolic in nature, with *p*-substituted methyl groups in higher concentration than *o*-substitution or any longer aliphatic substituents. The guayule bio-oil extract spectra (Supporting Information) indicate that both layers have a more complex composition than that of the corresponding horse manure materials, and each have more aliphatic character than those of the horse manure, as indicated by more upfield peaks in each spectrum. This observation is consistent with the higher H/C

DOI: 10.1021/acssuschemeng.5b00730
ACS Sustainable Chem. Eng. 2015, 3, 2809−2816

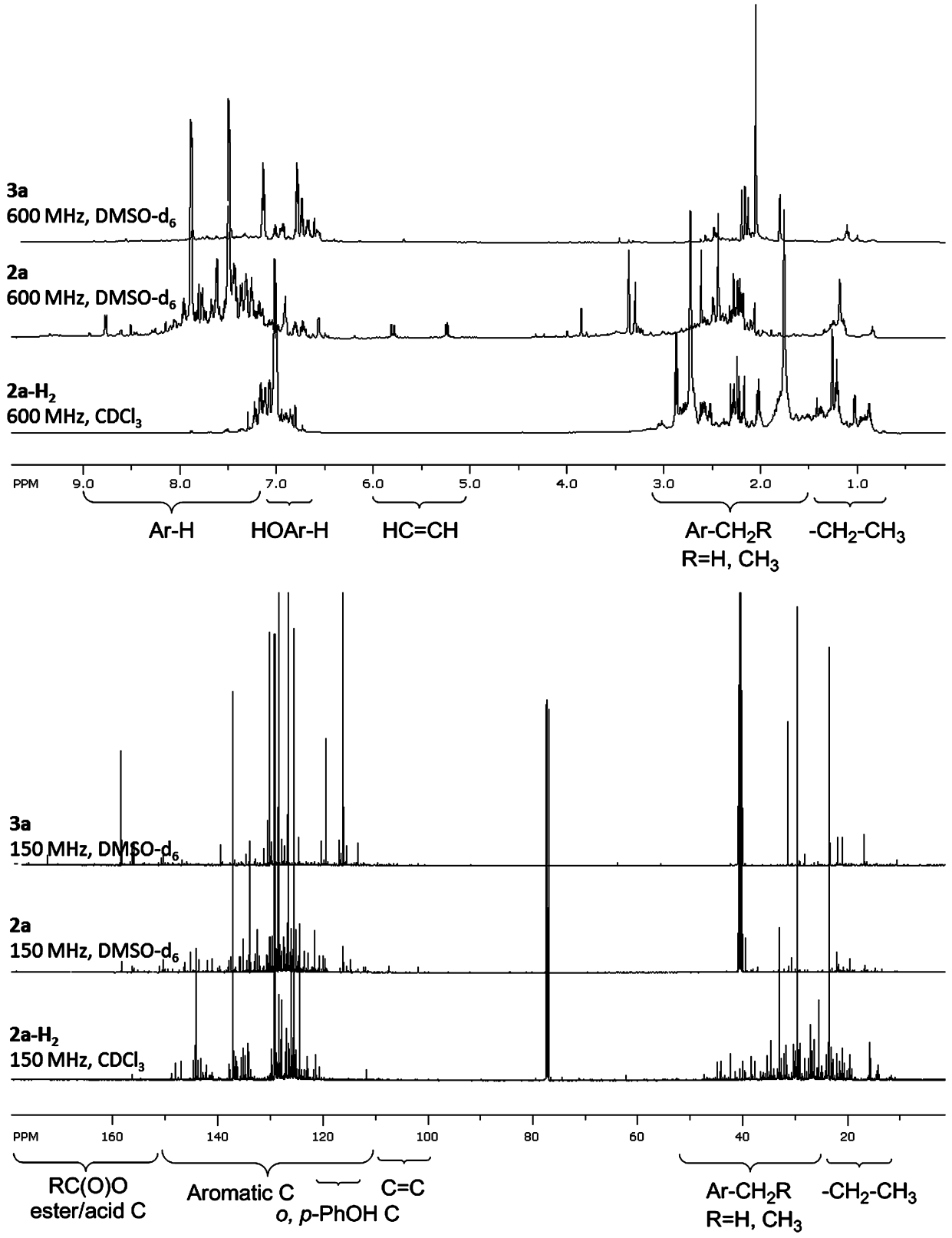


Figure 2. ^{1}H (top) and ^{13}C (bottom) spectra of phenolic layer (**3a**), hydrocarbon layer (**2a**), and hydrocarbon layer after hydrogenation over sponge Ni (**2a**-H_2) derived from horse manure TGRP oil.

ratio for the guayule based extracts, as noted above. All in all, the **3a** phenolics fractions represent a source of valuable commodity chemicals with opportunity for purification of individual compounds by fractional distillation.

Hydrogenation with Sponge Nickel. While the aforementioned extraction processes lend themselves toward isolation of hydrocarbons, direct use of the hydrocarbons (**2a**) as transportation fuel requires further upgrading into a

DOI: 10.1021/acssuschemeng.5b00730
ACS Sustainable Chem. Eng. 2015, 3, 2809−2816

hydrogen-rich product. We selected sponge nickel base metal catalyst due to its greatly reduced cost relative to traditional precious metal upgading catalysts and due to its environmentally benign nature. Furthermore, sponge nickel only performs hydrogenation, so upgrading would not emit any CO or CO_2 gases that are normally produced from HDO reactions. While our hydrogenation procedure primarily targets aromatic compounds, the procedure must consider olefins (e.g., styrene), which could either hydrogenate or polymerize at low temperatures. Hence, we employed a two-step hydrogenation procedure which consisted of (1) olefin hydrogenation at 80 °C and (2) aromatics hydrogenation at 200 °C.

Table 4 shows the characterized hydrogenation products. The moisture percentages decreased further to near 0.5 wt %, and the hydrogen increased to more than 10 wt %, which translates to significantly higher H/C ratios. Figure 3 summarizes the molar elemental ratios of the hydrogenated products, in relation to the characterized fractions and to typical values for gasoline and phenol. A significantly lower product density (0.86 g/mL, compared with 0.98) agrees with the extent of upgrading observed.[23] Interestingly, hydrogenation effectively decreased the products' nitrogen content, likely diluted by the increased abundance of hydrogen. For all hydrogenations, TAN values from horse litter and manure hydrocarbons read 7.6 mg KOH/g (end point values reported), whereas that of guayule and switchgrass gave TAN values of 4.9 and 5.5, respectively. Hydrogenation product yields consistently fell between 60 and 72% of the starting materials (except for guayule at 58%), with product losses due to factors such as reactor purging, catalyst entrainment, and filtering losses. When considering all steps of the process, the product constitutes as much as a 10% mass yield from the starting biomass. However, the isolated phenols can constitute between 8 and 15% of the original biomass, thus making the total liquid recovery more than 20% of biomass. On a bio-oil basis, the hydrogenation product constitutes 25% of the starting bio-oil. All the aforementioned yields are quite significant, considering that only a specific fraction of the bio-oil distillates undergoes the upgrading, with the rest of the product conceivably going toward commodity chemicals production. When we further include bio-oil distillate bottoms as coker feed[17,24] for producing green coke, the end biomass utilization increases to 30−35% (see Table S2).

Table 4. Characterization of TGRP Hydrocarbon Extracts after Hydrogenation with Sponge Nickel Catalyst[a]

		horse litter	horse manure	guayule bagasse	switchgrass
wt % (db)	N	0.23	0.74	0.81	0.80
	C	88.78	88.23	85.65	88.20
	H	10.52	10.56	12.1	9.50
	O	0.48	0.47	1.45	1.50
density (g/mL)		0.889	0.8751	0.864	0.937
wt % moisture		0.6	0.48	0.64	1.39
TAN (mg KOH/g) (R2)		7.6	7.6	4.9	5.5
theoretical HHV		44.1	44.2	44.9	42.4
wt % yield hydrogenation		60	72	58	72
wt %	pyridine	0	0	0.01	0
	indene	0	0	0	0.01
	styrene	0	0	0	0
	phenolics	0.34	0.08	0.04	0.02
	naphthalenes	0.06	0.01	0	0.03
	BTEX	3.31	7.87	6.57	3.61
	PAHs	0	0.01	0.00	0.00
	naphtha	0.85	1.71	23.89	5.67
	paraffins	0.44	0.64	18.07	3.33
	tetralin	14.00	33.23	3.32	16.57
	indane	8.17	11.32	2.34	8.23
	methyl tetralins	11.43	19.35	0.00	14.14

[a]TAN values are based on end point titration.

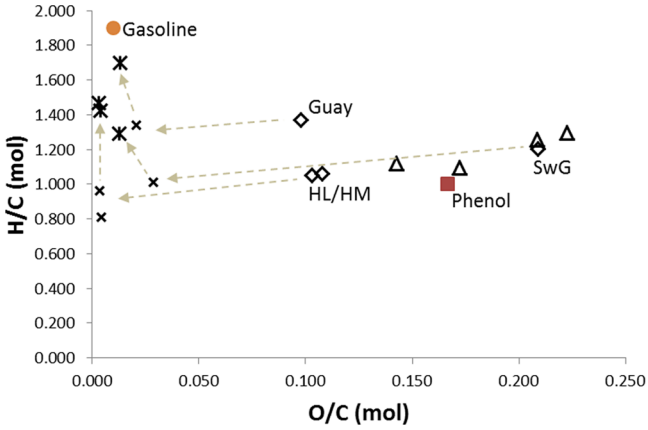


Figure 3. Van Krevelen diagram for the extraction of hydrocarbons and phenolics from various bio-oil distillates. Symbols are as follows: (◊) distillates, (×) **2a** HC extracts, (∗) hydrogenated HC extracts, (△) **3a** phenolic extracts. Gasoline (●) and phenol (■) are shown for reference.

Also in Table 4 are the associated GC-MS quantifications. For horse litter, horse manure, and switchgrass, naphthalenes predominantly converted into tetralin, with minor conversion into decalin. Similarly, indenes converted into indanes as well as the fully hydrogenated hexahydro-indane. While BTEXs mostly remained at the same concentrations, occasional increases in BTEX composition occurred due to the hydrogenation of styrene into ethylbenzene, with some ethylbenzene further converting into ethylcyclohexane. For switchgrass, hydrogenation produced comparable amounts of tetralins and saturated products (paraffin and naphtha). This is verified by the ^{1}H and ^{13}C NMR analysis of the horse manure products (Figure 2), where increased aliphatic/aromatic signal ratios after hydrotreatment are apparent. Also, the elimination of olefins is evidenced by disappearance of the peaks at 5−6 ppm in the ^{1}H spectra. Quantitatively, ^{1}H NMR analysis shows that the ratio of aliphatic to aromatic protons present increases from ∼0.5/1 to ∼3.2/1 via the Ni catalyzed hydrogenation. Qualitatively, the upgraded hydrocarbons exhibit a transparent yellow color that does not change with time, indicative of oxidative stability and lack of any reactive groups. While the products require further hydrogenation to attain fuel-quality H/C ratios, this could be mitigated by increasing the catalyst loading ratio and/or reaction time. Unlike nickel used in hydrogenolysis, the catalyst does not require acid, but only a small amount of water is required to both mitigate the reaction and to prevent the catalyst from exposure to air.

A higher quality fuel product was produced from hydrogenation of guayule-based hydrocarbons. Since the extracted hydrocarbons (**2a**) from guayule bio-oil exhibited higher H/C ratios to start than those from other biomasses, their hydrogenation product possessed even higher H/C ratios, so

DOI: 10.1021/acssuschemeng.5b00730
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much so that the Van Krevelen coordinate lands very close to that of gasoline. In this case, ^{1}H NMR analysis shows that the ratio of aliphatic to aromatic protons present increases from ~6:1 to ~12:1 via the Ni catalyzed hydrogenation. These improved atomic ratios align well with the associated GC-MS product distribution, which greatly differs from that of horse manure/litter. Measured products consisted primarily of naphtha and straight-chain paraffins, with small amounts of BTEX aromatics and tetralin. This type of a mixture suits many of the requirements for stringent fuels like aviation fuel,[25,26] wherein straight-chain compounds constitute a significant portion of both the light and heavier boiling ranges.

CONCLUSIONS

In summary, we have outlined a procedure for isolation of hydrocarbons from bio-oil distillates in significant yields, originating from the TGRP process. The procedure translates well across different feedstocks, with the feedstock difference mainly affecting the types of hydrocarbon compounds and the ratio of hydrocarbons/phenolics isolated. Guayule-based hydrocarbons contained paraffinic compounds which increased the overall H/C ratio, before and after hydrogenation. Compositions of hydrogenated hydrocarbons approached those of gasoline hydrocarbons. Due to the near-complete absence of oxygen, the extracted hydrocarbons (before and/or after hydrogenation) could conceivably enter a petroleum refinery as-is, so no further deoxygenation is required. Using only nickel hydrogenation brings several environmental and cost benefits, such as the absence of CO/CO_2 production, extended life through absence of coking, and low cost due to its natural abundance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00730.

Information on GC-MS compounds, NMR spectra, and extraction product yields (PDF)

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Notes

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to acknowledge Christina Gallo (Drexel University co-op student, 2014) for assistance with the extraction experiments, as well as Craig Einfeldt for the fast pyrolysis bio-oil production. We also thank Dr. Gary Strahan for NMR experiments. USDA-NIFA-BRDI grant 2012-10008-20271 is hereby acknowledged.

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