Catalytic Cracking of Fast and Tail Gas Reactive Pyrolysis Bio-oils over HZSM-5

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ABSTRACT

While hydrodeoxygenation (HDO) of pyrolysis oil is well understood as an upgrading method, the high processing pressures associated with it alone justify the exploration of alternative upgrading solutions, especially those that could adapt pyrolysis oils into the existing refinery infrastructure. Catalytic cracking is one such alternative industrial practice that is carried out at near-atmospheric pressure using zeolite-based FCC catalysts. The present study focuses on the catalytic cracking of pyrolysis oil of different starting compositions over HZSM-5 to inform the extent of upgrading in the liquid phase. After establishing a catalyst bed temperature of 500 °C as optimum operating condition with regard to deoxygenation and yield of mono-aromatics in the products obtained the performance of the use of conventional pyrolysis and TGRP bio-oils as starting liquids for the cracking were compared. The results indicate that the formation of naphthalenes was favored, while the formation of BTEX compounds was slightly depressed in the case of the TGRP oil. We attribute this finding to the formation of naphthalenes from BTEX molecules already found in the TGRP oil. Subsequent reuse of the catalysts showed that the cracking of TGRP bio-oil exhibited slightly greater deactivation after a third cycle, likely due to the increased formation of naphthalenes and coke which block HZSM-5 pores. The results obtained from this study will help determine the issues that need to be addressed when developing a catalytic cracker with HZSM-5 for regular pyrolysis oil and TGRP oil.

INTRODUCTION

Fast pyrolysis generates a crude liquid oil (pyrolysis oil, or bio-oil), solid biochar, and non-condensable gases[1, 2]. The liquid pyrolysis oil can be catalytically upgraded to value-added chemicals and transportation fuels. Unfortunately, pyrolysis oil has a low energy density and chemical stability relative to petroleum fuels due to high oxygen content and acidity. In fact, pyrolysis oil is known to contain over 300 highly oxygenated compounds, the most prominent being acetic acid, glycolaldehyde, phenol, and levoglucosan [3, 4]. Therefore, bio-oils must be deoxygenated before they can be blended with or replace crude petroleum oils. Currently, there are two main routes widely investigated for the

upgrading of pyrolysis oil. One is catalytic hydrotreating, in which pyrolysis oil is treated with catalysts under high pressures of hydrogen (30-140 bar) and elevated temperatures ($>300\text{ }^{\circ}\text{C}$). Catalytic hydrotreating in petroleum refineries removes heteroatoms present in the crude oil, such as nitrogen (hydrodenitrogenation) and sulfur (hydrodesulphurization), while catalytic hydrotreating of pyrolysis oil removes mainly oxygen (hydrodeoxygenation) from the pyrolysis oils[5-7]. While these processes may be performed analogously with pyrolysis oil, HDO, in particular, may result in excessive and costly consumption of hydrogen. Alternatively, pyrolysis oil can be upgraded through catalytic cracking with solid acid catalysts, typically zeolites, at atmospheric pressure without hydrogen consumption [8-10], which may make catalytic cracking more economical than HDO if acceptable yields can be achieved. In fact, catalytic cracking technology has been widely used in petroleum refineries to convert high molecular weight hydrocarbons, such as vacuum gas oil, into more valuable lighter hydrocarbons including olefins, gasoline, and diesel. Due to the high content of heavy molecules, primarily pyrolytic lignin, in pyrolysis oil many efforts have been made to introduce pyrolysis oil or to co-process pyrolysis oil with heavy petroleum distillates in a catalytic cracker for upgrading [8, 11]. Co-processing of raw pyrolysis oils and vacuum gas oil (VGO) was performed in a demonstration-scale FCC reactor (150 kg/hr), and the system generated similar product distributions as obtained from VGO cracking, such as LPG and gasoline. It was reported that about 30% of carbon in pyrolysis oils ended up in liquid products[12]. Additionally, Lindfors et al. conducted smaller scale co-processing of raw or upgraded pyrolysis oils with VGO in a micro activity test (MAT) unit[11]. The experiments demonstrated that coke increased with increasing pyrolysis oil in the feedstock, and the upgraded pyrolysis oils generated lower amounts of coke due to the lighter chemical compositions.

Zeolites have been the most active and widely used catalysts for cracking of biomass-derived feedstocks (vapors/liquids) as well as petroleum-based feedstocks. Many researchers have investigated the impacts of zeolite catalyst pore size on product yields and selectivities [8, 13] when cracking biomass-derived feedstocks. Shape selectivity of zeolites – i.e. the selective mass transfer limitations of specific compounds – is important in generating aromatic hydrocarbons from biomass-derived oxygenated

compounds. For example, shape selectivity prevents large reactants from entering the pores, thus preventing the formation of high molecular weight compounds which are larger than the pore size. For this reason, the medium pore size of HZSM-5 (~ 6.3 Å) generates small BTEX-type compounds (benzene, toluene, ethylbenzene, xylenes; kinetic diameter of ~ 6.0 Å) rather than large polyaromatic compounds (kinetic diameter of 6.2 Å– 6.8 Å), as compared to other zeolites[13, 14]. Additionally, catalytic pyrolysis of glucose using zeolites with small pore sizes, such as ZK-5 and SAPO-34 (3.9 Å and 4.3 Å, respectively), produces high amounts of coke without any aromatic hydrocarbon formation[13]. Others have studied the catalytic cracking of pyrolysis oil model compounds over HZMS-5 to probe overall reaction pathways of pyrolysis oil cracking[10, 15]. For example, carboxylic acids were proposed to undergo two reaction pathways during catalytic cracking: 1) decarboxylation to form carbon dioxide and ethane and 2) deoxygenation followed by condensation and aromatization to form water and aromatic hydrocarbons.

Highly deoxygenated, stable tail-gas reactive pyrolysis (TGRP) oil has been generated at USDA-ARS, a pyrolysis process that provides a reducing environment for pyrolysis by recycling the product gases[16, 17]. TGRP bio-oils overall possess lower molecular weights and narrower chemical compound distributions. Therefore, based on the aforementioned HZSM-5 structural properties, we hypothesize that TGRP oils could more effectively undergo cracking for production of mono-aromatics. To compare the performance of TGRP oil with that of fast pyrolysis oil for catalytic cracking, two different pyrolysis oils having different chemical speciations were catalytically cracked using HZSM-5 (Si/Al=30) and the elemental/chemical compositions, product yields and aromatic selectivities were compared. We also investigated the impact of catalyst bed conditions on the yield and selectivity of BTEX and naphthalenes.

EXPERIMENTAL

Pyrolysis oil production. Fast pyrolysis and TGRP of switchgrass was conducted at the Eastern Regional Research Center (ERRC) using a bubbling fluidized bed reactor system to obtain pyrolysis oil (as described previously[18]). Briefly, 2 kg/hr of ground and dried biomass feedstock was fed into the

fluidized bed reactor set at 500 °C. Solid biochar particles generated during pyrolysis were collected using a cyclone. The hot vapors exiting the reactor and cyclone were condensed in a series of condensers and electrostatic precipitators (ESP). Non-condensable gases leaving the condenser system were analyzed using an online micro-GC/TCD. For the TGRP process, a fraction of the product gases was mixed with the N₂ stream and introduced into the reactor bed as the fluidizing gas[16].

Catalytic cracking. *Ex-situ* catalytic cracking of pyrolysis oil was performed in a catalyst bed externally coupled with a microwave heater (Milestone RotoSYNTH); Figure 1 depicts the *ex situ* microwave arrangement. The system consists of a 300 ml quartz reaction vessel to for pyrolysis oil vaporization, a quartz catalyst bed for catalytic cracking of the vapors, a series of condensers (cold water condenser and liquid nitrogen trap) for liquid collection, and a gas reservoir for non-condensable gases collection. Approximately 30 g of pyrolysis oil and 1.5 g of activated charcoal (Darco®, 20-40 mesh particle size, granular) were placed into the vessel. The charcoal acts as a microwave absorber and heat transfer medium. In the case of TGRP experiments, additional water was added to the pyrolysis oil to match the contents of the fast pyrolysis oil. To evaluate the longevity of the catalyst while cracking two pyrolysis oils, each catalyst bed was re-used without regeneration for catalytic cracking at 500 °C twice after the original experiment. Prior to catalytic cracking, the reaction system was purged with N₂ three times. The microwave power was set to 1200 W during a run (for 15 minutes). Experiments were performed in duplicate and the average yields are reported.

Product characterization. Liquid products were collected from the cold water condenser (CW) and liquid nitrogen traps (LN) after each run. Liquid products in the CW fraction were isolated using acetone, and then the organic phase was separated from the aqueous phase via extraction with ethyl acetate. The extraction solvent was removed by rotary evaporation (at 35 °C) to obtain the solvent-free liquid products. For the LN fraction, the liquid products were collected by decanting from the liquid nitrogen

trap, due to negligible water content in the LN fraction. The CW fraction contained less volatile compounds, such as naphthalenes and phenolic compounds, while the LN fraction contained mainly volatile compounds like benzene, toluene, ethyl benzene, and xylenes (BTEX). To obtain overall liquid product yields and selectivities, concentrations in the two fractions were added while considering yields of each fraction. GC-MS analyses of the organic phases were performed on a Shimadzu GCMS QC-2010. The column used for chromatographic separation was a DB-1701 with dimensions of (60 m length $\times$ 0.25 mm ID $\times$ 0.25 μ m film thickness). The GC oven was programmed to hold at 45 $^{\circ}$ C for 4 min, ramp at 3 $^{\circ}$ C/min to 280 $^{\circ}$ C, and then hold for 20 min. The injector was maintained at 250 $^{\circ}$ C and used a split ratio of 30:1. Quantification of individual compounds was determined by calibration curves for pure compounds. Elemental analysis of the pyrolysis oils and the liquid products was performed using a Thermo EA1112 CHNS/O analyzer. The water content of the liquid products was measured by Karl-Fischer titration. For non-condensable gases, the volume of the gas products was measured by displacement using a gas collection reservoir, and its composition was determined using a micro-GC/TCD.

RESULTS AND DISCUSSION

Pyrolysis oils. The properties of the pyrolysis oils used for catalytic cracking are shown in Table 1. The TGRP oil contains over 2 wt% aromatic hydrocarbons, based upon select compounds for which GC-MS calibrations were created, and smaller amounts of highly oxygenated compounds (acetic acid and levoglucosan) in comparison to fast pyrolysis oil. TGRP oil also has higher concentrations of phenolic compounds, which are less oxygenated compared to most carbohydrate derived compounds. Furthermore, the moisture content of the TGRP oil is approximately one-third of that of the fast pyrolysis oil. In the case of fast pyrolysis oil, the oil has 11 wt% highly oxygenated compounds, 20 wt% water, and no quantified hydrocarbons. As a result, the TGRP oil contains only 21 wt% oxygen, while the regular fast pyrolysis oil has 35 wt% oxygen. The reduced oxygen content of the TGRP oil is also reflected in the

higher carbon and hydrogen content of the oil. The changes in carbon and hydrogen content make the TGRP oil more hydrogen deficient (smaller H/C ratio), relative to the fast pyrolysis oil.

Catalyst-to-oil ratio. We tested various catalyst loading ratios at 400 °C, the temperature at which HZSM-5 begins to show significant activity[19, 20]. Typically, higher temperatures will exhibit greater activity, regardless of catalyst loading ratio. Product distributions from three catalyst loadings are shown in Table 2. The carbon yield of measured aromatic hydrocarbons increased from 5.7 % to 11.0 % and carbon yield of measured oxygenated compounds decreased from 2 wt% to 0.5 wt%, as catalyst loading was increased from 1 to 2. This indicates that the 2:1 ratio successfully converted the oxygenated compounds to hydrocarbons, more so than the lower loading ratio. Further increasing the loading slightly increased hydrocarbon yields from 11.0 to 12.9 %, and resulted in 0.3 wt% oxygenated compounds. This relatively minor change in the product yields for the further increased (4:1) catalyst/bio-oil ratio suggested that the effect of catalyst loading had plateaued. Therefore, a catalyst-to-pyrolysis oil ratio of 2 was employed for subsequent experiments.

Catalyst bed temperatures

The temperature of the catalyst bed was varied from 400 °C to 600 °C during individual catalytic cracking experiments of fast pyrolysis oil to determine the best operating temperature for cracking. According to the overall mass balance (shown in Figure 2), the carbon yields of liquid products and coke display inverse trends with varying catalyst bed temperature. This suggests that the formation of deoxygenated liquid range molecules and coke products are competing pathways. The non-condensable gases continue to increase over the temperatures tested. At each catalyst bed temperature, elemental and chemical analyses of the liquid products were performed and aromatic selectivities of the products were determined.

At 400 °C, the oxygen content of the liquid products was 8 %, which is quite low compared to the starting oil (35 %) shown in Table 3. As a result, the calculated HHV values for the liquid products

increased to 38 MJ/kg from 18 MJ/kg for fast pyrolysis oil. However, as shown in the Van Krevelen diagram (Figure 4) the H/C ratio of the products decreased from 1.22 for fast pyrolysis oil to 1.17, which is undesirable for energy content and other fuel properties. The decrease in the H/C ratio is due to the loss of hydrogen during zeolite cracking. During the process, hydrogen is typically lost when aromatic hydrocarbons are formed through dehydration and final dehydrogenative aromatization [9, 21, 22]. As a result, a decrease in the H/C ratio is unavoidable during catalytic cracking with HZSM-5. The chemical compositions of the liquid products were characterized using GC-MS (Figure 5). It was observed that the fraction was primarily composed of aromatic hydrocarbons such as benzene, toluene, ethyl benzene, and xylenes (BTEX), naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene (naphthalenes), styrene, and indene. The rest was mainly monomeric phenols, lignin-derived oxygenated compounds, and non-volatile molecules that were not detectable by GC-MS. The large presence of non-volatile products indicates that the temperature was not sufficient for the cracking of heavy compounds (most likely phenolic oligomers from lignin) from the oil. In terms of aromatic selectivity (Figure 6), over 80 % of the hydrocarbons generated during cracking are mono-aromatics (BTEX) with a small amount of polyaromatics, such as naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene.

At 500 °C, the level of deoxygenation became more significant and the liquid products predominantly consisted of hydrocarbons with only trace amounts of oxygen, ~1 wt%, (Table 3). As shown in the Van Krevelen diagram (Figure 4), the O/C ratio for the products further decreased from 0.07 to 0.01 as the bed temperature increased from 400 °C to 500 °C and the HHV value increased to 42 MJ/kg, which is close to that of petroleum oil (44 MJ/kg). Similarly, it is noted in the diagram that the H/C ratio of the products decreased to 1.11 from 1.17 as temperature increased to 500 °C. A low H/C ratio can be related to a higher degree of catalytic cracking (indicated by higher yield of hydrocarbons in Table 4) at this temperature. In terms of chemical composition (shown in Figure 5), the products were predominantly composed of hydrocarbons (BTEX, styrene, indene, and naphthalenes) with only trace amounts of phenolic compounds. It is noted that non-volatile compounds present in the products formed

at 400 °C were not observed as the temperature increased, indicating that higher temperatures are required to crack high molecular weight compounds found in pyrolysis oil. Formation of mono-aromatics is still preferred, but the selectivities for BTEX compounds were slightly decreased. This was accompanied by increased formation of bicyclic compounds (naphthalenes) in comparison to results obtained at 400 °C (Figure 6). From this observation, it seems that higher temperatures favor bicyclic compounds over mono-aromatics. Given the opposing trends of selectivity for BTEX type compounds and naphthalenes as temperature increases and other studies[23], the BTEX compounds are intermediates for generating naphthalenes at this temperature.

At 600 °C, the oxygen content was reduced to less than 1 % (Table 3), which is even lower than what we observed at 500 °C (1.2 %). However, due to a decrease in the H/C ratio compared to the results obtained at 500 °C (Figure 4), the HHV value was not significantly improved despite further deoxygenation. In terms of chemical composition (Figure 5), the liquid products contained predominantly hydrocarbons, 72 wt% BTEX and 23 wt% naphthalenes, with small amounts of phenolic compounds (2 wt%). There is a non-volatile fraction present at 600 °C, which was not present at 500 °C, and this could be due to enhanced reoligomerization/repolymerization of monomeric compounds at higher temperatures. Consistent with the trend observed as temperature was increased from 400 °C to 500 °C, a decrease in the amount of BTEX-type compounds and an increase in the amount of naphthalenes were generated. It is important to note that unconverted phenolic compounds are present in the liquid products. This indicates that these compounds are resistant to cracking with HZSM-5 even at elevated temperatures, when compared to other oxygenated compounds such as levoglucosan and acetic acid. Phenolic compounds generally gain stability through resonance structures and, as a consequence, are less reactive under catalytic cracking conditions. This also suggests that the elevated temperature will not increase the conversion of oxygenates contained in TGRP bio-oil which has high concentrations of phenolics. In terms of aromatic selectivity (Figure 6), the formation of xylenes was depressed, whereas toluene remained

relatively constant. On the other hand, the formation of benzene and bicyclic compounds was promoted as temperature increased.

The changes in O/C and H/C ratios as temperature was varied are clearly demonstrated in the Van Krevelen diagram (Figure 4). The catalytic cracking of fast pyrolysis oil moved towards the y- (lower O/C ratio) and x-axes (lower H/C ratio) as temperature was increased from 400 °C to 500 °C. However, as temperature further increased to 600 °C, the position of the product moved only slightly more towards the y- (smaller O/C ratio) and x-axes (smaller H/C ratio) than that for 500 °C. The yield of aromatic hydrocarbons was significantly enhanced as the temperature was increased to 500 °C, but further increasing temperature resulted in lower yields (Table 4). From a chemical composition standpoint, both temperatures (500 °C and 600 °C) provided liquid products that are predominantly hydrocarbon, but the liquid products contained more BTEX-type compounds than bicyclic compounds when cracked at 500 °C (Figure 5). Typically, BTEX-type compounds are more desirable than bicyclic compounds. Therefore, 500 °C was selected as the optimum bed temperature for catalytic cracking with HZSM-5 because of the optimized yield and composition of the products.

In addition to the catalytic cracking experiments, control cracking experiment was performed by replacing the catalyst bed with inert quartz bead at 500 °C to see a role of thermal decomposition in a hydrocarbon formation and deoxygenation. As shown in Table S1 (Supporting Information), the non-catalytic cracking provided a small yield of hydrocarbons (~ 1%) and slight decrease in oxygen content (30%) of the product oils. It can be concluded that a large presence of aromatic hydrocarbons and a high degree of deoxygenation observed in the resulting oils are predominantly achieved by catalytic cracking rather than thermal cracking.

Fast pyrolysis oil vs. TGRP oil at 500 °C

In order to compare the performances of fast pyrolysis oil and TGRP oil, catalytic cracking of the TGRP oil was performed using the same experimental setup at the optimum catalyst bed temperature (500 °C),

which was determined from the fast pyrolysis oil experiments and also is expected to be optimal for TGRP bio-oil because of the behavior of phenolics in cracking as noted above. In terms of the overall mass balance (Figure 2), the catalytic cracking of TGRP oil provided a slightly higher carbon yield of liquid and lower carbon yield of coke, in comparison to fast pyrolysis oil cracked at 500°C. The lower amount of coke is probably due to a low quantity of reactive oxygenated compounds (Table 1). For a better understanding of a comparison of performance of each pyrolysis oil for catalytic cracking, the pyrolysis oil yields from biomass pyrolysis (conventional or TGRP) were considered (Figure 3). Due to the decrease in organics in the pyrolysis oil for TGRP process [16], less carbon in biomass ended up in liquid products in the case of TGRP-cracking process, compared to regular pyrolysis-cracking process.

The liquid products contained approximately 2 wt% oxygen which is slightly higher than the fast pyrolysis oil case (0.6 %), although a higher level of deoxygenation in the products is anticipated given the initial low oxygen content in the TGRP oil. As noted above, the decreased extent of deoxygenation with the TGRP oil could be due to higher concentrations of relatively stable phenolic compounds, as compared to the regular fast pyrolysis oil (Table 1). On the Van Krevelen diagram (Figure 4), the position of the product obtained from TGRP oil cracking is slightly lower (lower H/C ratio) and to the right (higher O/C ratio) when compared to the fast pyrolysis oil experiments at this temperature. This means that the quality of the products obtained from TGRP oil are of slightly lower quality than that of the fast pyrolysis oil. In fact, the calculated HHV value was 41 MJ/kg, which is slightly lower than that of the fast pyrolysis oil (42 MJ/kg). The hydrocarbon yield from the TGRP oil is approximately equal to that of the fast pyrolysis oil (Table 4). However, it should be noted that 4 % of the hydrocarbons were present in the TGRP oil prior to catalytic cracking. Therefore, less hydrocarbon product was generated during the catalytic processing in the case of the TGRP when compared to fast pyrolysis oil. More phenolic compounds remained in the case of the TGRP bio-oil than in the fast pyrolysis oil, which is due to the higher concentration of phenolic compounds in the starting material. In terms of selectivity for aromatic hydrocarbons, significantly lower amounts of BTEX (particularly, xylenes) were generated, while formation of naphthalenes was favored in comparison to the fast pyrolysis oil experiments. The

differences in selectivity between the two pyrolysis oils for BTEX and naphthalenes are likely the result of the different overall chemical compositions of each pyrolysis oil (Table 1). We propose that a portion of the naphthalenes were formed by reaction of monoaromatics, such as xylenes and benzene, with oxygenates present in the TGRP oil. Carlson *et al.* reported that monoaromatics from catalytic pyrolysis of glucose reacted with oxygenates to form naphthalenes via a Diels-Alder reaction followed by dehydration [23]. Therefore, it is likely that the BTEX compounds in the TGRP oil contribute to the naphthalenes observed in the products from the catalytic cracking of TGRP oil. Due to the initial BTEX content of the TGRP oil, it would be a one step process to convert BTEX to naphthalenes (step 2); whereas the fast pyrolysis oil containing no hydrocarbons would need to generate the BTEX compounds prior to the formation of naphthalenes via the aforementioned pathway (steps 1 and 2 in Figure 7).

It is important to note that all the liquid products obtained from catalytic cracking are located below not only petroleum but also the feedstock oils (lower H/C ratio) on the Van Krevelen diagram (Figure 4). This means that the products are hydrogen deficient, which is not surprising considering that the catalytic cracking over HZSM-5 traditionally leads to hydrogen loss and the pyrolysis oils, especially the TGRP bio-oils, are already more hydrogen-deficient. On the other hand, HDO processing, where hydrogen is introduced during upgrading, results in more saturated products [5, 6]. Additionally, when the catalyst was reused both regular and TGRP oils induced some gradual decline in catalyst activity, but the third cycle of catalyst re-use for TGRP oil resulted in a sharper decline than that of regular pyrolysis oil cracking (Figure 8). At the same time, coke formation was higher and the liquid production was lower with TGRP oil cracking as the catalyst was reused. This high coke production with TGRP oil is consistent with the hydrogen deficiency of the oil (lower H/C ratio). This study among others has shown that hydrogen deficiency negatively affects the yields of hydrocarbons and coke via catalytic cracking of pyrolysis oils.

In order to increase the hydrogen content of the products for catalytic cracking, it is necessary to introduce a hydrogen-rich feed into the catalytic cracking process. Therefore, co-processing of pyrolysis oil with vacuum gas oil (VGO), or heavy petroleum distillates, traditional FCC feedstocks, would be a

possible way to increase hydrogen content. However, for fast pyrolysis oils the immiscibility of the bio-oil and petroleum distillates may be a limiting factor. However, TGRP bio-oil will have more compatible solubility properties with hydrocarbons and therefore may be a more promising bio-oil for this purpose. During co-processing, VGO could provide a source of hydrogen to the pyrolysis oil, so that hydrogen loss during catalytic cracking would be less severe. The presence of linear or branched reactive hydrocarbon intermediates (i.e. olefins) from the initial cracking of the petroleum distillates may allow existing aromatic hydrocarbons in the TGRP oil to undergo alkylation to form higher alkyl benzenes rather than ring growth and minimize formation of polyaromatics and coke. In fact, the co-processing could be more economical, since it avoids the use of high pressure gaseous hydrogen.

CONCLUSIONS

The product qualities were investigated in terms of elemental/chemical compositions, product yields, and aromatics selectivities, as the catalyst bed temperatures increased from 400 °C to 600 °C for catalytic cracking of fast pyrolysis oil. From the temperature study, 500 °C was selected as the optimum temperature. Pyrolysis oils produced by “the tail-gas reactive pyrolysis” process are more stable than traditional pyrolysis oil but also more H-deficient to begin with, and the oil underwent the same catalytic cracking with HZSM-5 at 500 °C for comparison. Although abundant concentrations of deoxygenated one-ring aromatic compounds (BTX) were produced, yields were slightly less than those from fast pyrolysis oil. Based on the product distribution for TGRP oil cracking, we proposed that naphthalenes are a result of conversion of BTX type compounds initially present in the TGRP oil. For the products obtained from TGRP cracking, less deoxygenation and more hydrogen loss were observed due to high concentrations of phenolic compounds and to lower hydrogen (H/C ratio) content in the oil, respectively. Thus, the quality of TGRP oil renders deoxygenation less important during cracking; however, the need for a hydrogen rich co-reactant is greater than it is for fast pyrolysis oil. In cracking experiments of both regular and TGRP oil using spent catalysts, more rapid deactivation was observed in the case of TGRP

oil, thus requiring more frequent catalyst regeneration. In consideration of all process variables examined, catalytic cracking of TGRP oils would provide more benefit if the cracking was conducted with hydrogen source.

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Figure 1. Schematic diagram of microwave system with *ex-situ* catalytic cracking and product collection system.

Table 1. Elemental analysis and chemical composition of starting pyrolysis oils created by conventional pyrolysis and TGRP systems

	Fast pyrolysis oil	TGRP oil
<i>Elemental analysis</i>		
wt% db N	0.3	1.1
C	58.9	71.2
H	6.0	6.3
O	34.8	21.3
O/C (mol)	0.44	0.22
H/C (mol)	1.22	1.06
water, wt%	20.3	7.2
HHV, MJ/kg	18.1	26.6
Conradson carbon residue, wt%	35.0	17.0
Acidity, mg KOH/mg	74.8	59.2
Viscosity at 40 °C, cP	27.6	71.7
<i>Chemical composition (C wt%)</i>		
BTEX	-	1.8
Naphthalenes	-	0.6
Phenolics	1.4	7.5
Acetic acid	4.2	3.3
Levogluconan	3.1	-
Acetol	2.8	1.0
Furfural	1.0	0.6

BTEX includes benzene, toluene, ethyl benzene, p-xylene and o-xylene. Naphthalenes include naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene. Phenolics include phenol, guaiacol, o-cresol, m-cresol, and p-cresol.

Table 2. Effect of catalyst loading on product distribution for *ex-situ* catalytic cracking at 400 °C of fast pyrolysis oil (C mol%)

Catalyst:oil ratio	1:1	2:1	4:1
Total hydrocarbons	5.72	11.03	12.97
BTEX	4.85±0.97	9.20±1.38	11.26±2.14
Naphthalenes	0.87±0.16	1.83±0.20	1.71±0.25
Phenolics	1.45±0.31	0.51±0.08	0.34±0.04
Acetic acid	0.51±0.06	0.02	-
Levoglucosan	0.03	-	-
Acetol	-	-	-
Furfural	-	-	-

BTEX includes benzene, toluene, ethyl benzene, p-xylene and o-xylene. Naphthalenes include naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene. Phenolics include phenol, guaiacol, o-cresol, m-cresol, and p-cresol.

Figure 2. Effects of catalysis temperature on the overall mass balance of bio-oil cracking (C mol% at 2:1 loading ratio).

Figure 3. Product distributions based on the starting biomass (pyrolysis-cracking process).

Table 3. Elemental analysis and HHV data for the liquid products obtained from LN trap

	Fast pyrolysis oil				TGRP oil	
	Pyrolysis oil	400 °C	500 °C	600 °C	Pyrolysis oil	500 °C
%N, db	0.3	-	-	-	1.1	-
%C, db	58.9	83.6±0.2	90.4±0.1	91.3±0.2	71.2	89.5±0.1
%H, db	6.0	8.2±0.1	8.4±0.1	8.1±0.2	6.3	8.1±0.1
%O, db	34.8	8.2±0.3	1.2±0.2	0.6±0.4	21.3	2.4±0.2
H/C, mole	1.22	1.17±0.01	1.11±0.01	1.07±0.02	1.06	1.08±0.01
O/C, mole	0.44	0.07±0.00	0.01±0.00	0.01±0.00	0.22	0.02±0.00
HHV, MJ/kg	18.1	38.5±0.26	42.1±0.21	42.1±0.42	26.6	41.1±0.21

All numbers in wt% based on dry feedstock bio-oil. Oxygen was calculated by difference. HHV was calculated by the formula, $HHV = \{33.5[C] + 143.2[H] - 15.4[O] - 14.5[N]\} \times 10^{-2}$.

Figure 4. Van Krevelen-type plot of bio-oils and liquid products. Petroleum composition is added for comparison.

Figure 5. Chemical composition of the liquid products obtained from catalytic cracking of fast pyrolysis oil at different catalyst bed temperatures

Figure 6. Aromatic selectivity at different catalysis temperatures and pyrolysis oils (C mol% and 2:1 loading ratio)

Table 4. Chemical composition of liquid products at different catalyst temperatures (C mol% based on dry feedstock bio-oil and catalyst-to-bio-oil ratio of 2).

	400 °C	500 °C	600 °C	500 °C with TGRP
Acetic acid	0.02	-	-	-
Phenolics	0.51±0.08	0.27±0.03	0.14±0.01	2.30±0.36
Hydrocarbons	11.03±1.58	32.32±3.55	25.77±4.09	32.18±3.10

Phenolics include phenol, guaiacol, o-cresol, m-cresol, and p-cresol. Hydrocarbons include benzene, toluene, ethyl benzene, p-xylene, o-xylene, naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene.

Figure 7. Proposed reaction pathways leading to naphthalenes during catalytic cracking with HZSM-5.

Figure 8. Composition of hydrocarbons produced, with respect to re-use of spent catalysts for traditional and TGRP bio-oils (C mol%, 2:1 loading ratio).