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NOVEL SEPARATION STRATEGY FOR PROCESSING BIOPYROLYSIS LIQUIDS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

Cain Department of Chemical Engineering

by
Chuanlin Zhao
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The separation of pyrolysis bio-oil is important for its role in upgrading oil quality and acquiring commercial byproducts. A selective separation method for biopyrolysis liquids is developed in this work. Two parts in succession are involved as the first one aims at selectively removing some of the heaviest fractions from bio-oil. Chromatographic adsorption results show that Class C Fly ash and pyrolysis Bio-char have potential for this goal at <300 ºC, byproduct like combined adsorbates / adsorbents could also be used directly in asphalt cement processes. Thereafter, the second part focuses on adsorbing light fractions like lighter acids and aldehydes selectively. Basic (modified) activated carbons display relatively low selectivity at ~250ºC, but they have better selectivity compared to unmodified activated carbons. Thus some carbon-coated mesoporous silica and alumina materials are also prepared for the adsorption of these light compounds in the future. The combination of the two parts of adsorptions would leave behind a middle distillate fraction which is the bio-oil fraction most amenable to catalytic upgrading, to either a fuel or chemical feed.

1. LITERATURE REVIEW

1.1 Definition of Bio-pyrolysis

Bio-pyrolysis is the thermal decomposition of biomass at elevated temperatures in the absence of oxygen, or when significantly less oxygen is present than required for complete combustion. Nowadays, pyrolysis describes processes where pyrolysis oils are the preferred products [1]. The bio-oils from a pyrolysis process can contain a large number of chemicals. Upon condensation, there is always an oil phase, but sometimes also a separate aqueous phase containing some of the more water-soluble products. Bio-oils have shown some significant environmental advantages over traditional fossil fuels [2], such as CO_2 neutral and low sulfur content, so they can be a logical choice for the next generation fuels.

1.2 Typical Composition of Pyrolysis Liquid Products

Fast pyrolysis is a high-temperature process in which biomass is rapidly heated in the absence of oxygen, producing 60-75 wt% of liquid bio-oil, 15-25 wt% of solid char, and 10-20 wt% of non-condensable gases, depending on the feedstock used [1]. Figure 1.1 shows a generic product breakdown from the pyrolysis process. Mullen and Boateng analyzed bio-oil from pyrolyzed switchgrass, for cellulose- and hemicellulose-derived compounds. Using HPLC they found acetic acid (2.9 wt%), hydroxyacetaldehyde (2.4 wt%), acetol (2.7 wt%), and levoglucosan (6.4 wt%) as major identifiable compounds. For lignin-derived compounds they found less than 3% phenolics [3]. Mullen et al. also studied the pyrolysis of three biomass feeds derived from barley, straw, hulls, and distiller's dried grains with solubles (DDGS). The bio-oils were produced by fluidized-bed fast pyrolysis.

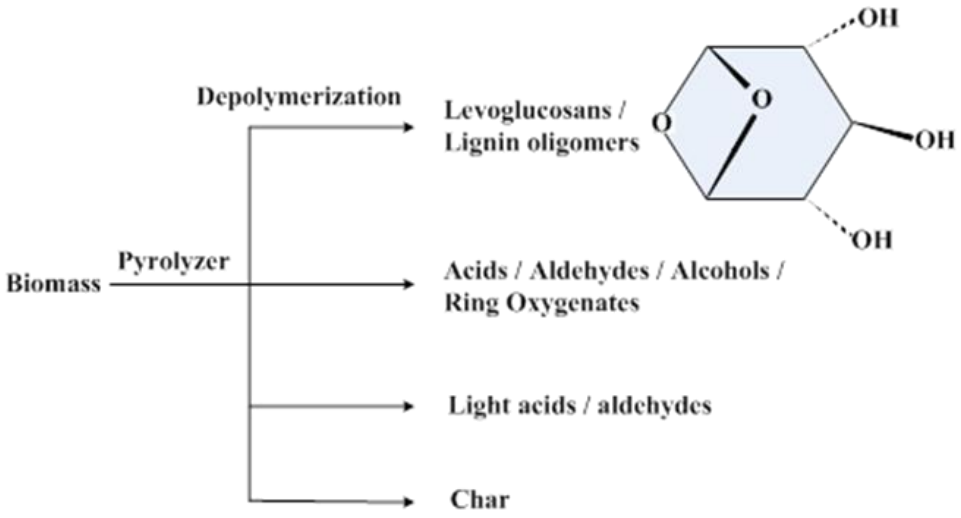

Figure 1.1 - Breakdown of Fast Pyrolysis Products (Principal Fractions)

Their results for major identifiable compounds as determined by GC/MS and aqueous HPLC were showed in Table 1.1, and the elemental analysis results of Table 1.2 also illustrate main elements distribution in the pyrolysis products from the biomass[4]. The ration of the conversion of carbon (Bio-oil) to the conversion of oxygen (Bio-oil) is about 7.36, which gives a high energy density (~32MJ/kg) in the bio-oil product.

Table 1.1 - Composition of Three Fast-pyrolyzed Bio-oils

Compound	Straw bio-oil, wt%	Hulls bio-oil, wt%	DDGS bio-oil, wt%
Acetic acid	8.56	7.56	0.75
Furfural	0.39	0.53	0.00
Acetol	6.31	4.79	0.00
Levoglucosan	2.06	3.15	2.24
Phenolics	0.97	1.43	0.46

Table 1.2 - Elemental Balance on Biomass (DDGS) and Pyrolysis Products

	Biomass	Bio-oil	Biochar	Non-condensed Gas (NCG)	Water
C	100%	76.6%	16.2%	7.3%	
H	100%	59.7%	4.4%	1.3%	36.9%
O	100%	10.4%	3.8%	24.0%	63.0%
N	100%	79.4%	20.7%		

Oasmaa et al. found, that for the fast pyrolysis liquid products, the water content was about 20-30 wt%, and that its composition increased with pyrolysis time. The pyrolysis oils contained less than 10 wt% volatile carboxylic acids, among which the main ones were acetic and formic acids [5]. Piskorz et al. analyzed bio-oils pyrolyzed from four different kinds of biomass (Brockville Poplar, White Spruce, Red maple, and IEA Poplar), and found weight percentages (based on the weight of the feed) as follows: aldehydes (e.g., hydroxyacetaldehyde and formaldehyde) less than 10 %; heavy phenolics from 16.2 to 24.8 %; disaccharides (e.g., cellobiosan) from 1.1-2.5%; monosaccharides (e.g., fructose and glucose) from 1.7 to 3.5% [6]. Zheng analyzed the bio-oil produced from the fast pyrolysis (fixed at 520 ℃) of torrefied pine in a fluidized bed. The analytical results showed that when the torrefaction temperature was 240 ℃, the acetic acid fraction of the bio-oil was 4.88 wt%, ketone group 3.23 wt%, furan group 0.83 wt%, and phenolic compounds 2.86 wt% [7].

1.3 Current Separation Methods for Pyrolysis Bio-Oils

According to the literature, bio-oil solvent fractionation is a promising method for separating pyrolysis liquids, and there exist many specific solvent fractionation methods [1]. However, one common idea in these works is they combine inorganic solvents (such

as water, sodium hydroxide, or inorganic acids) with organic solvents (such as ethers, esters, methanol, hydrocarbons, or halogenated hydrocarbons) to manage the separation process. For example, in a bench scale experiment at room temperature, vacuum-pyrolyzed birchwood bio-oil was extracted three times with an equal volume of pentane, then the pentane insoluble fraction was dissolved in two volumes of toluene and extracted three times with an equal volume of water. The toluene solution can be evaporated to obtain a syringol-rich fraction. The water solution must be extracted three times with twice the volume of ethyl acetate, to give another syringol fraction in the ethyl acetate [8]. Similarly, in another bench-scale phase separation of vacuum-pyrolyzed softwood bark bio-oil, which was not produced by fast pyrolysis (heating rate of $12\ ℃/min$), centrifugation was applied first to get two layers. For 1.0 g of either upper layer, bottom layer or whole bio-oil samples, 100 mL of the following extraction solvents were used: pentane, benzene, dichloromethane, ethyl acetate and methanol. The results of extraction are shown in Table 1.3 [9]. Pentane was applied to extract nonpolar to less-polar compounds like hydrocarbons and olefins, benzene and dichloromethane targeted moderately polar compounds such as phenols and similar oxygenates, while ethyl acetate and methanol were aimed at more polar compounds such as ketones, aldehydes, sugars and acids [9].

Some investigations have focused on an initial phase separation of bio-oils, the idea being that a water-soluble fraction can be separated from the rest of the bio-oil by adding a salt solution [10]. After condensation of vapor bio-oil, Chen et al. added about 20 different kinds of salt solutions to bio-oil samples (mass ratio of salt solution to bio-oil was 1/10, at below 15 ℃), and found that the mass ratio of the bottom (aqueous) layer to the whole

Table 1.3 - Results of Extractions

	Fractionation (wt%, on total sample basis)					
component	pentane	benzene	CH_2Cl_2	Ethyl acetate	MeOH	total
upper layer	4.0	11.4	7.2	63.3	14.1	100
bottom layer	0.2	1.4	3.0	49.4	46.0	100
whole bio-oil	1.0	3.2	3.4	51.9	40.5	100

bio-oil increased with increasing concentration of solution. They also found that for more acidic (or less basic) salts like $NaHCO_3$, the rates of such increase were faster than those of more alkaline salts like Na_2CO_3. In addition, some metal ions can form complexes with phenols in bio-oil and affect the phase separation. However, after phase separation, solvent fractionation is usually needed for further separation.

Water is the easiest liquid to use for these initial phase separations of bio-oil liquids. Piskorz et al. added water to bio-oil sample in a 30% weight ratio to obtain phase separation. The water-insoluble fraction is called “pyrolytic lignin” and the water-soluble fraction contained such compounds as cellobiosan (4.0 wt%), glucose (1.5 wt%), fructose (3.6 wt%), glyoxal (4.0 wt%), levoglucosan (6.3 wt%), hydroxyacetaldehyde (12.4 wt%), formic acid (11.5 wt%), acetic acid (6.2 wt%), ethylene glycol (1.4 wt%), and acetol (1.9 wt%) [11].

Another method adopted for rough separation of bio-oils is distillation of the condensed bio-oil. Murwanashyaka et al. used steam distillation and further vacuum distillation to separate the lighter phenolic compounds (phenol and guaiacol) from heavy phenolic compounds (syringols) of vacuum-pyrolyzed softwood bark bio-oil [8]. In the steam distillation section, using a steam-to-pyrolytic oil ratio of 27, 88.2% of the total phenols

present in the initial bio-oil were recovered. The further vacuum distillation of the products from the steam distillation at 25℃-135 ℃ (total pressure of 0.67 kPa) resulted in 16 different distillate fractions in different temperature ranges. Then they used solvent fractionation as discussed previously to obtain concentrated syringols.

The reverse of the distillation process discussed above is the fractional condensation of the biomass pyrolysis vapors leaving the continuous flow reactor. Westerhof et al. controlled the reactor and the first condenser temperatures to get bio-oils of different compositions [12]. When the reactor temperature was 480 ℃, they got more sugars, mid-boilers, and water-insoluble lignin-derived oligomers; when the reactor temperature was 330 ℃ they obtained a light oil. Bio-oils collected from the first condenser at 70 − 90 ℃ have less water and acetic acid than if it is operated at 20 ℃, and this is good for further refining of the bio-oil.

In summary, solvent fractionation, phase separation, distillation of condensed bio-oil, and condensation of pyrolysis vapors are four of the current separation methods for processing bio-pyrolysis liquids. The selectivity of separation for interested compounds is the key point of all the four separation strategies.

1.4 Char from Biomass Pyrolysis

Mohan et al. in their review noted that the hemicellulose fraction of biomass (25-35 wt% of dry wood) usually decomposes at from 200 − 260 ℃ , producing less char than the cellulose fraction (40-50 wt% of dry wood) [1]. Pyrolysis of the lignin fraction (20-30 wt% of wood) can produce even more residual char than the pyrolysis of cellulose, which means that some of all three major fractions of the original biomass fed to the pyrolyzer end up as char. Imam and Capareda found that in the pyrolysis of switchgrass (32 wt %

cellulose, 19.2% hemicellulose and 18.8% lignin) at 600 ℃, the product contained 25% bio-char, and the bio-char yield decreased from 48% to 25% when temperature increased from 400 to 600 ℃ [13]. Piskorz et al. mentioned that in their bench scale fast pyrolysis of sweet sorghum (dry basis: 14-16 wt% lignin, 46-48 wt% cellulose/hemicellulose), the char yield is 21 wt% (feed basis) with the reactor temperature at 427 ℃. This is near the temperature where the maximum liquid product yield was obtained [14]. Scott et al. in their research of fast pyrolysis of White spruce (softwood) and Poplar (hardwood) noted that the char yields are 12.2 and 11.8 wt% of the mass of the wood feeds, respectively [15].

Because so much char is produced in either biomass fast pyrolysis or biomass gasification processes, one goal of biomass-to-fuels or -chemicals process development is to find some uses for it. One possible use could be to regard them as one kind of adsorbent material, as shown in the following section.

1.5 Current Separation Work: Economical Solid Adsorption

Solid-phase selective adsorption could be a promising frontier in the separation of bio-oil fractions. But economic considerations are most important: the adsorbents used must either be cheap (waste solids) or completely regenerable. In the waste solids category, Junk et al. showed that fly ash can remove aromatic hydrocarbons (20–50 ppb) from water [16]. Vapor phase pyrene (a PAH) was successfully adsorbed on coal ash [17]. Subsequent pyrene recovery using methanol extraction ranged from 0 to 100% depending on the fly ash source. This evidence gives the idea that some waste solids like fly ash might be used to adsorb some of the organic compounds of a pyrolyzed bio-oil, and that an adsorptive separation might have commercial application. Meanwhile, some more

basic solid adsorbents may be worth further study to see if they can separate light acids from the residual bio-oils.

The separation strategy studied in this thesis is to first try to adsorb the relatively heavier components of the bio-oils on cheap adsorbents. For this purpose four different kinds of waste solids were tested, on two different synthetic bio-oil mixtures. The four adsorbents were Class C fly ash (FAC), fumed silica (FS), a pyrolysis biochar (BC) that was a product of biomass gasification, and a blast furnace slag (BFS). If successful, the solid mixture of adsorbates / adsorbent could be used directly in asphalt cement processes, or as fuel. In other words, heavier components don't need to be recovered after separation process.

After separating out the heavier components, the lighter acids and aldehydes could then possibly be adsorbed in a second step on basic (modified) activated carbons or other basic adsorbents. Then water wash and light organic solvents can be manipulated to recover and further purify light acids from the mixture of adsorbates / adsorbent. For these batch adsorption experiments, "reduced" bio-oil, in which all of the heavier compounds were excluded, were tested. These experiments were designed to determine the selectivity of the adsorbents for light acids relative to the middle distillates.

The combination of the two adsorption steps in succession, if both were successful, would leave behind a middle distillate fraction which is the bio-oil fraction most amenable to catalytic upgrading, to either a fuel or chemical feedstock. As the dominant acids in the parent bio-oil are low molecular weight, the middle distillates would also be greatly reduced in acidity, and so more stable and compatible with current hydrodeoxygenation catalysts.

The heaviest cut bio-oil components are replacements for at least some of the petroleum-based asphalt in cement [18, 19] or roofing shingles.[19-21] The bio-oil can actually improve the cement's low temperature [18] mechanical properties. Here the limestone dust (~10%) or other fine aggregate used as filler in asphalt would be replaced with the collected bio-fly ash, slag, etc., containing the adsorbed bio-oil. Fly ash, blast furnace slag and similar waste materials have been shown to be effective asphalt fillers [22-31], in many cases improving the mix's moisture resistance, cohesion, and stiffness, while reducing energy requirements. However, additional research is required in order to confirm that VOC emissions remain low during asphalt processing, that long-term asphalt mechanical performance is suitable, and that the optimal amount of bio-binder is used. Binder anti-stripping properties could actually be improved by the attraction of slightly acidic phenolic –OH groups of the heavier bio-oil fraction to the basic groups on the ash or slag.

2. EXPERIMENTAL METHODS

2.1 Materials

2.1.1 Bio-oils

The feeds for these studies were two synthetic bio-oils of the following compositions on a dry basis (Table 2.1). Working with such mixtures was easier than using actual unrefined pyrolysis oil, especially for analytical purposes. The synthetic composition duplicates the major compound classes (including water) in raw switchgrass and similar lignocellulosic bio-oils, based on previous studies [5, 32, 33]. The final mixture is a homogeneous liquid with much better stability than raw bio-oil, although only small amounts were made up at any time. Among the major compounds in both Mix. #2 and Mix. #3, the composition of furfural compounds are different because we want to make both synthetic bio-oils stable. And if too much furfural presented in Mix. #2, it proved to be too unstable.

Table 2.1- Synthetic Bio-Oils, Wet Basis

Mix #2	**wt %**	**Mix #3**	**wt %**
formaldehyde	14	hydroxyacetone	5
acetic acid	14	2-methylfuran	5
acetone	14	furfuryl alcohol	5
ethanol	3.5	acetic acid	15
furfural	3.5	isobutyric acid	5
4-hydroxybenzaldehyde	3.5	furfural	10
phenol	3.5	guaiacol	10
glucose	14	glucose	15
water	30	water	30

The sources and purities of these chemicals were as follows:

Formaldehyde – Sigma-Aldrich, 37% in water/methanol

Acetic acid – Fischer, reagent

Acetone – Sigma-Aldrich, HPLC

Ethanol – Alfa-Aesar, anhydrous denatured, 95%

Furfural (2-furaldehyde) – Acros, 99%

Hydroxyacetone – Acros, Tech

Phenol – Liquefied, 90% (bal. water), Mallinckrodt

Furfuryl alcohol – Acros, 98%

Glucose (dextrose) – Anhydrous, B&A

Isobutyric acid – Aldrich, 99%

Guaiacol (2-methoxyphenol) – Alfa-Aesar, 98%

2.1.2 Adsorbent Materials

The adsorbents (potential asphalt fillers) tested in the first part of the study were class C fly ash (FAC), blast furnace slag (BFS), waste fumed silica (FS), mullite, and a switchgrass biochar (BC). The granulated BFS was supplied by Lone Star, type Aucem, 28-38% SiO_2, 8-18% Al_2O_3, 35-45% CaO, up to 16% MgO. The Class C FAC was supplied by Bayou Ash, CaO >5% and the sum of SiO_2, Al_2O_3, and Fe_2O_3 between 50-70%. The biochar was produced at the pilot-plant gasifier of Oklahoma St. University (steam/air, ~870 ºC). The fumed silica was provided by PPG (now Axiall) as a waste product from its food-grade silica operations.

We worked with three common activated carbons (Calgon PCB, Nuchar CEE and Darco G-60) as base materials. These carbons were characterized for total acid and base sites

using Boehm titration. The Boehm procedures were taken from standard literature sources [34-36]. BET surface areas, pore volumes and pore size distributions were measured by N_2 adsorption-desorption (Quantachrome AS-1) with pore sizes calculated by the BJH method.

More highly basic groups were incorporated into these carbons by reacting them with alkali, adapting the procedure of Suppes [37]. After thorough washing to reach a wash pH near 7, each carbon was ground in a porcelain mortar and pestle with double the weight of KOH, adding water as necessary to make a paste. The pastes were loaded into Vycor crucibles, dried overnight at 100 ºC, then at 400ºC for 1 h, then 800 ºC for 1 h. After cooling excess water was added to dissolve the unreacted KOH, then the solid was filtered, vacuum dried at 140 ºC, then an additional 2 h at 400 ºC under vacuum.

Three different kinds of carbon-coated silica and a kind of carbon-coated alumina were also synthesized for batch adsorption experiments. The stepwise synthesis procedures are as follows. To 5.0 g of each support material enough sucrose solution (0.1 g/ml) was added to give 10 wt% carbon on each support. The solutions were contacted with the supports in Petri dishes and stirred with a glass rod until no visible liquid phase remained. These materials were carbonized in a tube furnace (Thermolyne 21100) using an alumina tube starting at 100 ºC, raising to 400 ºC over 2 h, then holding at 400 ºC for 2 h. The N_2 flow through the furnace was >200 mL/min. The final products were named CC-1 to CC-4 with the ordering the same as in Table 2.2 below.

2.2 Chromatographic and Batch Adsorption Studies

Chromatographic adsorption tests were conducted using ¼" diameter stainless steel

Table 2.2 - Support Materials for Carbon-Coated Adsorbents

Support Name	Material	Surface area / (m^2/g)	Pore volume / (cm^3/g)	Average Pore size / nm
Perlkat 29-3[a]	Silica	300-500	0.79	10.0
MEA-5[b]	Alumina	430	1.15	4.0
RYOO-4[b]	Silica	770	0.70	4.4
SBA-16[b]	Silica	550	0.94	9.4

[a]Manufacturer's (BASF) specifications

[b]Personal communication, Kerry Dooley, 3/18/2013.

packed columns of varying lengths. Temperature was controlled by a GC oven (HP 5890). Mullite (an aluminosilicate mineral, size >20 mesh) was used as an inert column filler. It was verified that mullite adsorbed very little bio-oil at temperatures up to 350ºC. The bio-oil samples injected from the normal GC inlet (0.2-0.6 μl) were either single components at the same wt% as in the mixtures of Table 2.1 (balance methanol), or the feed mixtures themselves (0.05-0.5 μl). All runs were isothermal. An FID detector was used to quantify the amounts eluting. There was no calibration, so all results are reported as raw intensity (detector signal voltage).

Batch adsorption experiments made use of a glass apparatus and a Schlenk line under no-air conditions. The adsorbents were added to thick-walled glass tubes (0.75" O.D.), each of which was sealed (by O-ring and spring clamp) to a glass vacuum adapter. The tubes were evacuated and dried for 30 min at 200 ºC. Then a fixed ratio of liquid/adsorbent (at least 4 on a weight basis) was added under N_2, the tube evacuated, and then immersed in a hot sand bath for times of at least 2 min. It was sealed almost immediately after

immersion. The time to reach the desired adsorption temperature was calculated using Eq. (1):

$$t = \frac{\rho C_p}{U_i (2 / R_i)} \ln\{\frac{T_o - T_1}{T_o - T_2}\} \quad (1)$$

Where U_i is the estimated overall heat transfer coefficient, R_i the tube inner radius, T_o the sand bath temperature, T_1 and T_2 the tube initial and final temperatures, and the other symbols have their usual meanings. For the highest nominal temperature, assuming a U_i of at least 500 W/(m^2-K), the tube would be within 20 ºC of the desired adsorption temperature in <1 min, with a desired residence time at the adsorption temperature of ~1 min. In the batch adsorption experiments, the temperature of sand bath was measured by a K-type thermocouple and readout (Omega).

2.3 Analytical Methods

The gas chromatography method for the chromatographic adsorption tests is given in Table 2.3.

The feed samples and the samples taken after the batch adsorption experiments were dissolved in HPLC methanol, 10% by volume. Methanol was also used as the internal standard. These samples were analyzed by gas chromatography using a 0.53 mm, 30 m long Nukol column (Supelco). The method is given in Table 2.4. The retention times and calibration factors are given in Tables 2.5 (mixture #2) and 2.6 (mixture #3). The factors were computed by repeated shots of the feeds themselves – at least 5, but more for those presenting analytical problems such as sample decomposition or oligomerization. Of these, glucose presents the most problems (it decomposes in the inlet port) and it is further discussed in third part of this thesis. Furfuryl alcohol and furfural can interconvert

Table 2.3 - GC Method (Chromatographic Adsorption)

Parameter	Setting
Injector Temperature	280 ℃
Detector Temperature	330 ℃
Initial Temperature	320 ℃
Final Temperature	320 ℃
Isothermal Time	15 min
Carrier Gas Flow Rate	30 mL/min
Injection Volume	0.05 μL

to some extent, but both peaks were quantified when present. Formaldehyde and hydroxyacetone can undergo facile aldol-type condensations, so the dimer was also quantified when present. The identities of the compounds were confirmed by injections of single component standards in methanol.

The amounts of each compound were computed using the following equations:

$$\frac{WT_i}{WT_{i.s.}} = \frac{A_i}{A_{i.s.}} \frac{(^{WT_i}/_{WT_{i.s.}})_{Avg.In\ Mix}}{(^{A_i}/_{A_{i.s.}})_{Avg.In\ Mix}} \quad (2)$$

Where WT_i represents the weight of component i, and $WT_{i.s.}$ means the weight of the internal standard, which is methanol.

$\mathrm{A_{i.s.}} = \text{Area of Internal Standard} = \text{Area of Methanol}$

$\mathrm{A_i} = \text{Area of Detected Compound}$

So both $\mathrm{A_{i.s.}}$ and $\mathrm{A_i}$ are acquired from GC integration, both $(^{\mathrm{WT_i}}/_{\mathrm{WT_{i.s.}}})_{\mathrm{Avg.In\ Mix}}$ and $(^{\mathrm{A_i}}/_{\mathrm{A_{i.s.}}})_{\mathrm{Avg.In\ Mix}}$ are known values, representative of the feed.

Table 2.4 - GC Method (Batch Adsorption)

Parameter	Setting
Injector Temperature	220 ℃
Detector Temperature	210 ℃
Initial Temperature	40 ℃
Initial Time	3 min
Ramping Rate 1	5 ℃/min
Final Temperature 1	80 ℃
Final Time 1	10 min
Ramping Rate 2	10 ℃/min
Final Temperature 2	200 ℃
Final Time 2	22 min
Carrier Gas Flow Rate	15 ml/min
Injection Volume	0.1 μL

Table 2.5 - Retention Times and Calibration Factors for Bio-Oil Mix#2 Standards

Compound	Retention Time /min	Calibration Factor / *area/area I.S.*[1]
Acetone	1.0-1.4	0.0028 ± 0.002
Ethanol	1.7-1.8	0.0057 ± 0.0022
Formaldehyde	7.4-7.7 (major) ; 9.5 (minor)	0.0020 ± 0.0008
Acetic acid	14.9-15.4	0.0142 ± 0.0009
Furfural (2-Furaldehyde)	12.8-13.1	0.010 ± 0.002

(Table 2.5 continued)

Compound	Retention Time $/min$	Calibration Factor / *area/area I.S.*[1]
Furfural alcohol	16-16.6	0.011 ± 0.001
Phenol	30.4-30.6	0.010 ± 0.003
Glucose	27.4-30.2 (major) ; 15.4, and 31.5 (minor)	0.0054 ± 0.0037
4-Hydroxybenzaldehyde	47.4	0.0094 ± 0.0035

Table 2.6 - Retention Times and Calibration Factors for Bio-Oil Mix#3 Standards

Compound	Retention Time $/min$	Calibration Factor / *area/area I.S.*[1]
2-Methylfuran	0.94	0.0048 ± 0.0002
Hydroxyacetone	9.3 (major) ; 11.9-12.3 (minor)	0.0073 ± 0.0004
Acetic acid	13.2-13.5	0.0020 ± 0.001
Furfural (2-Furaldehyde)	14.5-14.6	0.018 ± 0.0003
Furfuryl alcohol	16.9-17 (minor) ; 24.7-25 (major)	0.011 ± 0.001
Isobutyric acid	20-20.2	0.013 ± 0.001
Guaiacol(2-methoxyphenol)	28-28.2	0.033 ± 0.003
Glucose	30.8-31 (major) ; 29.9, 32.6-33.4, 35.2 (minor)	0.010 ± 0.002

[1]I.S. = internal standard, methanol

3. RESULTS AND DISCUSSION

3.1 Separation of a "Heavies" Fraction

Each individual component was mixed with methanol (at the wt. fraction the component has in the mixture, balance methanol) to determine its distribution coefficients and selectivity relative to methanol on longer (40 cm) ¼" columns of the adsorbents at 350ºC. The selectivity shows how strongly that compound can adsorb on the solid from the mixture:

α = adsorption selectivity = k_j / k_{MeOH} (3)

Where k is the solid-gas distribution coefficient. For chromatographic separation the distribution coefficient is determined from [38]:

$k_j = (t_{Rj} - t_0)/(t_0)$ (4)

Where t_{Rj} is the retention time of the bio-oil component and t_0 is the retention time of an unretained component (i.e., the gas phase residence time).

The biochar exhibited strong, irreversible adsorption of all components at these longer residence time conditions. The FAC and BFS irreversibly adsorbed all of the heavier glucose decomposition products even at the lowest loading. These decomposition products are 5-hydroxymethylfurfural, levulinic acid, levoglucosan and 1,6-anhydroglucose [39-42]. This suggests that most, if not all, of the heavy levoglucosans and lignin phenolics can be separated from the lighter materials using adsorbents like these at practical temperatures near those of the pyrolyzer. Results for the other compounds in mixture #2 are shown in Figure 3.1. The advantage of FAC over BFS as an adsorbent is more pronounced than Figure 3.1 suggests, because in other tests it was found that the total adsorption capacity of the FAC is 25% more than that of BFS at

350ºC. This was determined by comparing relative peak intensities for the mixture on a clean adsorbent in side-by-side chromatographic experiments on the two adsorbents.

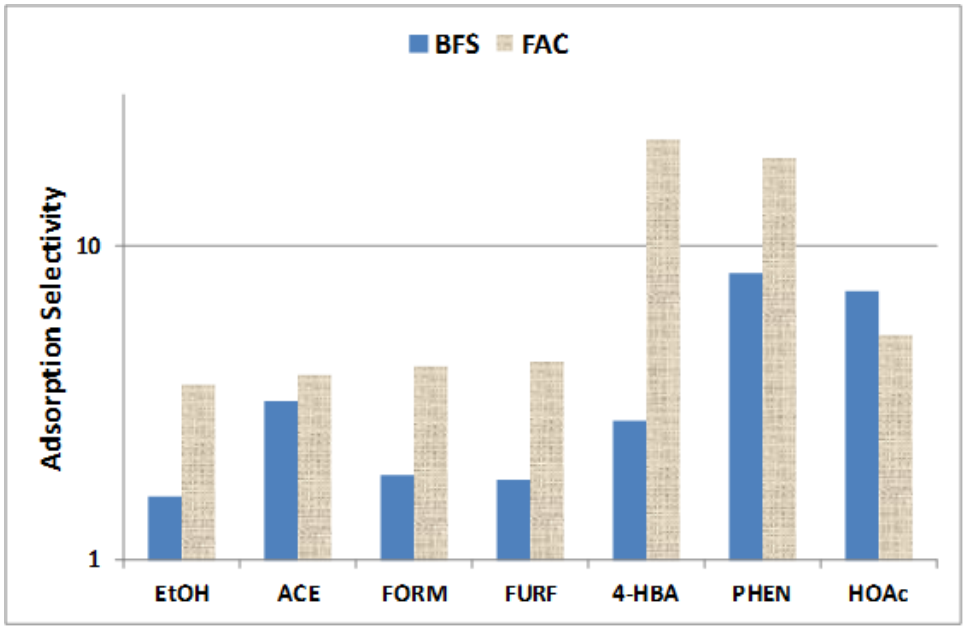

Figure 3.1 - Adsorption of individual bio-oil compounds from mix#2 on either fly ash (FAC) or blast furnace slag (BFS) at 350 ºC, using packed adsorption columns at low loading. Compounds are: EtOH, ethanol; ACE, acetone; FORM, formaldehyde; FURF, furfural; 4-HBA, 4-hydroxybenzaldehyde; PHEN = phenol; HOAc = acetic acid. A selectivity of 10 means the compound adsorbs 10 times more strongly than methanol

From Figure 3.1, it suggests that heavier oxygenates could possibly be separated from lighter compounds on such cheap adsorbents. This possibility was tested further by injecting the entire mixture into the columns, and, while separation was poor at 350 ºC, at a lower temperature three fractions were obtained as shown in Figure 3.2, 3.3, 3.4 (the glucose is the 3rd fraction and does not elute at all).

Examining Figs. 3.1, 3.2, and 3.3, it would seem a key separation is between phenol, furfural and acetic acid, representing phenolics, middle distillate oxygenates, and light acids, respectively. But the column retention times are too long to preclude extensive degradation, and there are practical limits on column lengths with this method, so it was

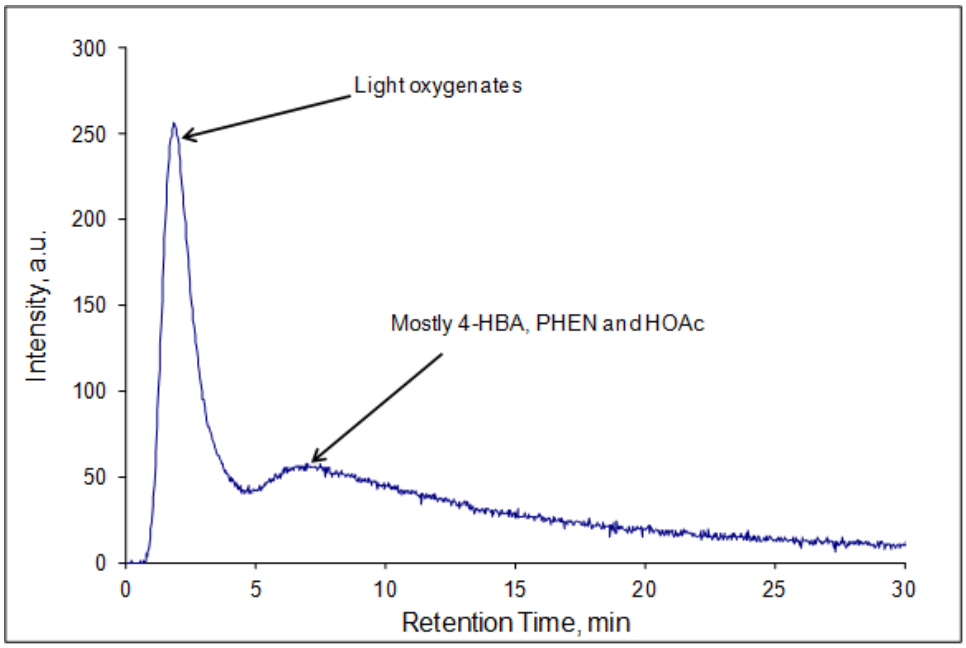

Figure 3.2 - Separation of mix#2 of Table 2.1 on FAC column at low loading, 320 ºC. The separation on BFS was similar and the selectivity of the 2nd peak relative to the 1st is ~5. Water was not detected (FID detector), and glucose's products were (mostly) irreversibly adsorbed

decided to move to a different method based on batch adsorption.

The samples analyzed by the batch adsorption method are from the residual liquid, and so give the amounts not adsorbed. But assuming mass balance the amounts adsorbed can be computed. The experiments were at too small a scale to elute and analyze the adsorbates.

The amounts adsorbed can be computed as follows.

$$Fraction\ Adsorbed\ \% = [1 - \frac{\left({WT_i}/{WT_{i.s.}}\right)_{Product}(V_{Product})}{\left({WT_i}/{WT_{i.s.}}\right)_{Avg.In\ Mix}(V_{Feed})}] \times 100 \quad (5)$$

Where the value of $\left({\mathrm{WT_i}}/{\mathrm{WT_{i.s.}}}\right)_{\mathrm{Product}}$ is acquired using Equation (2), $\left({\mathrm{WT_i}}/{\mathrm{WT_{i.s.}}}\right)_{\mathrm{Avg.In\ Mix}}$ is a known value the same as in Equation (2), and $V_{Product}$ and V_{Feed} are the volumes of the liquid product and the original liquid feed, respectively.

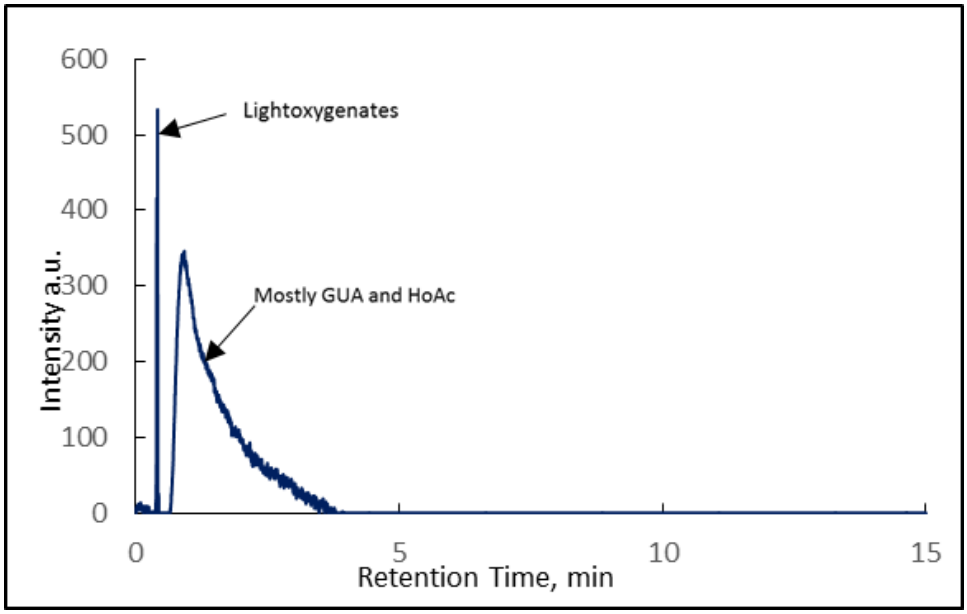

Figure 3.3 - Separation of mix#3 of Table 2.1 on FAC column at low loading, 320 ℃. The selectivity of the 2nd peak relative to the 1st is ~1.5; Water was not detected (FID detector), and glucose's products were (mostly) irreversibly adsorbed

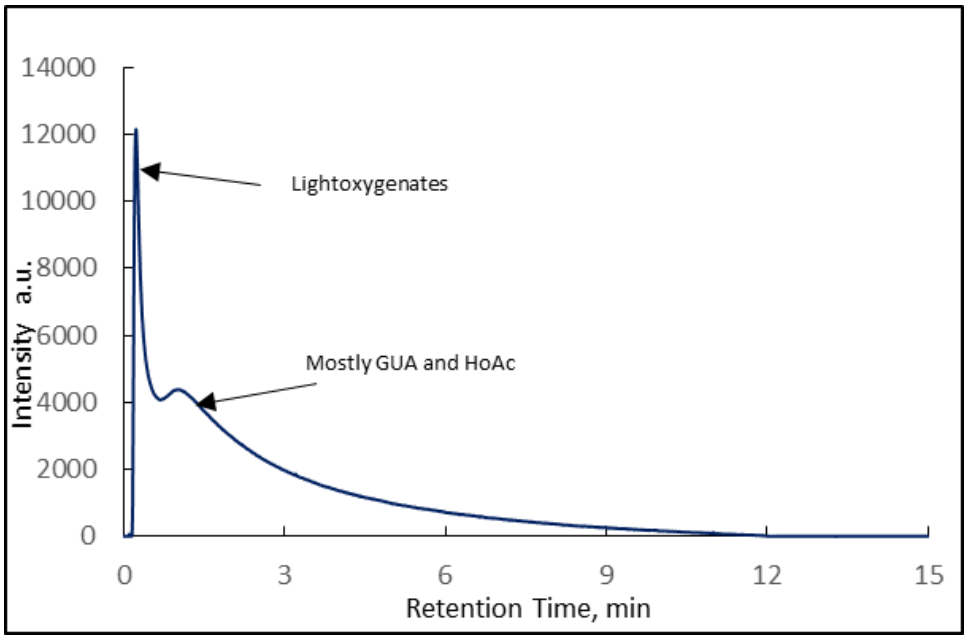

Figure 3.4 - Separation of mixture #3 of Table 2.1 on Biochar column at low loading, 320 ℃. The selectivity of the 2nd peak relative to the 1st is ~3.0; Water was not detected (FID detector), and glucose's products were (mostly) irreversibly adsorbed

$$WT_{Adsorbed}/_{WT_{Adsorbent}} = \frac{(\frac{Fraction\ Adsorbed\ \%}{100})(V_{Feed})w_j}{WT_{Adsorbent}} \quad (6)$$

Where $WT_{Adsorbed}$ represents the mass of the compound adsorbed, $WT_{Adsorbent}$ is the mass of adsorbent applied in the adsorption experiment, w_j is the weight percentage of compound j in the original feed. Note that the feed densities were near 1.0 g/mL, allowing the use of V_{Feed} in eq. (6).

Adsorbate amounts showing the key separation metric wt. furfural / wt. phenol for mix #2 are shown in Figure 3.3 below. Heavier compounds were (mostly) adsorbed, but typically less than 80% of the phenol was adsorbed, for any of the adsorbents tested. Some of the variation in Figure 3.5 can be attributed to imprecise control of residence time, but nonetheless it can be concluded that temperature is the important variable. Recognizing that smaller numbers on the y-axis mean better separation, the process would have to be operated at <300 ºC. The "lights" and "heavies" would be separated and compounds similar to furfural and phenol would behave (to use a distillation analogy) as the light and heavy keys, i.e., a clean split is not possible between them.

Recognizing that the wide range of compositions in typical bio-oils might result in different behavior than shown in Figure 3.5, the batch adsorption experiments were repeated with mixture #3, which consists of slightly different light and heavy compounds, but similar amounts of acetic acid, glucose and water. Results of these experiments are shown in Figure 3.6. Again, smaller numbers on the y-axis mean better separation of the middle distillates from the phenols, here represented by guaiacol. Similar amounts of guaiacol were adsorbed by all the solids.

It can still be concluded that temperatures <300ºC would be better for separation, although the effect for this mix is less marked. It appears that biochar (BC) is the best

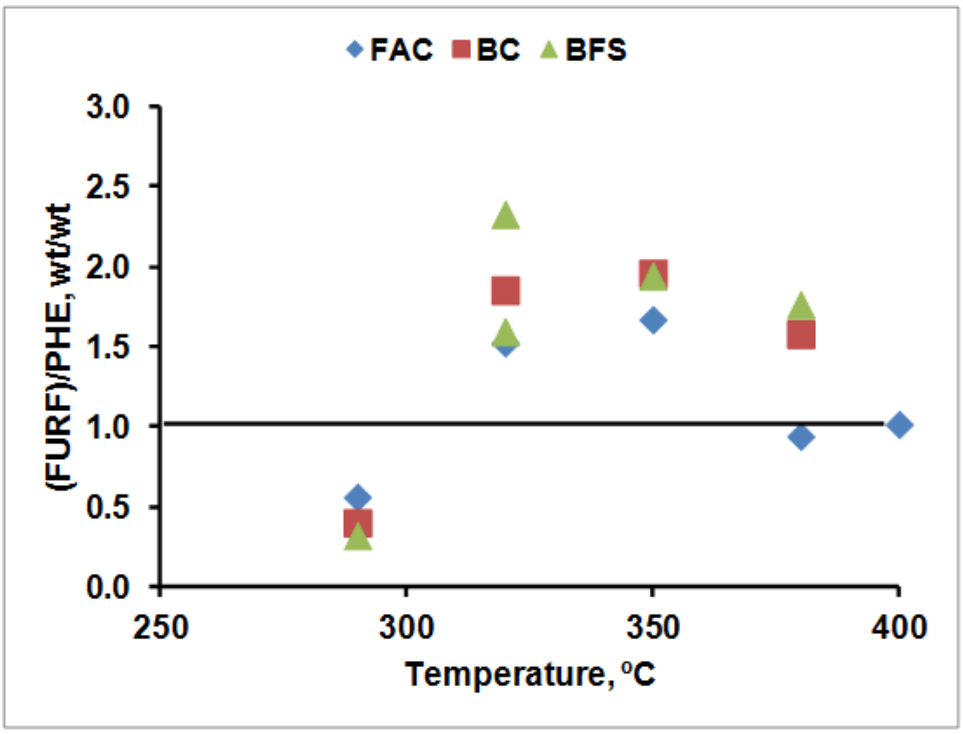

Figure 3.5 - Selectivity to middle distillates (represented by furfural) relative to heavies as represented by phenol (glucose and 4-hydroxybenzaldehyde products almost entirely adsorbed). The horizontal line shows the metric for the feed. Results for fused silica similar to FAC

adsorbent to adsorb the "heavies", with FAC a reasonable alternative. For no separation whatsoever, the wt/wt ratio = 3, so BFS and FS actually prefer the lighter compounds slightly over guaiacol.

3.2 Separation of a Light Acid/Aldehyde Fraction

The lightest pyrolysis bio-oil fraction is disproportionately acid/aldehyde. This suggests potential separations based on acid-base type interactions. A problem with such studies of this type in the past has been the preferential selectivity of adsorbents for the lignin oligomers[43]; the initial removal of the "heavies" fraction solves this problem. Organic acids can be removed from wastewaters by activated carbons, so this is a logical starting point for a more selective adsorption. But most activated carbons contain more acidic (e.g., carboxylic, phenolic) than basic (e.g., amino, quinone) groups. Boehm

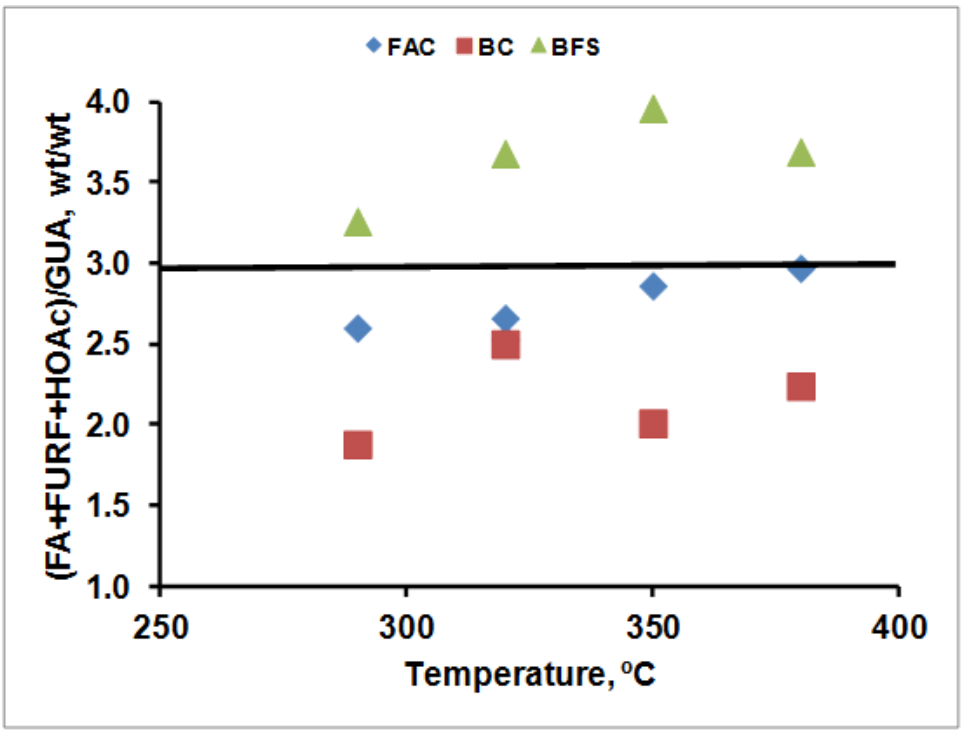

Figure 3.6 - Selectivity to middle distillates relative to heavies as represented by guaiacol (glucose products almost entirely adsorbed). Results for fused silica similar to BFS. The weight ratio of the feed is 3

titrations of the three starting carbons gave the following totals for acidic and basic groups, respectively (meq/g): Calgon PCB, 0.67 and 0.086; Nuchar CEE, 0.25 and 0.049; Darco, 0.20 and 0.018. Therefore it is unlikely that typical unmodified activated carbons could successfully separate lighter acids from middle distillates. The carbons could still show high adsorption capacities for all components because they all exhibit high surface areas and pore volumes (e.g., Calgon PCB, 830 m^2/g, 0.47 cm^3/g, ~1.6 nm dominant pore size; Nuchar CEE, 670 m^2/g, 0.54 cm^3/g, ~1.8 nm pore size), but the selectivities for light acids might be poor.

Potential separation of the light acids/aldehydes was tested at 280-350 ºC, target residence times of ~1 min, using the glass batch adsorption apparatus and both the initial and alkali-modified carbons. The batch adsorption experiments followed the same

procedures as before, except the mixtures used were "reduced", meaning that all of the heavier compounds (phenol, guaiacol, glucose, isobutyric acid, 4-hydroxybenzaldehyde) were not included. The remaining compounds were present in the same ratios as in mixtures #2 and #3. This non-inclusion was meant to simulate the initial stage of the separation process. The key separation metric for the second stage, with the carbon adsorbents, would be (furfuryl alcohol + furfural)/acetic acid, keeping in mind that the goal is to adsorb the acids selectively. The metric's values in the feeds are 0.25 (mix #2) and 1 (mix #3).

Initial batch tests confirmed that the unmodified carbons were not selective; all three of them preferred furfuryl alcohol and furfural to acetic acid. The results of batch adsorption tests for the other adsorbents using the "reduced" mixtures are shown in Figure 3.5. BAC-2 is the basic carbon made from Nuchar CEE, BAC-3 from Calgon PCB. Both of these adsorbed almost all of the acetic acid at 250 ºC, and from 40-70% at 300 ºC. For comparison a mildly basic supported oxide (Sud-Chemie T-2728, 20 wt% CeO_2/Al_2O_3, 170 m^2/g surface area) and a more basic pure oxide (MgO from decomposition of the carbonate, 125 m^2/g surface area) were also tested. The adsorbents made from the carbon Darco G-60 (BAC-1) and from the MgO proved too reactive, giving mostly tar product, and so these results are not shown. The CeO_2/Al_2O_3 appears to hold no advantage over the modified carbons.

Clearly the selectivities were improved at 250 ºC, along with the amount of acetic acid adsorbed. However, the best selectivities are still only in the ~2 range for mix #3, which had the more typical weight ratio of (FURF + FA)/(HOAc) in the feed. In Figure 3.7, a y-

axis value of 0.5 gives an adsorption selectivity = 2 for mix #3. While this is not an unreasonable value in a continuous adsorption process, and further improvement in selectivity may be possible at lower temperatures, it would appear that a more profitable approach might be to further increase the number of truly basic groups on the carbon surface. This might be better accomplished using organic modification reactions. Modification of silica with amino groups has been applied to a similar separation at much lower temperatures [44].

Another approach might be to use high surface area, high strength carbon-coated meso- and megaporous adsorbents. Initial syntheses of such carbon-coated adsorbents have been successful, except for the material derived from SBA-16 (sample CC-4, see Table 3.1 below), which underwent partial pore collapse. However, using a standard support SiO_2, a mesoporous Al_2O_3, and a MCM-48 mesoporous silica, carbonization at 400 ºC, proved successful. For 10 wt% carbon layer materials surface areas between 300-500 m^2/g were obtained while preserving most of the original pore structure – compare the values in Table 3.1 and Table 2.2. The specific results of three points BET tests are shown in Table 3.1:

Table 3.1 - Surface Area of Carbon-coated Materials

Sample Name	Support Name	Material	Surface Area / (m^2/g)	Pore Volume / (cm^3/g)
CC-1	Perlkat 29-3[a]	Silica	501.82	0.2532
CC-2	MEA-5[b]	Alumina	304.39	0.1578
CC-3	RYOO-4[b]	Silica	489.03	0.2433
CC-4	SBA-16[b]	Silica	150.9	0.0758

[a]Manufacturer's (BASF) specifications

[b]Personal communication, Kerry Dooley, 3/18/2013.

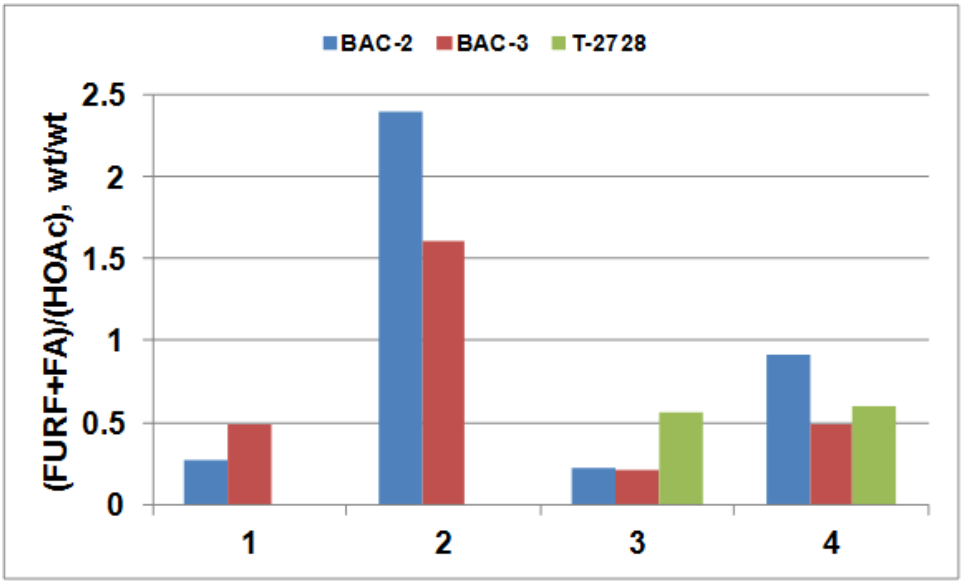

Figure 3.7 - Selectivity to middle distillates relative to acids, as represented by acetic acid. X-Axis labels: 1 = mix #2, 300 ºC; 2 = mix #3, 300 ºC, 3 = mix #2, 250 ºC; 4 = mix #3, 250 ºC. The weight ratios of the feeds are: mix #2, 0.25; mix #3, 1

4. CONCLUSIONS

(1) The chromatographic adsorption tests show that both FAC and BC have potential for separation of the heavier fraction of the bio-oils at short (~1 min) residence times, and that the selectivity for heavies is better at <300ºC. However, the BC exhibited strong, irreversible adsorption of all components at residence times >10 min, as measured by column chromatography. In batch adsorption experiments, the FAC and BFS irreversibly adsorbed all of the heavier glucose decomposition products even at the lowest loading, and also completely adsorbed all of the heavier glucose decomposition products at residence times >10 min.

(2) While the selectivity of light acids for adsorption on alkali-modified activated carbons is better at temperature near 250ºC, it is still relatively low.

(3) Unmodified activated carbons show poor selectivity for acetic acid, while strongly basic oxides generate tar via polymerization. A better approach to increasing the adsorption selectivity for light acids might be to further increase the number of truly basic groups on the carbon surface. This might be accomplished using organic modification reactions, possibly on carbon-coated adsorbents. Some high surface area carbon-coated adsorbents were prepared. The future plan is to modify these carbon-coated porous supports with both pyridine and Schiff base groups to give a more uniformly basic surface than can be provided by the alkali reaction method,[45, 46] in order to further improve the selectivity in the separation of the light acids from the middle distillates.

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VITA

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