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Parametric Study on the Production of Renewable Fuels and Chemicals from Phospholipid-Containing Biomass

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Abstract Heterogeneous catalytic cracking of lipids into transportation fuels and other specialty chemicals offers a unique opportunity to provide sustainable energy while utilizing the current petroleum infrastructure. This study addresses a possible route for the utilization of phospholipid-containing biomass for production of renewable fuels and chemicals. The first part of the study focused on reaction pathways associated with the catalytic cracking of model phospholipid into fuel-type compounds. The results indicated that phospholipid cracking proceeds via acidcatalyzed mechanisms, which resulted to cleavage of fatty acids and glycerol moieties. Microbial lipids, which contain large concentrations of phospholipids, are a potential non-food related feedstock to displace petroleum. Among possible sources of microbial lipids, activated sludge offers a distinct advantage for its availability and abundance at a potential fee. The second part of this work dealt with the conversion of activated sludge to chemicals of value as fuel components through fluidized-bed catalytic cracking. The effect of moisture level and catalyst loading were determined. Results indicated that moisture level of up to 15 %(weight) has no effect on total product yield. On the other

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hand, higher catalyst loading resulted to a higher yield of gaseous product. Significant coke deposition was inferred as indicated by the high proportion of phenolic compounds produced from pyrolytic reactions. The results of this study provide a potential route of utilizing bulk lipid feedstocks, without the removal of phosphorus-containing molecules, to produce fuel components.

1 Introduction

Development of renewable fuels and chemicals has become increasingly important over the last decade. Concerns about global warming and the approach to a peak in petroleum production have highlighted the need for alternative, renewable sources of transportation fuels. Biodiesel, a mixture of fatty acid alkyl esters, is a renewable fuel produced from the transesterification reaction of lipids (chiefly triglycerides) and an alcohol (commonly methanol) [1]. However, due to processing concerns and product quality specifications, biodiesel is limited to refined or high quality feedstocks, which account for 70-85 % of the total production cost of the fuel [2, 3]. This presents economic challenges for the biodiesel industry due to the quite limited inventory of usable feedstocks, which are mostly edible oils. The use of food grade oils, such as soy and canola, require biodiesel producers to compete with the food industry for the market share and to rely on federal subsidies to be profitable [4].

To eliminate concerns with using food type oils for fuel, researchers are considering other potential feedstocks for renewable fuel production. Among the alternative

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feedstocks include microalgae and oleaginous microorganisms [5–7]. Oils from these sources, however, contain other compounds (i.e. phospholipids, sphingolipids) that are not preferred for biodiesel processing. In fact, of the total lipid content, the yeast Rhodotorula glutinis contains about 25.60-33.80 % (weight) phospholipid, depending on culture conditions [8]. As phospholipids comprise a significant portion of extractable lipids from these microorganisms, an economical and efficient approach is to react the phospholipids alongside other lipidic materials (i.e. acylglycerides, free fatty acids, waxes, etc.) via robust conversion technologies such as catalytic cracking. Another option is to hydrolyze the mixture of lipidic materials to yield fatty acids, which could then be converted to biodiesel or green diesel. This could eliminate problematic compounds (i.e. phospholipids) and can be accomplished using chemical (mild acid or alkaline) or enzymatic hydrolysis [9].

One attractive alternative feedstock for biofuel production is waste activated sludge due to its availability in large quantity all year round. In the United States alone, current production of activated sludge is about 7.60-8.20 million U.S. dry tons annually [10]. One feature that makes activated sludge advantageous over other feedstocks is its inherent adaptability with economic and social changes. That is, as commercialization and population increases, fuel demand also increases, and so is the amount of activated sludge that can be converted to fuel. Activated sludge is composed mostly of heterotrophic bacteria, which are responsible for biological treatment of wastewater. Previous studies on the production of biodiesel from activated sludge obtained from a municipal wastewater treatment plant indicated that about 3-6 % (weight) of fuel could be obtained from this feedstock [3, 11, 12]. However, at this relatively low yield, this feedstock is not economically competitive at current petroleum prices. This is mainly due to the cost associated with dewatering the sludge prior to fuel conversion, which accounts for more than 50 % of the fuel conversion cost [11, 13]. Studies indicated that activated sludge contains significant quantities of polyhydroxyalkanoates, wax esters, sterols, steryl esters, free fatty acids, acylglycerides, and phospholipids [1, 14]. These compounds could be used in a wide range of applications both in the biofuel and oleochemical industries. They can also be cracked, without prior extraction, into fuel components and other chemicals, which could result in an increase in overall yield of products while minimizing solid management issues. The spent solids could be used as potential adsorbent for heavy metals (i.e. Cd, Cr, Pb and Ni), tar removal or recovery and as soil conditioner [15–19].

Prior to disposal, wastewater sludge could be treated by fluidized-bed drying, which operates around 300–900 °C.

Commonly, drying time varies from 10 to 15 min with air or steam as fluidizing hot gas [20]. Waste activated sludge contains about 0.4-1.5 % (weight) solids and thus, it needs to be partially dewatered by mechanical means (i.e. centrifuge, belt, screw and filter press) prior to drying to ensure good fluidization [21]. Furthermore, fluidized-bed drying of waste sludge utilizes an inert material (sometimes referred to as fluidization medium), which is normally quartz sand or slag. Due to high water content of waste activated sludge, inert materials are used as heat carriers and as dispenser/fluidization enhancers [20, 22]. Studies on the fluidization of wet biomasses indicated that, even in the presence of inert material, there was a moisture content limit by which good fluidization could be achieved. For sawdust for example, this moisture content limit was 33-54 % (dry weight) depending on the diameter of the inert glass particles [23].

In general, cell walls of gram-negative bacteria contain 20–30 % lipids while those of gram-positive bacteria contain 2–4 % lipids. For both gram-negative and positive bacteria, most of the lipids are phospholipids [24]. In a catalyst-sludge mixture, these phospholipid-containing cell walls are the first point of contact. Thus, it is of utmost importance to study how these phospholipids will react in the presence of several catalysts. This is a key step to maximize production of fuel from activated sludge. Once a mechanism for catalytic conversion of phospholipid(s) to fuel has been established, process integration can be strategized. That is, utilization of existing fluid-bed dryer for simultaneous sludge drying (or biosolid production) and fuel conversion with catalyst acting as a fluidization/reaction enhancer.

This work initially focused on the establishment of reaction pathways towards the transformation of a model phospholipid into fuel-type compounds. Using this model compound (phosphatidylglycerol) with H⁺ZSM5 as catalyst, possible cracking reaction pathway was determined. The second part has focused on fluidized-bed catalytic cracking (FCC) of activated sludge using the same catalyst. The effect of two parameters (catalyst to sludge ratio and moisture content) was evaluated with respect to yield of gaseous and liquid products.

2 Experimental Section

2.1 Preliminary Study on Phospholipid Cracking Using Model Compounds

2.1.1 Chemicals

The model phospholipids (Fig. 1) were obtained from Avanti Polar Lipids (Alabaster, AL, USA). Analytical



Fig. 1 Illustration of the model phospholipid molecules used in this study: **a** Phosphatidylglycerol (MW = 771), **b** Phosphatidic Acid (MW = 697). Note that both have one saturated ($C_{16:0}$) and one unsaturated ($C_{18:1}$) fatty acid chains

standards used for product identification and quantitation were obtained from Sigma-Aldrich (St. Louis, MO, USA) at their highest available purity and were used without further purification. All gases (H₂ and He) were purchased from nexAir (Columbus, MS, USA) and were of ultra high purity grade.

2.1.2 Catalysts

The ZSM5 (CBV 8014) catalyst was obtained from Zeolyst International (Valley Forge, PA, USA) in the ammonium form having SiO_2/Al_2O_3 ratio of 80, as determined by the supplier. The catalyst was calcined at 550 °C for 2.5 h in air to develop the protonated form: H⁺ZSM5 [25].

2.1.3 Reactions

A reactor/analyzer device, known as the Quatra C, was used for rapid, online analysis of reaction products. A complete description of the Quatra C can be found elsewhere [26]. Products were identified and quantitated using GC–MS, which is an integral part of the Quatra C. Both electron impact ionization (EI) and chemical ionization (CI) techniques were employed for product characterization. Acetonitrile was used as the CI reagent gas. The chromatographic column used was a Restek Rxi[®]-1ms (30 m × 0.52 mm with 1.50 µm film thickness) (Restek, Bellefonte, PA, USA). For a detailed experimental procedure and analytical conditions, (see section S1 of Electronic Supplementary Material).

2.2 FCC of Activated Sludge

2.2.1 Material Collection and Preparation

Activated sludge samples were collected from the Hilliard Fletcher wastewater treatment plant in Tuscaloosa, AL, USA, during the plant's normal operation [27]. The solids were concentrated by gravity-settling overnight in ice bath, followed by vacuum filtration using a P8-creped cellulose fiber filter (Fisher Scientific, Pittsburgh, PA, USA). The concentrated sludge was frozen at -23 °C and was freezedried in a Freezone 6 Bulk Tray freeze dry system (Labconco, Kansas City, MO, USA). Sludge samples with 4.55 ± 0.26 and 14.70 ± 0.30 % (weight) moisture, as measured by an Ohaus MB45 infrared heater (Ohaus, Pine Brook, NJ, USA), were used for the experiments. The freeze-dried sludges were then ground using mortar and pestle followed by sieving. Intermediate particles with sizes 48/100 mesh were collected for fuel conversion.

Prior to calcination, the H⁺ZSM5 was also sieved to collect particles with sizes 100/115 mesh. The intermediate particle size ranges were decided based on preliminary estimation of the minimum fluidization velocities of both the sludge and catalyst (see section S2 of Electronic Supplementary Material for detailed calculations).

2.2.2 FCC Experimental Design

A two-level design was considered to determine the effect of two variables on the FCC of activated sludge. Catalyst to sludge mass ratio (5 and 10) and moisture content (\sim 5 and 15 % weight) were considered as variables for this study. Control runs (without catalyst) were also conducted to evaluate the effect of H⁺ZSM5 on the FCC of activated sludge with respect to product yields.

2.2.3 Fluidized-bed Reactions and Product Analyses

FCC reactions were conducted using a Parr flow reactor equipped with 4871 process controller and 4876 power controller (Parr Instrument Company, Moline, IL, USA). The schematic of the instrument used in this study is shown in Fig. 2. The reactor was a stainless steel having dimensions of 1 in. OD \times 8 in. height with 0.083 in. wall thickness. Both ends of the reactor were welded to a $\frac{1}{2}$ in.



Fig. 2 Diagram of the fluidized-bed system for the catalytic cracking of activated sludge. *TIC* temperature indicator controller, *T/C* temperature reading in °C, *PT* total pressure, *PG* gauge pressure, *BPR* back pressure regulator, *MFC* mass flow controller, *S* software-controlled valve

OD stainless steel tubing. Glass beads (2 mm diameter) were used to fill up the $\frac{1}{2}$ in. tubing and reducer weld fitting at the bottom of the reactor. A layer of glass wool was then placed on top of the glass beads. Stainless steel frit discs (2 μ m porosity) were used at the top and bottom ends of the $\frac{1}{2}$ in. tubing to ensure solid-free products.

FCC reactions were conducted with H/D (bed aspect ratio) of around 3, which has been suggested for homogeneous fluidization conditions and for minimizing the experimental difference between total bed pressure drop and bed weight per unit section [28]. The activated sludge and catalyst were loaded to the reactor and then purged with low He flow. The reactor was then placed inside the pre-heated (500 °C) furnace. The temperature inside the reactor was allowed to equilibrate for 30 min, during which, the back pressure regulator (BPR) was kept closed. After equilibration, BPR was opened and He flow was started which was set at 150 cm³/min equivalent to \sim 7.14 mm/s flow through the reactor.

The products coming out of the reactor passed through a stainless steel collector which was in an acetone bath

maintained at -23 to -30 °C using a CryoCool CC-60 dip chiller (Neslab Instrument Inc.). Uncondensed or gaseous products were collected in a gas-sampling bag for the first 4 min of the reaction. After 4 min, gas-tight syringes were used to withdraw gaseous samples from the sampling port at different times until 50 min, by which the reaction was halted.

Analysis of gaseous products was conducted using two-Agilent 6890 N gas chromatographs (GC), both equipped with single filament thermal conductivity detector (TCD). Hydrocarbons were analyzed using an 80/100 mesh, 6 ft. × $\frac{1}{8}$ in. Porapak-Q column (Agilent, Santa Clara, CA, USA), while permanent gases were analyzed using an 80/100 mesh, 6 ft. × $\frac{1}{8}$ in. Porapak-Q and 45/60 mesh and 10 ft. × $\frac{1}{8}$ in. mol sieve 5A columns in series. Liquid products, on the other hand, were analyzed on an Agilent 6890 N GC coupled to a 5975 inert Mass Selective Detector (MS). The column was a Restek Rxi[®]-5Sil MS having dimensions of 30 m × 0.25 mm with 0.25 µm film thickness (Restek, Bellefonte, PA, USA). For detailed analytical procedures, (see section S3 of the Electronic Supplementary Material).

3 Results and Discussion

3.1 Model Phospholipid to Fuel Mechanisms

Gram-negative bacteria, in general, have outer membranes containing 25 % phospholipids with 75 % phosphatidylethanolamine, 20 % phosphatidylglycerol and 5 % cardiolipin. Gram-positive bacteria contain the same phospholipids but in different proportions. For example, phospholipids from Bacillus megaterium contains 16 % phosphatidylethanolamine, 40 % phosphatidylglycerol, 40 % cardiolipin and 4 % other [1]. It should be noted that initial studies with phosphatidylethanolamine showed physical/chemical changes, implied by color change. However, no phosphatidylethanolamine was transferred to the reactor, as indicated by weight difference between the initial amount loaded and the amount after Quatra C run. The manner by which the Quatra C operates is that the reactant is vaporized in a flowing stream of Helium, which transports the reactant to the reactor. This suggests that phosphatidylethanolamine is not a suitable model compound for evaluation of catalytic reaction involving bacterial membrane. This was not the case for phosphatidylglycerol and thus, it was chosen as surrogate for bacterial cell wall.

As previously mentioned, phospholipids are the first point of contact in a catalyst-sludge mixture. However, activated sludge contains other organic compounds in addition to phospholipids. H⁺ZSM5 was chosen as catalyst for this study since cracking of these compounds, especially acylglycerides and fatty acids (using either model lipid compounds or pre-extracted oils), have been studied with this catalyst [29–32]. This study is an extension of these previous studies, applied without the pre-extraction step on an actual feedstock containing various contaminants. Furthermore, the process employed on this study has the goal of integration with current sludge treatment option.

3.1.1 Identification and Quantitation of Reaction Products

Products from catalytic cracking of model phospholipids were tentatively identified using NIST spectral library (see Figure S1). Standard compounds were then used for further verification of the peak's identity. Reaction conversions for this study are not available due to inherent limitations of the chromatographic column, which is not designed for phospholipid analysis. Products from empty bed reactions (i.e. no catalyst) were qualitatively identified as diacylglycerides with C16 and C18 fatty acid chains corresponding to the parent molecule, which probably cleaved from the phosphate head group of the phospholipid molecule. These products were not found in the catalytic runs. The results presented here, therefore, are mainly due to catalytic reactions, rather than pyrolysistype reactions.

Figure 3 shows the product distributions for the catalytic cracking of phosphatidylglycerol. Of particular interest was the formation of 2-propenal. Reactions at two different temperatures with the same catalyst loading resulted to lower 2-propenal yield at higher temperature. To verify whether 2-propenal was coming from the "glycerol" portion of the phosphatidylglycerol, reactions were carried out using phosphatidic acid (see Fig. 1 for structure). Results showed undetected level of 2-propenal, which indicates that this molecule originates from the "glycerol" portion of phosphatidylglycerol and not from the fatty acid chains. This was further supported by the reactions with two different catalyst loadings at the same reaction temperature, which showed that the yield of 2-propenal was higher at lower catalyst loading where catalyst contact time was lower. Due to molecular size inhibitions, protonation of phospholipid molecules on H⁺ZSM5 catalyst is believed to occur on the outside surface of the catalyst and not within the pores. Smaller, intermediate species (i.e. 2-propenal) can then enter the catalyst pores where additional reactions take place, resulting to a lower yield at higher catalyst contact. Table 1 shows the yield of aromatic hydrocarbons from cracking of phosphatidylglycerol over H⁺ZSM5. It can be deduced from the results that primary cracking resulted to fatty acids and 2-propenal as main products. These products then underwent secondary and tertiary cracking, producing aromatic compounds.

No phosphorus-containing products were found for the cracking reactions with the analysis techniques used. Most probably, the phosphorus adsorbed onto the catalyst where it would remain until catalyst regeneration. It was beyond



Fig. 3 Product distribution for the cracking reaction of phosphatidylglycerol (PG) and phosphatidic acid (PA) on H⁺ZSM5 catalyst

Table 1 Composition profile of aromatic compounds from phosphatidylglycerol cracking on H^+ZSM -5 catalyst reacted at 400 °C

Aromatic compound	Percent weight of total aromatics	
	5 mg catalyst	10 mg catalyst
Toluene	9.9 ± 0.7	9.8 ± 1.8
Ethyl benzene	9.4 ± 3.1	17.6 ± 5.1
Xylenes	9.0 ± 1.6	14.8 ± 3.2
Trimethyl benzene	38.7 ± 0.2	18.8 ± 2.2
Propenylbenzene	12.1 ± 0.5	10.7 ± 5.6
Phenylbutene	12.7 ± 3.8	15.8 ± 4.3
Naphthalene	4.6 ± 0.4	7.3 ± 1.8
Methyl naphthalene	3.7 ± 1.8	4.9 ± 0.9

the scope of this study to determine the effect of phosphorus on the life of the catalyst or product distribution.

3.1.2 Proposed Reaction Schemes

From the results presented in Fig. 3, a pathway for the catalytic cracking of phosphatidylglycerol is proposed (Fig. 4). Primary cracking resulted in the cleavage of fatty acid constituents from the phospholipid molecule. This indicates that acyl-oxygen cleavage readily occurred, probably due to a

Fig. 4 Primary products from catalytic cracking of phosphatidylglycerol using H⁺ZSM5 stabilization of the tertiary carbocation [33, 34]. A similar pathway was shown by Benson et al. [29] for the cracking behavior of unsaturated triacylglycerides in which the fatty acid chains cleave and further react.

The aromatic products seen in Fig. 3 (composition profile relative to total aromatics given in Table 2) arise from the shape-selectivity of the zeolite catalyst, which includes combinations of C_2 - C_4 intermediates that oligomerize to form benzene and methyl-substituted aromatics. Polycyclic aromatic hydrocarbons ensue from additional combinations and are precursors to coke formation. The complete reaction scheme for aromatics formation within zeolites can be found elsewhere [33-35].

Propanediol is believed to be the primary product originating from the cleavage of the glycerol component of the phosphatidylglycerol. Propanediol was then converted to 2-propenal probably via dehydration followed by an intramolecular hydride transfer mechanism. These findings are consistent with previous studies [36–39].

 H^+ZSM5 catalyst is high in Brønsted and Lewis acidities and readily accept lone electron pairs [40]. Recent study indicated that the catalyst (CBV 8014) used in this study has about 0.40 mmol/g Brønsted acid sites [41], which is about the same as the concentration of Al in the catalyst. During cracking reactions involving R–O–C



Table 2 Composition of liquid products from pyrolysis of activated sludge at 500 $^{\circ}$ C in addition to PAHs and FAMEs presented in Fig. 6

Compound class	Yield (μg/g activated sludge)
Alcohols	72.8 ± 27.5
Aliphatic hydrocarbons	1822.3 ± 578.8
Indolic compounds	166.8 ± 41.7
Nitriles	866.3 ± 227.0
Phenolic compounds	5362.3 ± 1528.0
Pyridine compounds	38.4 ± 11.1
Pyrrolic compounds	69.9 ± 22.7
Sulfur compound	116.2 ± 18.2

scissions where the O–C bond is cleaved, the Brønsted sites are able to bind to the R–O⁻ for electron stability. Products such as palmitic and oleic acids (H⁺ZSM5 reactions) are plausible products of lipid reactions on cracking catalysts, as depicted in Fig. 4. Although not measured for these reactions, decarboxylation and decarbonylation reactions probably do occur, resulting in the formation of hydrocarbon compounds. Similar results were found by Benson et al. [29] for the cracking of acylglycerides, along with the formation of aromatic compounds on H⁺ZSM5.

3.2 FCC of Activated Sludge

To prevent gradual build-up of deposits of impurities onto the catalyst, a fluidized-bed was chosen over fixed-bed for the catalytic cracking of activated sludge. The activated sludge used in this study contains on the average (dry weight); 41.41 % C, 5.48 % H, 22.27 % O, 7.59 % N, 0.98 % S, 0.12 % Cl and 21.32 % Ash [1]. This indicated that the phosphorus content of the sludge ranges from 1.5 to 2.5 % (dry weight) [42]. Preliminary studies on catalytic cracking of model phospholipid compounds showed that phosphatidylethanolamine was unreactive in the "Quatra C operating environment", where volatilization of material to be reacted is necessary prior to reaction. This might not be the case for fluidized-bed catalysis, where the material and catalyst are always directly in contact regardless of whether the material could be vaporized or not. As previously mentioned, the catalyst was chosen for this study since catalytic studies involving acylglycerides and fatty acids on H⁺ZSM5 showed significant yield of wide range of products (i.e. paraffins, olefins and aromatics), which could be used as transportation fuel [29, 30]. Furthermore, a previous study on the conversion of methanol to dimethyl ether indicated that H⁺ZSM5 was the most active in terms of methanol conversion. Furthermore, water was found to have little influence on catalytic activity (methanol conversion) of H⁺ZSM5 [43, 44].

Helium was chosen as the fluidizing gas to prevent any side reactions as for the case of other gases such as N_2 . At temperatures below 950 °C, the formation of NO_x from atmospheric N_2 is almost eliminated. However, they can still be formed from feedstock-bound nitrogen, which could be affected if N_2 is used as fluidizing gas [22]. Consequently, this could affect the performance of the system.

Preliminary experiments indicated that, with respect to hydrocarbon selectivity, temperatures of 500 and 600 °C were not significantly different (see Figure S6). This could be explained by the study conducted by Chao et al. [45] on the kinetics of sludge pyrolysis. They found that from 500 to 700 °C the residual C, N and S on the spent solid were statistically similar. Thus, all FCC reactions were conducted at 500 °C. The experimental runs without catalyst serve as positive control. Although there might be catalytic reactions involved due to presence of contaminants such as heavy metals, products from these reactions were considered to be coming from pyrolysis or thermal cracking since they are inherent to the feedstock.

3.2.1 Gaseous Products

The profile of products present in the gaseous stream of fluidized-bed system is shown in Fig. 5. It can be seen from the results that the amount of CO_2 produced were not significantly different for all the treatments considered, including the control run. Thus, the CO_2 produced can be accounted to decarboxylation due mainly to pyrolytic reactions. On the other hand, the amount of CO produced was lowest for the control followed by the treatments with a catalyst to sludge mass ratio (C:S) of 5, regardless of the moisture content (M) of the activated sludge. These results indicated that decarbonylation was the main reaction leading to deoxygenation of the sludge using H⁺ZSM5. This was supported by the results obtained from treatments with C:S = 10, where the highest production of CO was observed. Again, this was irrespective of M.

For all the treatments, production of small amount of hydrogen gas and methane were observed. These are common products of biomass pyrolysis at the reaction temperature employed in this study [46]. This was supported by the results obtained showing that the yields of hydrogen gas and methane were statistically similar for all the treatments (Fig. 5). Regarding the production of alkanes and alkenes (C_2 – C_6), no apparent trend can be observed from the results. If one looks at Fig. 5, it seems that in general, the amount of aliphatic hydrocarbons produced were lower for the control run. Nevertheless, they seemed to be not significantly different from other treatments. Thus, a statistical analysis was performed on the total aliphatic hydrocarbon production of all the treatments. Fig. 5 Profiles of gaseous product obtained from FCC of activated sludge using H⁺ZSM5. C:S—catalyst to sludge mass ratio, M—weight percent moisture content



This was performed using a general linear model (GLM) at a significance level of 0.05, utilizing $SAS^{\otimes 1}$ software [47]. This analysis revealed that the total aliphatic hydrocarbon production was not significantly different for all treatments. However, on the average, a general trend regarding aliphatic hydrocarbon production was observed, which was: [Control] < [C:S = 10, M = 15] < [C:S = 5, M = 15] <[C:S = 10, M = 5] < [C:S = 5, M = 5]. This trend indicates catalytic activity, which was not high enough to significantly increase the yield of aliphatic hydrocarbons. This was probably due to catalytic conversion of the aliphatic to aromatic hydrocarbons. Low molecular weight hydrocarbons in C₂-C₄ range, in the presence of shapeselective H⁺ZSM5, act as intermediates to production of aromatics. This can be seen on the trend observed as well, which suggests that at the same sample moisture content, aliphatic hydrocarbon production was higher at lower C:S. Lower C:S translates to lesser contact between catalyst and reacting compound. Lesser contact between C2-C4 and H⁺ZSM5 means lesser chance of producing aromatic hydrocarbons and the reacting species will go out of the reactor unreacted.

It can be clearly seen from Fig. 5 that all the treatments with catalyst significantly increased the yield of aromatics from activated sludge. The effect of catalyst loading was as expected, which was higher aromatics yield at higher C:S. This was, as previously stated, due to higher contact between reactant and catalyst at higher C:S. The effect of moisture, however, is not apparent from the results.

For all the treatments with catalyst, the moisture content of the activated sludge has no significant effect on the yield of aliphatic and aromatic hydrocarbons. Several studies suggested that water could either regenerate H^+ZSM5 by removal of carbon deposits or by attenuating coke deposition [48–50]. This could be true also for activated sludge. However, the deposits coming from other contaminants (i.e. phosphorus and other metals) present in activated sludge could have prevented effective regeneration of catalytic sites to significantly affect the yields of hydrocarbon.

Another compound that was produced in significant quantity was acetonitrile (see Figure S4). Though this was also detected in the control run, the yields on the treatments with catalyst were substantially higher (Fig. 5). Acetonitrile is generally used as solvent in organic and inorganic syntheses. There is no commercial-scale production process to produce this compound other than as by-product of propylene ammoxidation to produce acrylonitrile. Due to worldwide economic downturn, there is a global shortage of acetonitrile [51]. Thus, its production from activated sludge is advantageous for this feedstock to attain economic competitiveness.

Pyrolysis of nitrogen-containing biomasses is known to release acetonitrile, ammonia and HCN [52, 53]. Acetonitrile, in H⁺ZSM5, could be produce from ammonia and low molecular weight hydrocarbon or alcohol [54, 55]. Thus, the marked increase in acetonitrile in treatments with

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 H^+ZSM5 could be accounted for catalytic activity. The effect of moisture is also not significant with respect to acetonitrile yield, as was the case for hydrocarbons. However, higher catalyst loading resulted to substantial reduction in acetonitrile yield. Studies on the co-adsorption of acetonitrile and olefins in H^+ZSM5 showed formation of *N*-alkylnitrilium cation, which is a persistent species inside a zeolite [56]. This could have cause the lower acetonitrile yield at higher catalyst loading, where contact between reactants (olefins and acetonitrile) and H^+ZSM5 was higher.

3.2.2 Liquid Products

The results of gaseous product analysis did not show any indication of severe catalyst coking. However, the results of the analysis of the liquid product revealed otherwise (Fig. 6). It can be seen from the results that the polycyclic aromatic hydrocarbons (PAHs) yield of the control was about six fold higher than the treatments with C:S = 5. It is well established that PAHs are precursor to coke formation. This suggests that the difference between the two values was deposited as coke on the catalyst. This is supported by the results obtained on treatments with C:S = 10, which yielded PAHs of less than half of the treatments with C:S = 5. Regardless of the moisture level of the activated sludge, similar trend was observed.

PAHs are common products of pyrolysis of sewage sludge. In a study conducted by Domínguez et al. [57], they



Fig. 6 Profiles of liquid product obtained from FCC of activated sludge using H⁺ZSM5. C:S—catalyst to sludge mass ratio, M— weight percent moisture content, PAH—polycyclic aromatic hydro-carbons, FAMEs—fatty acid methyl esters

found that PAHs such as quinolone, 1H-indene, naphthalene, methylnapthalenes, acenaphthylene and phenanthrene are present in pyrolysis oil from sewage sludge. In this study, some PAHs that were detected include naphthalene, azulene, methylnaphthalenes, ethylnaphthalenes, propylnaphthalenes, fluorene, phenanthrene and methyl phenanthrenes. Also detected were methyl ester of monoand di-unsaturated C_{18} fatty acids (see Figure S5). And if one looks at Fig. 6, it is apparent that these fatty acid methyl esters FAMEs) were products from pyrolytic reactions.

In addition to PAHs and FAMEs, other compounds in significant concentration were also detected on the control run, but not on treatments with catalyst. These compounds include alcohols, aliphatic hydrocarbons, nitriles, indolic compounds, pyrrolic compounds, pyridine compounds, phenolic compounds and sulfur-containing compound. Previous works on the pyrolysis of sewage sludge also detected these compounds [15, 57–60]. Sulfur-containing compound was also detected on the catalytic runs with levels similar to the control (see Figure S5).

As shown in Table 2, phenolic compounds have the highest concentration among the compounds detected on the control. According to Gayubo et al. [61], phenol and 2-methoxyphenol have low reactivities to hydrocarbon using H^+ZSM5 as catalyst. Furthermore, they concluded that deposition of coke due to condensation of 2-methoxyphenol was noticeable. Thermally, PAHs could also be formed from phenolic compounds via secondary pyrolytic reactions [62]. The liquid products from treatments with catalyst contain no detectable levels of phenolic compounds. This suggests that these compounds were probably deposited also as coke on the catalyst.

Overall, the total average yield (gaseous and liquid products) of the control was 24.60 % (weight). This was significantly lower than the values reported in the literature, which ranges from 50 to 90 % (weight) with N₂ (0.6–7.4 cm/s) as fluidizing gas at 400–550 °C [59, 63]. However, unlike what was observed by Park et al. [59] with metal oxide (CaO and La₂O₃) catalysts at 450 °C, the product yield increased for the catalytic reaction runs. Specifically, total average product yields were around 34 and 38 % (weight) for C:S = 5 and C:S = 10, respectively, irrespective of moisture level in the activated sludge.

The study involving model phospholipids was conducted employing fixed bed reactor. Studies indicated that in fixed bed reactors, phosphates were deposited on both sides (top and bottom) of the bed, which lead to blockage and deactivation of the catalyst [64]. This was probably the main reason why the primary cracking products of the model phospholipid were not observed in the fluidized-bed reactor. Although FAMEs were detected, results indicated that they were from pyrolytic reactions. The deactivation of the catalyst on the fixed bed reactor probably resulted to a gradual shortening of the catalytically active bed and thus, primary cracking products were detected in relatively high concentrations. Catalyst deactivation is expected to be almost equally distributed among the catalyst particles involved in the fluidized-bed reactor. Thus, the effect would not be as severe as the fixed bed reactor. This could result to a more catalytically active catalyst system as indicated by the results obtained.

Another possible condition that contributed to the differences in the results obtained was the He gas velocities, which were about 10 and 7.14 mm/s for fixed and fluidized-bed, respectively. Lower velocity translates to higher retention (or contact) time, which could have significantly increase reaction conversion of the primary cracking products into smaller hydrocarbon compounds. This, combined with excessive catalyst deactivation of the fixed bed reactor as well as the presence of other organic and inorganic compounds in the activated sludge, could have caused the results obtained. Nevertheless, this study provided a key step for the conversion of phospholipid-containing biomass into fuel-type compounds.

4 Conclusions

Catalytic cracking of lipids into transportation fuels and other specialty chemicals offers a unique opportunity to provide sustainable fuel while utilizing the current petroleum infrastructure. A possible route for the utilization of phospholipid-containing biomass for production of renewable fuels and chemicals was proposed in this study.

Initial study focused on reaction pathways associated with the catalytic cracking of model phospholipid (phosphatidylglycerol) into fuel-type compounds using H⁺ZSM5. Reactions were carried out using a pulse-type micro-reactor utilizing online GC–MS analysis, allowing real-time evaluation of reaction products. The results indicated that phosphatidylglycerol cracking proceeds via acid-catalyzed mechanisms, which resulted to cleavage of fatty acids and glycerol moieties. These products then underwent further reactions producing aromatic hydrocarbons.

Microbial lipids, which contain large concentrations of phospholipids as cellular constituents, are a potential nonfood related feedstock for renewable fuel production. Among possible sources of microbial lipids, activated sludge offers a clear advantage for its availability in abundance year-round at little to no cost. Activated sludge is an unwanted by-product of biological wastewater treatment. In fact, 25–65 % of operating expenses of wastewater treatment facilities are associated with excess sludge disposal [65]. Thus, the second part of this work dealt with the conversion of activated sludge to fuels and chemicals through FCC. This process was sought with the aim of integration with current sludge treatment to produce salable biosolids, which is fluidized-bed dryer. The effect of moisture level and catalyst loading were determined. Results indicated that moisture level of up to 15 % (weight) has no effect on total product formation. On the other hand, higher catalyst loading resulted to a higher gaseous product yield. Significant coke deposition was inferred as indicated by the high proportion of phenolic compounds from control run where pyrolytic reactions alone were present.

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