Attique, S., Batool, M., Goerke, O., Abbas, G., Saeed, F. A., Din, M. I., Jalees, I., Ahmad, I., Gregory, D. H. and Shah, A. T. (2022) Fe-POM/ attapulgite composite materials: efficient catalysts for plastic pyrolysis. Waste Management and Research, (doi: 10.1177/0734242X221080084)

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

https://eprints.gla.ac.uk/264206/

Deposited on: 28 January 2022

Enlighten – Research publications by members of the University of Glasgow
https://eprints.gla.ac.uk

Fe-POM/ Attapulgite Composite Materials: Efficient catalysts for plastic pyrolysis

Journal:	*Waste Management & Research: The Journal for a Sustainable Circular Economy*
Manuscript ID	WMR-21-0732.R1
Manuscript Type:	Original article: 35,000 characters
Date Submitted by the Author:	29-Nov-2021
Complete List of Authors:	Attique, Saira; University of the Punjab Quaid-i-Azam Campus, Institute of Chemistry Batool, Madeeha; University of the Punjab Quaid-i-Azam Campus, Institute of Chemistry Goerke, Oilver; Technical University of Berlin, Department of Ceramic Materials Abbas, Ghayur; The Islamia University of Bahawalpur Pakistan Saeed, Faraz; COMSATS Institute of Information Technology - Lahore Campus Din, Muhammad; University of the Punjab Quaid-i-Azam Campus, Institute of Chemistry Jalees, Irfan; University of Engineering and Technology Ahmad, Irfan; King Khalid University Gregory, Duncan; University of Glasgow, WestCHEM, School of Chemistry Tufail Shah, Asma; COMSATS Institute of Information Technology - Lahore Campus,
Keywords:	Waste recycling, Pyrolysis, Tungstophosphate, Liquid Hydrocarbon, Polyethylene, GC-MS, Clay
Abstract:	This manuscript describes the catalytic cracking of low-density polyethylene over attapulgite clay and iron substituted tungstophosphate/attapulgite clay (Fe-POM/attapulgite) composite materials to evaluate their suitability and performance for recycling of plastic waste into liquid fuel. These catalysts enhanced the yield of liquid fuel (hydrocarbons) produced in cracking process. A maximum yield of 82% liquid oil fraction with a negligible amount of coke was obtained for 50% Fe-POM/attapulgite composite.. Whereas, only 68% liquid oil fractions with a large amount of solid black residue was produced in case of non-catalytic pyrolysis. Moreover, Fe-POM/attapulgite clay composites showed higher selectivity towards lower hydrocarbons (C5–C12) with aliphatic hydrocarbons as major fractions. These synthesized composite catalysts significantly lowered the pyrolysis temperature The from 375 ºC to 310 °C. Hence, recovery of valuable fuel oil from polyethylene using these synthesized catalysts suggested their applicability for energy production from plastic waste at industrial level as well as for effective environment pollution control.

SCHOLARONE™
Manuscripts

Fe-POM/ Attapulgite Composite Materials: Efficient catalysts for plastic pyrolysis

Saira Attique[1], Madeeha Batool[1], Oliver Goerke[2], Ghayoor Abbas[3], Faraz Ahmad Saeed[4], Muhammad Imran Din[1], Irfan Jalees[5], Irfan Ahmad[6], Duncan H. Gregory[7], Asma Tufail Shah[2,8†]

[1]Institute of Chemistry, University of the Punjab, New Campus, Lahore-54000, Pakistan

[2]Fachgebiet Keramische Werkstoffe/Chair of Advanced Ceramic Materials, Technische Universität Berlin, Hardenbergstr. 40, 10623 Berlin, Germany

[3]Faculty of Pharmacy and Alternative Medicine, Islamia University Bahawalpur, Bahawalpur, Pakistan

[4]Ahmad Saeed & Co Pvt. Ltd. 473 G3, Johar Town, Lahore, 54000, Pakistan

[5]Institute of Environmental Engineering And Research, University of Engineering and Technology, Lahore 54890, Pakistan

[6]Department of Chemistry, College of Science, King Khalid University, Abha, Saudi Arabia

[7]WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, G12 8QQ,United Kingdom

[8]Interdisciplinary Research Centre in Biomedical Materials (IRCBM), COMSATS University Islamabad, Lahore Campus, Lahore-54600, Pakistan

Corresponding Author:

1. **Dr. Asma Tufail Shah**

Telephone # +92 (0) 42-111-001-007 Ext. 828

Fax: +92-42-35321090

Email: drasmashah@cuilahore.edu.pk

2. **Dr.Madeeha Batool**

For Peer Review

Email: madeeha.chem@pu.edu.pk

Abstract

This manuscript describes the catalytic cracking of low-density polyethylene over attapulgite clay and iron substituted tungstophosphate/attapulgite clay (Fe-POM/attapulgite) composite materials to evaluate their suitability and performance for recycling of plastic waste into liquid fuel. These catalysts enhanced the yield of liquid fuel (hydrocarbons) produced in cracking process. A maximum yield of 82% liquid oil fraction with a negligible amount of coke was obtained for 50% Fe-POM/attapulgite composite. Whereas, only 68% liquid oil fractions with a large amount of solid black residue was produced in case of non-catalytic pyrolysis. Moreover, Fe-POM/attapulgite clay composites showed higher selectivity towards lower hydrocarbons (C_5–C_{12}) with aliphatic hydrocarbons as major fractions. These synthesized composite catalysts significantly lowered the pyrolysis temperature The from 375 ºC to 310 °C. Hence, recovery of valuable fuel oil from polyethylene using these synthesized catalysts suggested their applicability for energy production from plastic waste at industrial level as well as for effective environment pollution control.

Keywords: Waste recycling; Pyrolysis; Tungstophosphate; Liquid Hydrocarbon; Polyethylene; GC-MS.

Introduction

Thermal and thermo-catalytic degradation of waste polymers into valuable hydrocarbons, like fuel oil, is an area of great interest due to depletion of natural resources (Gaca, Drzewiecka et al. 2008). Thermal degradation requires a very high temperature (500 ºC – 900 ºC). It produces

For Peer Review

liquid products that mainly contain heavier hydrocarbons (C_6 – C_{25}) (Lin, Yang et al. 2004, Akpanudoh, Gobin et al. 2005). The use of catalyst not only decreases the degradation temperature but also maximizes the yield of lower hydrocarbons (Bobek-Nagy, Gao et al. 2020, Chai, Wang et al. 2020, Shah, Attique et al. 2021). Various catalysts including, silica, alumina, zeolites, mesoporous materials, and heteropolyacids have been tested for polymer degradation to get valuable hydrocarbons (Serrano, Aguado et al. 2000, Mastral, Berrueco et al. 2006, Aguado, Serrano et al. 2007, Shah, Attique et al. 2021, Wang, Jiang et al. 2021). Heteropolyacids, also known as polyoxometalates (POMs), have been reported for catalytic cracking of plastic. POMs are molecular metal oxide clusters that possess larger number of Brönsted acid sites that accelerate the cracking process (Shah, Attique et al. 2021).

Natural clays have acidic sites which made them suitable for catalytic applications. Various types of clays, such as bentonite, smectite, montmorillonite, and kaolin have been used as a catalyst/support due to their porosity, active surface elements.They have good thermal stability which ensures their use in applications at high temperature. Kaolin and Fire clay had been reported for catalytic cracking of polyethylene with liquid yield 73 % and 43 %, respectively (Patil, Varma et al. 2018, Saira Attique 2018). Wei Luo et al. reported kaolin clay for pyrolysis of PE at 600 °C to get liquid and oil products (Luo, Fan et al. 2021). Clays impregnated with POMs had been reported to enhance oil yield upto 81 % (Saira Attique 2018, Attique, Batool et al. 2020). Thus, POM increase the polymer conversion that in turn enhances the liquid oil formation that is more useful fuel.

In the present study, attapulgite clay has been impregated with Cs salt of iron substituted POM (tungstophosphate) to develop highly efficient acidic cracking catalyst. Attapulgite is a hydrated magnesium-aluminum silicate material that consists of tetrahedrally arranged double

For Peer Review

chains of silica interconnected by octahedral oxygen and hydroxyl groups enclosing aluminum and magnesium ions in a chain-like structure (Araújo Melo, Ruiz et al. 2002). This tetrahedral arrangement extends throughout the chain and forms channels through the structure (Murray 1999). Due to its exceptional structural properties, attapulgite has been selected as a support which has been loaded with the Cs salt of iron substituted tungstophosphate. The resultant hybrid material shows excellent results for plastic degradation reactions and produces a high amount of liquid fuel. Moreover, the synthesized catalysts distinctly affect the pyrolysis temperature and thus cracking process starts at 310 ºC that is significantly lower than non-catalytic cracking at 375 ºC. Therefore, the prepared hybrid materials are remarkably effective for conversion of waste plastic materials into value added chemicals.

Materials and Methods

Materials

Sodium tungstate dihydrate (98 %), disodium hydrogen phosphate (98 %), iron nitrate nonahydrate (99 %), cesium chloride (99 %) and acetic acid (99.5 %) were supplied by Sigma Aldrich. All chemicals were used as received without further purification unless otherwise stated. Attapulgite clay was obtained from Ahmad Saeed & Co Pvt Ltd. Low-density polyethylene pellets (20 µm thickness) were purchased from the local market.

Methods

Synthesis of Cs salt of iron substituted tungstophosphate (Fe-POM)

Iron substituted Keggin tungstophosphate was synthesized by a simple method as reported in the literature(Simões, Conceição et al. 1999). Briefly, 15.156 mmol (5 g) of sodium tungstate ($Na_2WO_4 \cdot 2H_2O$)and 1.38 mmol (0.246 g) of disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$)

For Peer Review

were dissolved in 31 mL of deionized water. Then, 1.82 mmol (0.735 g) of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were added to the above mixture,and pH was adjusted to 4.8 with glacial acetic acid. The resultant mixture was heated to 80-85 ºC, filtered if needed, and then 6.82 mmol of cesium chloride (CsCl) dissolved in 5 mL of deionized water was added to this mixture dropwise. The solution was cooled to room temperature and 150 mL of ethanol was added as an antisolvent. The resultant solid was separated and dissolved in 60 mL of water at 60 ºC and recrystallized using ethanol, filtered, washed many times with ethanol, and dried at 100 ºC for 10 hours. For simplification, the product ($Cs_6[FePW_{11}O_{39}] \cdot 12H_2O$) was abbreviated as Fe-POM.

Synthesis of Fe-POM/Attapugite Composites

A series of catalysts were prepared by impregnating with different concentrations (10, 30 and 50 wt.% relative to attapulgite) of Fe-POM as follows; aqueous suspension of attapulgite clay (1 g) was prepared in 50 mL of water. Then, an aqueous solution of the calculated amount of $Cs_6[FePW_{11}O_{39}] \cdot 12\ H_2O$ was added into it under constant stirring followed by heating till complete evaporation of water. Finally, the composites were dried in an oven at 110 ºC (overnight). The synthesized composites were symbolized as Fe-POM-10, Fe-POM-30, and Fe-POM-50 corresponding to attapulgite impregnated with 10, 30, and 50% of $Cs_6[FePW_{11}O_{39}] \cdot 12\ H_2O$.

Cracking Experiment

Polyethylene (PE) cracking experiment was performed by batch operation using apyrex glass reactor (280 mm x 50 mm) as shown in Fig. 1. PE pellets were mixed with the catalyst in a weight ratio 20:1 and placed in the reactor for catalytic cracking. Heating of reactor was done in two steps: in the former step, it was heated at 2 ºC /min to 120 ºC under the flow of nitrogen (30 ml/min) to remove any adsorbed water molecules however in the latter, N_2 supply was disconnected and the temperature was increased to cracking temperature (heating rate 5 ºC/min).

For Peer Review

The experiment was carried out up to three hours. Liquid products and solid residue were weighed directly, however, the amount of gaseous products was determined indirectly by measuring the difference in weight of both liquid products and solid residues from the total weight of PE feed. Total polymer conversion was estimated by the ratio of polymer converted to liquid fuel and the amount of sample fed initially. Liquid hydrocarbons were analyzed by a Gas Chromatograph-Mass Spectrometer(GC-MS QP2010S) using the ZB-5 MS column with dimensions of 30 m × 0.32 mm × 0.25 μm.

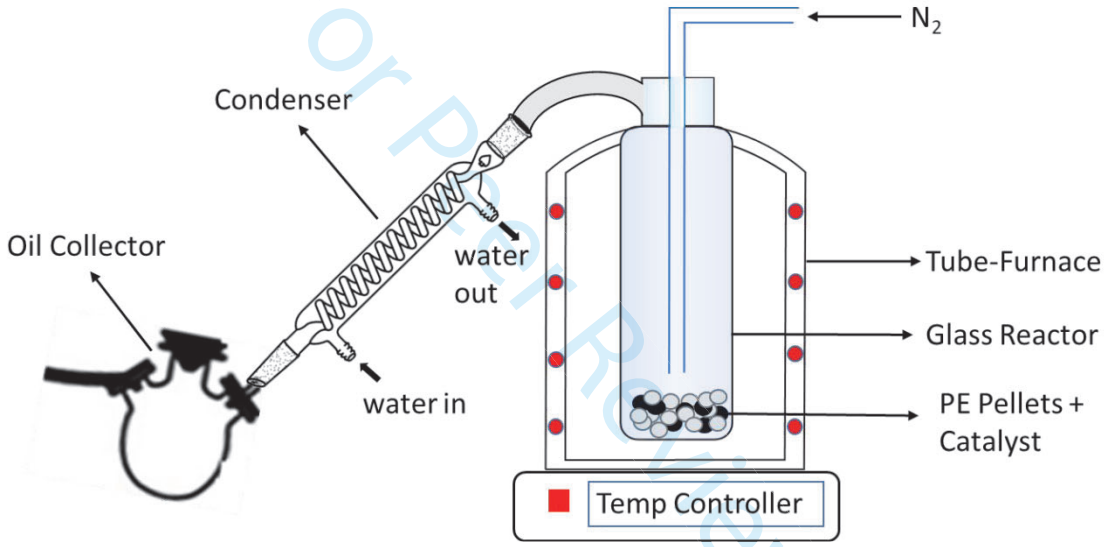


Figure 1: Schematic diagram for set up used for PE cracking experiments.

Characterization Techniques

Characterization of synthesized catalysts was accomplished by various analytical techniques like Fourier Transform Infrared (FTIR) spectroscopy, Powder X-ray Diffraction (PXRD), Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy (SEM-EDX), and Thermogravimetric analysis (TGA). FTIR spectroscopy was used to identify functional groups with the help of an FTIR Spectrometer (model 41630 by Agilent technology) operating in the ATR

For Peer Review

mode. Spectra were recorded at room temperature (4 cm^{-1} resolution, 256 scans/sample). TGA was performed on Netzsch STA 409 instrument: *approx*. 20 mg sample was placed in alumina crucibles and the temperature program was set to rise at a rate of 10 ºC/min upto 1000 ºC in the argon environment (flow rate: 60 ml/min). The surface morphology of prepared composites was examined by an XL30 ESEM instrument. Gold targets were used for the pre-coating of samples by a Polaron SC7640 sputter coater. The elemental composition of the samples was obtained with the help of INCA X-Act EDX detector. The crystalline structure of prepared composites was evaluated by PXRD performed on a PANalytical XPERT-PRO system working at 40 kV and 40 mA utilizing Cu Kα radiation. The scanning rate was set at 0.02º over 2θ range of 5º-85º. Liquid products were analyzed by a GCMS-QP2010S instrument usingthe ZB-5 MS column (30 m × 0.32 mm × 0.25 μm) under flow of He gas. GC and MS conditions were as follows: Initial GC oven temperature was kept at 40 ºC for 1 min, then heated to 310 ºC at a heating rate of 3 °C/min and held constant for 30 min. The temperature of the injector was maintained at 280 ºC while the detector was held at 310 ºC. EI ionization mode was used to record mass m/z from 30 to 500. Ion source and interface temperatures were kept at 180 ºC and 250 ºC, respectively. All compounds were identified from NIST/EPA/NIH MS Library.

For Peer Review

Results and Discussion

Characterization of catalysts

FTIR

FTIR spectrum (Fig. 2) of attapulgite clay exhibited characteristic asymmetric vibrations at 920 and 800 cm^{-1} corresponding to Si–O–H and Al–O–Si bonds, respectively.A shoulder peak

at 1193 cm^{-1} is ascribed to Si–O–Si bond in clay (MENDELOVICI 1973, Araújo Melo, Ruiz et al. 2002). The vibrational band at 1600 cm^{-1} is attributed to coordinated water molecules (Fig. 2). Fe-POM/attapulgite clay samples exhibit only a few characteristic vibration bands of POM. FTIR spectrum of bulk Fe-POM shows typical asymmetric vibrations for $P–O_a–W$, $W=O_d$, $W–O_b–W$ bridges between corner-sharing WO_6 octahedra, and $W–O_c–W$ bridges between edge-sharing WO_6 octahedra at 1084, 982, 895 and 789 cm^{-1}, respectively (Rocchiccioli-Deltcheff, Fournier et al. 1983, Shah, Mujahid et al. 2012).W–O–Fe vibrations are located at 666 cm^{-1} (Gamelas, Soares et al. 2003). In case of 50 % POM/attapulgite, only $P–O_a–W$ and $W–O_c–W$ stretching vibrations can be seen at 1080 and 789 cm^{-1}, which are characteristic of Fe-POM Keggin structure. However, $W=O_d$ and $W–O_b–W$ vibrations of Fe-POM structure located at 982 and 895 cm^{-1} are not obvious due to overlapping with the strong bands of silica present in clay's structure.

For Peer Review

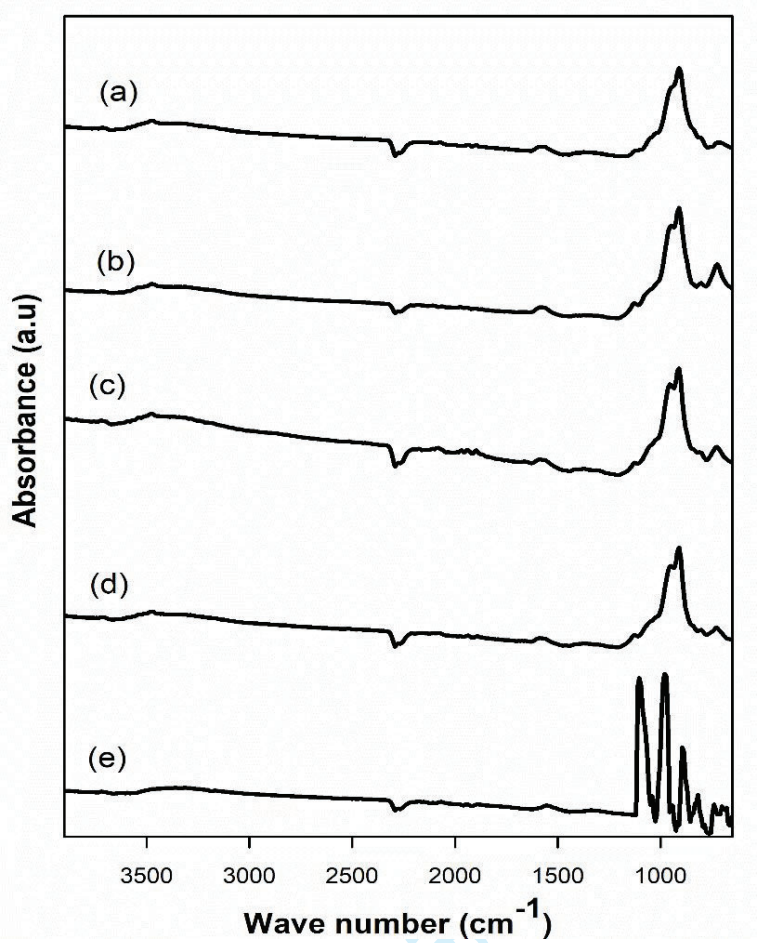


Figure 2: FT-IR spectra of (a) Attapulgite, (b) Fe-POM-50, (c) Fe-POM-30, (d) Fe-POM-10, and (e) Fe-POM samples.

XRD

Attapulgite clay exhibited a high degree of crystallinity as shown in Fig. 3. The diffraction peak observed at 2θ values of 8.5º, 20.2º, and 35.0 are ascribed to basal space of attapulgite framework (PDF No. 02–0018). The peaks located at 2θ values 13º, 16.4º, 20.8º, and 50.1º correspond to silica layers of the clay. The most intense peak corresponding to quartz (PDF No. 33–1161) impurities is located at 2θ = 26.8º (Shepard, Christ et al. 1969, Araújo Melo, Ruiz et al. 2002, Suki, Azahari et al. 2013). XRD patterns of Fe-POM exhibits a cubic crystalline phase that is characteristic of Keggin tungstophosphate (Dias, Caliman et al. 2004, Zhang, Yue et al. 2013).

Diffraction patterns of Fe-POM/attapulgite clay composites present all the characteristic peaks of attapulgite but only a few diffraction peaks of Fe-POM Keggin structure. Attapulgite impregnated with 50 % Fe-POM exhibit characteristic peak of Fe-POM at 2θ value of 8.3º but in 10 % and 30 % Fe-POM /clay samples this peak is masked by intense diffraction peaks of silica present in clay structure.

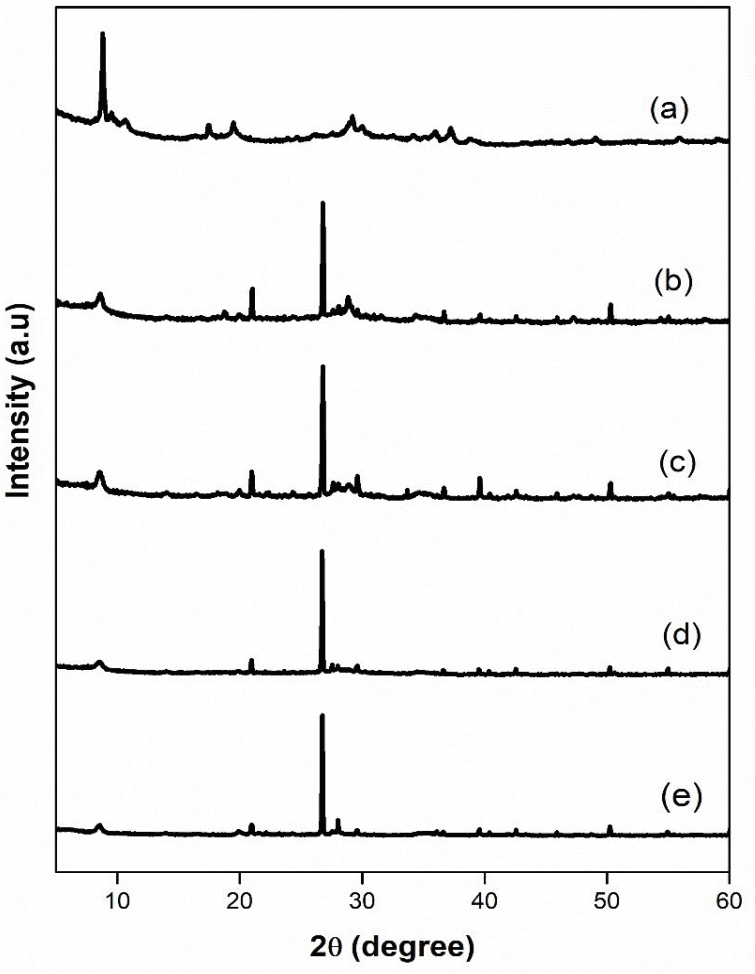


Figure 3: Powder XRD patterns of(a) Fe-POM.(b) Fe-POM 50, (c) FePOM-30, (d) Fe-POM 10 and (e) Attapulgite.

TGA

Thermogravimetric analysis of Fe-POM, attapulgite, and Fe-POM impregnated attapulgite-composites is shown in Fig. 4. TGA data collected for attapulgite exhibited weight loss in four distinct steps. The first two steps are attributed to dehydration and the next two steps correspond to dehydroxylation. During the first step, which starts at ~ 50 ºC, physiosorbed water molecules are lost (4 wt.%). The second step (located at 245 ºC) corresponds to the loss of hydrated water molecules (~ 2 %). The last two steps are complex comprising overlying weight loss steps. The third step is related to two concurring reactions occurring at 450 and 495 ºC (comprising weight loss of ~ 4 %). The last step is also completed in two steps occurring at 786 and 820 ºC (weight loss ~ 3 %). Nagata et al. have also proposed that the dehydration and dehydroxylation of attapulgite take place in a series of steps (Vágvölgyi, Daniel et al. 2008). These steps are ascribed to the loss of (i) adsorbed water molecules (ii) water molecules of hydration (iii) coordinated water molecules and (iv) the loss of water molecules through dehydroxylation.

Fe-POM showed a weight loss of 6 % upto 250 ºC that was ascribed to water molecules of crystallization and no further noticeable weight loss was observed upto 1000 ºC. Fe-POM/attapulgite composites also exhibited thermal behavior analogous to attapulgite clay, the weight loss observed during thermal analysis could be ascribed to the loss of coordinated H_2O molecules and dehydroxylation of silica sheets in attapulgite. However, compared to attapulgite, Attapulgite impregnated with Fe-POM exhibited reduced weight loss in the dihydroxylation phase and this weight loss kept on reducing by increasing the amount of Fe-POM. Attapulgite impregnated with 50 % Fe-POM showed least weight loss during this dehydroxylation step due to

For Peer Review

reduced percentage of attapulgite clay (from 100 to 50 %) and increased percentage of Fe-POM (from 0 to 50 %) compared to bare attapulgite, Fe-POM did not lose any water in this region.

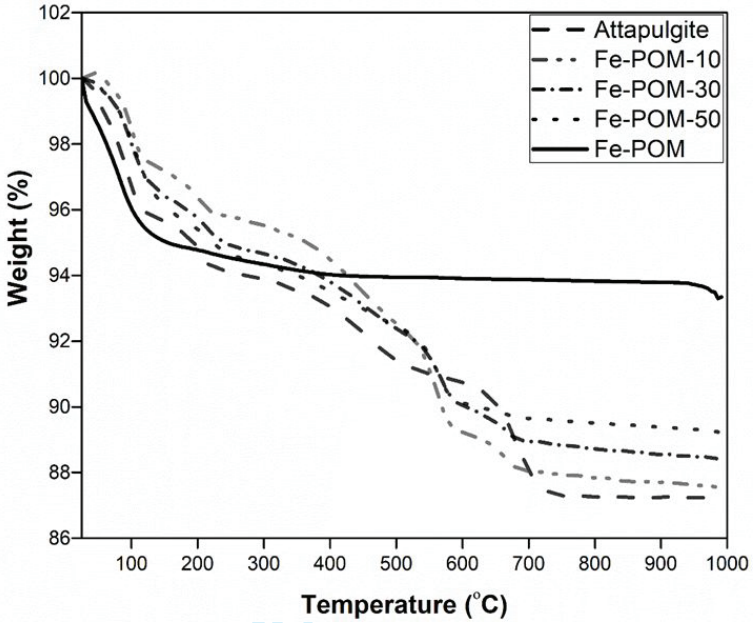


Figure 4: Thermal gravimetric analysis of Fe-POM/attapulgite composites.

SEM-EDX analysis

SEM analysis was conducted to investigate the morphology of prepared catalysts. Attapulgite clay showed crystalline morphology as can be seen in Fig. 5. Fe-POM exhibited a cubic crystalline structure as reported for cesium and silver salts of Keggin tungstophosphate (Dias, Caliman et al. 2004, Zhu, Gao et al. 2013). However, SEM images of Fe-POM/attapulgite composites did not show this crystalline morphology, indicating the uniform distribution of Fe-POM on the attapulgite surface due to the interaction of Fe-POM particles with the clay. Another distinct change in the morphology of Fe-POM/attapulgite composites was the change in the luster of pure attapulgite and Fe-POM loaded attapulgite. Fe-POM impregnated attapulgite samples were more lustrous compared to pure attapulgite. Furthermore, EDX analysis was performed to

determine the elemental composition of these composite materials. EDX analysis of attapulgite shows that the major components of attapulgite are Mg-Al silicate, while iron and titanium are present in trace amounts (Araújo Melo, Ruiz et al. 2002). EDX spectrum of Fe-POM/attapulgite composites revealed that in addition to Mg-Al silicate, tungsten and cesium were also present, confirming the successful loading of Fe-POM on the attapulgite substrate. Moreover, the weight percentage of W and Cs increased by increasing the percentage of Fe-POM. The highest percentage of W and Cs were observed for the 50 % Fe-POM loaded attapulgite composite. Atomic and weight percentages of elements found in all composites are shown in Table S1.

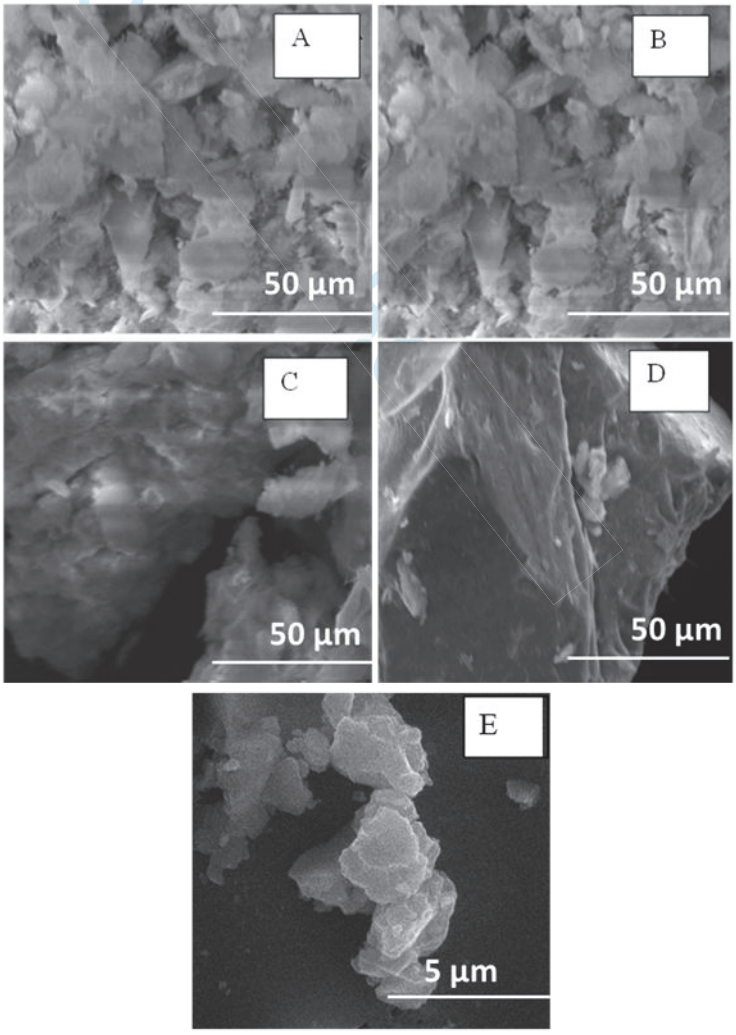


Figure 5: SEM images of (A) Fe-POM-50, (B) Fe-POM-30, (C) Fe-POM-10 and (D) attapulgite clay.

Thermal Catalytic Cracking of Polyethylene

The results of polyethylene cracking in the absence and presence of catalysts are summarized in Table 1. Thermal cracking took place at a very high temperature (375 ºC) while in presence of catalysts the cracking temperature was dropped to a great extent. However, various catalysts showed different behavior for the cracking of polyethylene. Fe-POM exhibited lesser yield of liquid oil products and the cracking started at a higher temperature i.e., 350 ºC. Impregnation of Fe-POM on attapulgite clay decreased the cracking temperature to 310 ºC and enhanced the liquid yield by large amounts. At the same time, the amount of residue was lowered considerably. The liquid yield was enhanced by increasing the amount of Fe-POM loading. 50 % Fe-POM impregnated attapulgite produced 82 % liquid hydrocarbons, while solid residue was reduced to ≤ 2 %. On the other hand, pure attapulgite produced 72 % liquid oil that was far less than the Fe-POM/clay composite samples. POM impregnated on attapulgite creates extra Brönsted acid sites that synergistically enhance catalyst activity for cracking of polyethylene. The enhancement in catalyst acidity would have reduced the cracking temperature and degraded heavier hydrocarbons into smaller ones. PE cracking reactions proceed over the Bronsted acidic sites, as described earlier and therefore with increasing acidic sites the temperature required for cracking decreases (Aydemir and Sezgi 2013). Moreover, recycled 50 % Fe-POM/attapulgite sample exhibited negligible activity loss when applied for LDPE cracking that proved it to be a truly heterogeneous catalyst.

For Peer Review

Table1: Percentage yield of degradation products over various catalysts

Catalyst	Cracking temperature (°C)	Liquid Oil (%)	Gas (%)	Residue (%)
No Catalyst	375	68	10	22
Fe-POM	350	74.67	15.83	9.5
Attapulgite	310	72.7	17.3	10
Fe-POM-10	310	78.4	16.5	5.1
Fe-POM-30	310	80.1	16.7	3.2
Fe-POM-50	310	82.0	15.9	2.1
Recycled Fe-POM-50	310	81.8	15.8	2.4

3.2.1 Composition of liquid Products

The oil fraction obtained by PE cracking was analyzed by GC-MS. Every single peak in the chromatogram corresponded to a specific compound. The molecular weight and structure of these compounds were identified by mass spectrometer. It was found that the oil acquired over all prepared catalysts contained hydrocarbons distribution between C_5─C_{21} (Fig. 6). Nearly 60 % hydrocarbons comprised of petroleum fractions (C_5–C_{12}), while ≥ 35 % fractions were Kerosene-like hydrocarbons (C_{13}–C_{18}). High molecular weight hydrocarbons (C_{19}–C_{21}) were ≤ 5 %. All the tested catalysts shifted the product distribution towards lower hydrocarbons and the effect was most profound in oil obtained using 50 % Fe-POM/attapulgite sample. Although, C_5–C_8 are produced in enormous amounts in oil obtained using 50 % POM loaded sample but the maximum is observed for C_9–C_{10} hydrocarbon fraction. On the contrary, Fe-POM gave maximum distribution of C_{10}–C_{13} fractions, while oil obtained by thermal cracking showed the maximum at C_{12}–C_{14} fractions (Fig. 6).

For Peer Review

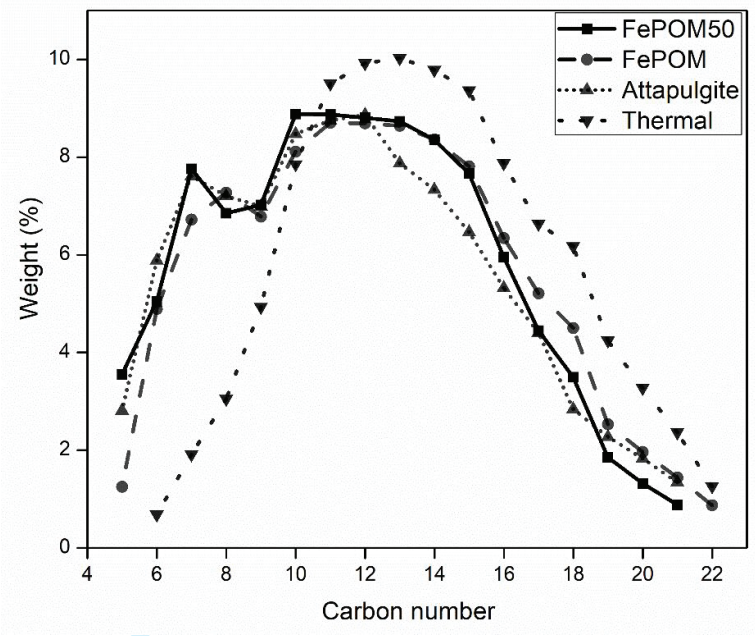


Figure 6: Comparioson of distribution of carbon number for various oil samples obtained by thermal, Fe-POM, attapulgite and 50 % Fe-POM/attapulgite catalysts.

Detailed GC-MS analysis revealed that oil produced by catalytic cracking contained mainly aliphatic hydrocarbons (paraffins and olefins). The relative abundance of paraffins and olefins produced by different catalysts are given in Table S-2 (Supplementary file). Among the lower hydrocarbons (C_5–C_{12}), olefins were more abundant, while in case of heavier hydrocarbons paraffins were prominent. Non-catalytic oil produced a higher percentage of paraffinic hydrocarbons (Table 2), as non-catalytic degradation occurred at a higher temperature, which favors paraffin formation (Rahimi and Karimzadeh 2011). The formation of olefins during non-catalytic and catalytic cracking is also explained by Haag-Dessau mechanism (Kotrel, Knözinger et al. 2000). For catalytic cracking, Si/Al ratio also affects the olefin and paraffin distribution (Yoshimura, Kijima et al. 2001, Han, Lee et al. 2004, Wei, Liu et al. 2005). The maximum percentage of olefin was achieved over50% Fe-POM/attapulgite catalyst that could be attributed

to the creation of protonic acidified sites (from Fe-POM) and incorporation of Si and Al (from attapulgite) in catalyst. However, no aromatic compounds could be detected in oil samples, the exclusion of aromatics is of great importance from environmental point of view (Artetxe, Lopez et al. 2012). Thus, the prepared catalysts Fe-POM/attapulgite could be regarded as an efficient and cost-effective catalysts for degradation of waste polymeric materials.

Table 2: Product Distribution in oil obtained by different catalysts.

Catalyst	Carbon number	Weight Percent (%)	
		Alkanes	Alkenes
No Catalyst	C_5–C_{12}	19.1	16.62
	C_{13}–C_{18}	21.35	21.20
	>C_{18}	14.67	----
Fe-POM	C_5–C_{12}	24.85	26.18
	C_{13}–C_{18}	25.04	16.09
	>C_{18}	6.80	----
Fe-POM-50	C_5–C_{12}	27.03	28.79
	C_{13}–C_{18}	23.83	14.79
	>C_{18}	4.05	----
Attapulgite	C_5–C_{12}	25.77	28.38
	C_{13}–C_{18}	27.37	12.47
	>C_{18}	5.44	----

For Peer Review

Conclusion

This research reports the synthesis and characterization of iron-substituted tungstophosphate (Fe-POM) impregnated attapulgite clay using various concentrations of Fe-POM (10 %, 30 % & 50 %). The synthesized materials have been successfully characterized by

FTIR, XRD and SEM-EDX analysis. TGA explains the thermal stability of these composite materials. Fe-POM imregnated attapulgite composites have been used as catalysts for polyethylene cracking. The synthesized composite materials exhibit extraordinary performance for the conversion of polyethylene to lower hydrocarbons, hence the yield of fuel oil was enhanced to a considerable extent. By increasing the amount of Fe-POM loading, oil yield enhances and therefore maximum oil yield is exhibited by 50 % Fe-POM/attapulgite sample. Furthermore, these composites also lower the pyrolysis temperature, hence make the cracking process economical. Moreover, valuable hydrocarbons have been recovered from waste polymeric materials by prepared catalysts for transportation fuels, suggesting the applicability of these catalysts for energy recovery from plastic waste along with the effective pollution control of the environment.

Acknowledgement

Higher Education Commission of Pakistan is greatly acknowledged for the grant of Indigenous PhD Scholarship (PIN# 213-66412-2PS2-074). We are also thankful to Higher Education Commssion for NRPU project grant (6776/NRPU/R&D/HEC) to complete this research work.

Supplementary material

GC-MS spectra, peak identification table and EDS elemental analysis is provided in supplementary material file.

Conflict of interest

The authors declare that they have no conflict of interest.

8. Refrences

For Peer Review

Aguado, J., D. P. Serrano, G. S. Miguel, J. M. Escola and J. M. Rodríguez (2007). "Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins." Journal of Analytical and Applied Pyrolysis **78**(1): 153-161.

Akpanudoh, N. S., K. Gobin and G. Manos (2005). "Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts: effect of polymer to catalyst ratio/acidity content." Journal of Molecular Catalysis A: Chemical **235**(1): 67-73.

Araújo Melo, D. M., J. A. C. Ruiz, M. A. F. Melo, E. V. Sobrinho and A. E. Martinelli (2002). "Preparation and characterization of lanthanum palygorskite clays as acid catalysts." Journal of Alloys and Compounds **344**(1): 352-355.

Artetxe, M., G. Lopez, M. Amutio, G. Elordi, J. Bilbao and M. Olazar (2012). "Light olefins from HDPE cracking in a two-step thermal and catalytic process." Chemical engineering journal **207**: 27-34.

Attique, S., M. Batool, M. Yaqub, O. Goerke, D. H. Gregory and A. T. Shah (2020). "Highly efficient catalytic pyrolysis of polyethylene waste to derive fuel products by novel polyoxometalate/kaolin composites." Waste Management & Research **38**(6): 689-695.

Aydemir, B. and N. A. Sezgi (2013). "Alumina and Tungstophosphoric Acid Loaded Mesoporous Catalysts for the Polyethylene Degradation Reaction." Industrial & Engineering Chemistry Research **52**(44): 15366-15371.

Bobek-Nagy, J., N. Gao, C. Quan, N. Miskolczi, D. Rippel-Pethő and K. Kovács (2020). "Catalytic co-pyrolysis of packaging plastic and wood waste to achieve H2 rich syngas." International Journal of Energy Research **44**(13): 10832-10845.

For Peer Review

Chai, Y., M. Wang, N. Gao, Y. Duan and J. Li (2020). "Experimental study on pyrolysis/gasification of biomass and plastics for H2 production under new dual-support catalyst." Chemical Engineering Journal **396**: 125260.

Dias, J. A., E. Caliman and S. C. Loureiro Dias (2004). "Effects of cesium ion exchange on acidity of 12-tungstophosphoric acid." Microporous and Mesoporous Materials **76**(1): 221-232.

Gaca, P., M. Drzewiecka, W. Kaleta, H. Kozubek and K. Nowinska (2008). "Catalytic degradation of polyethylene over mesoporous molecular sieve MCM-41 modified with heteropoly compounds." Polish Journal of Environmental Studies **17**(1): 25.

Gamelas, J. A. F., M. R. Soares, A. Ferreira and A. M. V. Cavaleiro (2003). "Polymorphism in tetra-butylammonium salts of Keggin-type polyoxotungstates." Inorganica Chimica Acta **342**: 16-22.

Han, S. Y., C. W. Lee, J. R. Kim, N. S. Han, W. C. Choi, C.-H. Shin and Y.-K. Park (2004). Selective Formation of Light Olefins by the Cracking of Heavy Naphtha. Carbon Dioxide Utilization for Global Sustainability: Proceedings of the 7th International Conference on Carbon Dioxide Utilization, Seoul, Korea, October 12-16, 2003, Elsevier.

Kotrel, S., H. Knözinger and B. Gates (2000). "The Haag–Dessau mechanism of protolytic cracking of alkanes." Microporous and mesoporous materials **35**: 11-20.

Lin, Y.-H., M.-H. Yang, T.-F. Yeh and M.-D. Ger (2004). "Catalytic degradation of high density polyethylene over mesoporous and microporous catalysts in a fluidised-bed reactor." Polymer degradation and stability **86**(1): 121-128.

Luo, W., Z. Fan, J. Wan, Q. Hu, H. Dong, X. Zhang and Z. Zhou (2021). "Study on the reusability of kaolin as catalysts for catalytic pyrolysis of low-density polyethylene." Fuel **302**: 121164.

For Peer Review

Mastral, J. F., C. Berrueco, M. Gea and J. Ceamanos (2006). "Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite." Polymer Degradation and Stability **91**(12): 3330-3338.

MENDELOVICI, E. (1973). "Infrared Study Of Attapulgite And HCl Treated Attapulgite " Clays and Clay Minerals **Vol. 21**: pp. 115-119.

Murray, H. H. (1999). Applied clay mineralogy today and tomorrow. Clay Minerals. **34:** 39.

Patil, L., A. K. Varma, G. Singh and P. Mondal (2018). "Thermocatalytic Degradation of High Density Polyethylene into Liquid Product." Journal of Polymers and the Environment **26**(5): 1920-1929.

Rahimi, N. and R. Karimzadeh (2011). "Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review." Applied Catalysis A: General **398**(1): 1-17.

Rocchiccioli-Deltcheff, C., M. Fournier, R. Franck and R. Thouvenot (1983). "Vibrational investigations of polyoxometalates. 2. Evidence for anion-anion interactions in molybdenum (VI) and tungsten (VI) compounds related to the Keggin structure." Inorganic Chemistry **22**(2): 207-216.

Saira Attique, M. B., Muhammad Irfan Jalees, Khurram Shehzad., Zakir Khan., Umar Farooq., Fawad Ashraf., Asma Tufail Shah. (2018). "Highly efficient catalytic degradation of low-density polyethylene Using a novel tungstophosphoric acid/kaolin clay composite catalyst." Turkish journal of Chemistry(42): p. 684-693.

Serrano, D. P., J. Aguado and J. M. Escola (2000). "Catalytic conversion of polystyrene over HMCM-41, HZSM-5 and amorphous SiO2–Al2O3: comparison with thermal cracking." Applied Catalysis B: Environmental **25**(2): 181-189.

For Peer Review

Shah, A., S. Attique, M. Batool, H. R. Godini and O. Görke (2021). Role of polyoxometalates in converting plastic waste into fuel oil**:** 333-355.

Shah, A. T., A. Mujahid, M. U. Farooq, W. Ahmad, B. Li, M. Irfan and M. A. Qadir (2012). "Micelle directed synthesis of (C19H42N)4H3(PW11O39) nanoparticles and their catalytic efficiency for oxidative degradation of azo dye." Journal of Sol-Gel Science and Technology **63**(1): 194-199.

Shepard, A. O., C. L. Christ, J. C. Hathaway and P. B. Hostetler (1969). "Palygorskite: New X-Ray data1." American Mineralogist **54**(1-2): 198-205.

Simões, M. M. Q., C. M. M. Conceição, J. A. F. Gamelas, P. M. D. N. Domingues, A. M. V. Cavaleiro, J. A. S. Cavaleiro, A. J. V. Ferrer-Correia and R. A. W. Johnstone (1999). "Keggin-type polyoxotungstates as catalysts in the oxidation of cyclohexane by dilute aqueous hydrogen peroxide." Journal of Molecular Catalysis A: Chemical **144**(3): 461-468.

Suki, F. M. M., N. A. Azahari, N. Othman and H. Ismail (2013). "XRD Analysis and Tensile Properties of Attapulgite Clay Filled Polyvinyl Alcohol/Corn Starch Blend Films." Advanced Materials Research **620**: 99-104.

Vágvölgyi, V., L. M. Daniel, C. Pinto, J. Kristóf, R. L. Frost and E. Horváth (2008). "Dynamic and controlled rate thermal analysis of attapulgite." Journal of Thermal Analysis and Calorimetry **92**(2): 589-594.

Wang, J., J. Jiang, Y. Sun, X. Wang, M. Li, S. Pang, R. Ruan, A. J. Ragauskas, Y. S. Ok and D. C. Tsang (2021). "Catalytic degradation of waste rubbers and plastics over zeolites to produce aromatic hydrocarbons." Journal of Cleaner Production **309**: 127469.

For Peer Review

Wei, Y., Z. Liu, G. Wang, Y. Qi, L. Xu, P. Xie and Y. He (2005). "Production of light olefins and aromatic hydrocarbons through catalytic cracking of naphtha at lowered temperature." Studies in Surface Science and Catalysis **158**: 1223-1230.

Yoshimura, Y., N. Kijima, T. Hayakawa, K. Murata, K. Suzuki, F. Mizukami, K. Matano, T. Konishi, T. Oikawa and M. Saito (2001). "Catalytic cracking of naphtha to light olefins." Catalysis Surveys from Japan **4**(2): 157-167.

Zhang, L., B. Yue, Y. Ren, X. Chen and H. He (2013). "An aluminum promoted cesium salt of 12-tungstophosphoric acid: a catalyst for butane isomerization." Catalysis Science & Technology **3**(8): 2113-2118.

Zhu, S., X. Gao, F. Dong, Y. Zhu, H. Zheng and Y. Li (2013). "Design of a highly active silver-exchanged phosphotungstic acid catalyst for glycerol esterification with acetic acid." Journal of Catalysis **306**: 155-163.

For Peer Review

Supplementary information for

Fe-POM/ Attapulgite Composite Materials: Efficient catalysts for plastic pyrolysis

Table S1: Weight % and atomic % of elements found in Fe-POM and Fe-POM/Attapugite composites.

Catalyst	Element	Weight %	Atomic %
Attapulgite	O	62.06	74.45
	Na	0.72	0.60
	Mg	4.24	3.35
	Al	5.67	4.03
	Si	23.93	16.35
	K	0.31	0.15
	Ti	0.28	0.11
	Fe	2.79	0.96
Fe-POM-50	O	42.97	71.90
	Na	0.60	0.70
	Mg	2.96	3.26
	Al	3.53	3.51
	Si	14.30	13.83
	Ca	1.18	0.79
	Fe	1.84	0.88
	Cs	7.59	1.53
	W	24.83	3.61
Fe-POM-30	O	44.21	70.19
	Na	0.53	0.58
	Mg	3.06	3.19
	Al	3.43	3.23

For Peer Review

	Si	14.65	13.24
	Ca	1.02	0.64
	Fe	1.85	0.84
	Cs	5.41	1.03
	W	19.69	2.72
Fe-POM-10	O	45.97	72.90
	Na	0.50	0.60
	Mg	2.96	3.26
	Al	3.53	3.51
	Si	14.50	13.83
	Ca	1.18	0.79
	Fe	1.84	0.88
	Cs	4.59	1.23
	W	17.83	2.41

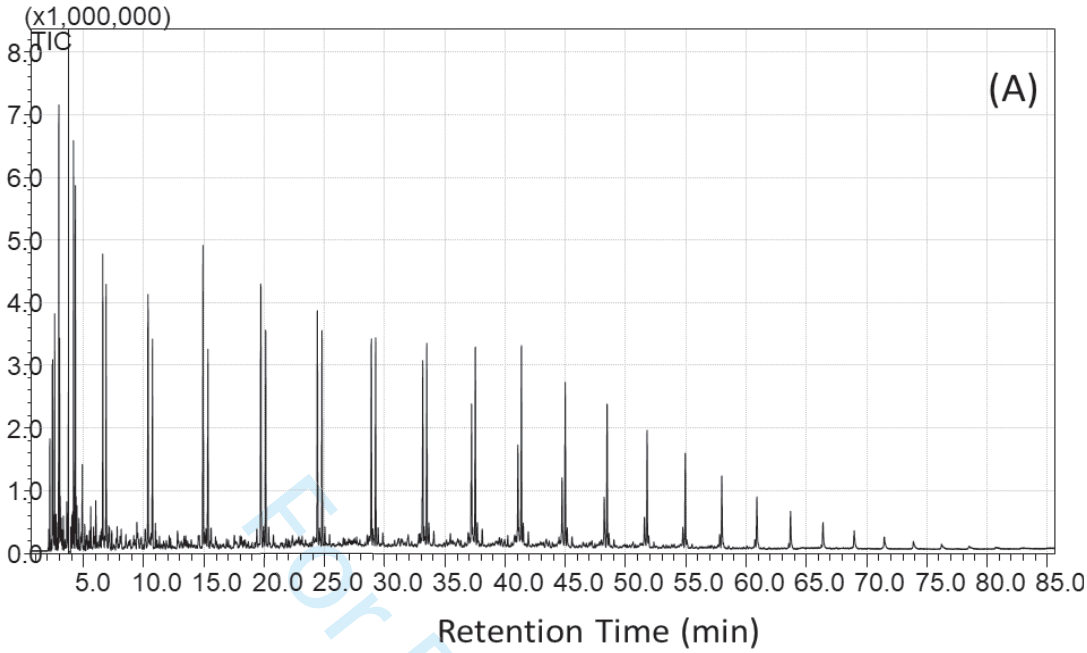
Table S-2: Identification of different compounds in the oil produced by various catalysts by GC-MS Analysis

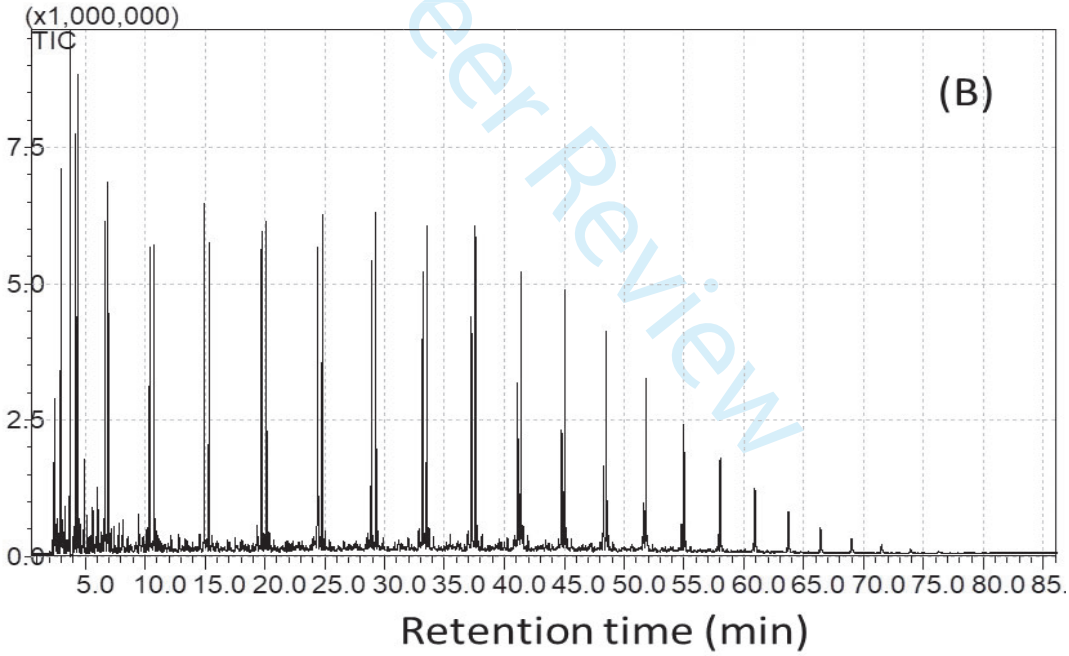
RT (min)	**Peak Name**	**Relative Abundance (%)**			
		No Catalyst	Fe-POM	Attapulgite	Fe-POM-50
2.196	1-Butene-2-methyl	----	0.50	0.96	1.02
2.401	1-Pentene	----	1.10	1.35	1.08
2.430	n-Pentane	----	0.75	1.46	1.45
2.618	1,3-Pentadiene	0.39	--	--	0.38
2.939	1-Hexene	0.29	2.43	2.87	3.04
3.007	n-Hexane	----	1.83	1.99	2.01
3.605	1,4 pentadiene-3-methyl	0.94	0.61	0.45	0.74
4.177	1-Heptene	0.97	2.81	3.17	3.14
4.327	n-Heptane	----	3.25	3.95	3.44

For Peer Review

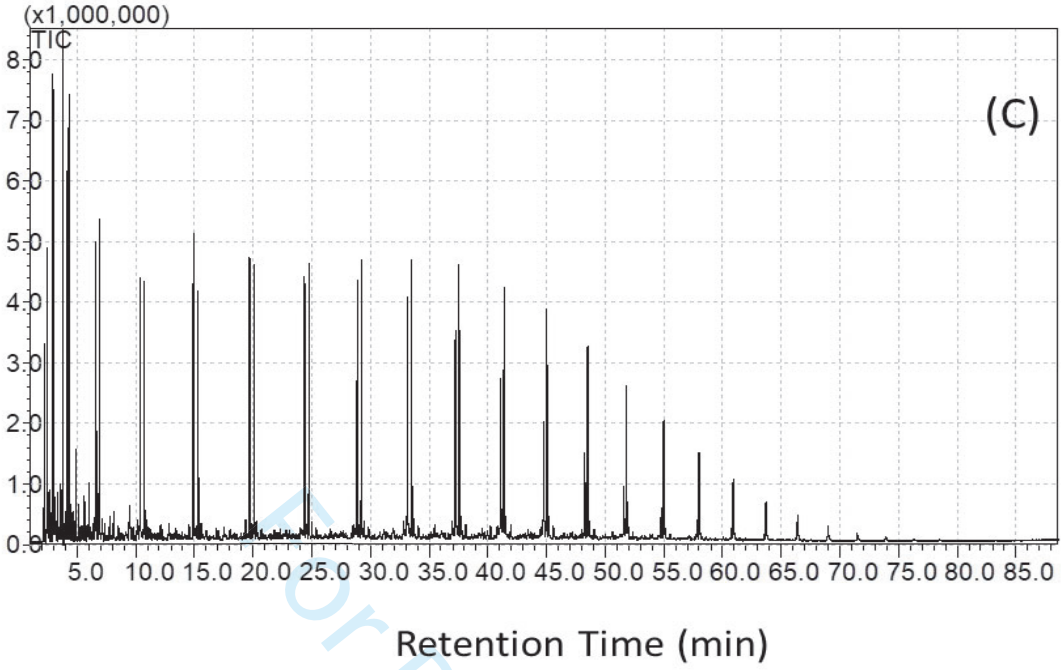
4.84	2-Pentene-4,4-dimethyl	----	0.66	0.62	0.74
6.013	Cyclohexane methylene	1.42	---	---	0.77
6.047	Heptane-3 methylene	1.63	---	---	0.74
6.600	1-Octene	2.51	2.92	3.57	3.10
6.876	n-Octane	2.42	3.61	3.73	3.75
10.349	1-Nonene	4.56	3.31	3.68	3.51
10.718	n-Nonane	3.29	3.47	3.11	3.51
14.900	Cis-3-decene	5.10	4.33	4.10	4.45
15.308	n-Decene	4.40	3.78	3.37	3.83
19.683	2-Undecene	5.12	4.34	4.32	4.46
20.090	n-Undecene	4.80	4.36	3.83	4.41
24.374	1-dodecene	5.04	4.14	4.01	4.23
24.762	n-dodecene	4.98	4.55	4.05	4.63
28.872	1-tridecene	4.89	3.94	3.92	3.98
29.235	n-tridecene	4.89	4.70	3.93	4.75
33.151	3-tetradecene	4.43	3.72	3.45	3.67
33.493	Tetradecane	4.93	4.64	3.88	4.68
37.216	1-Pentadecene	3.50	3.19	2.56	3.05
37.531	n-Pentadecene	4.37	4.62	3.90	4.61
41.074	1-Hexadecene	2.75	2.20	1.60	2.01
41.368	n-Hexadecene	3.88	4.14	3.72	3.94
44.744	1-Heptadecene	2.43	1.51	0.94	1.22
45.012	n-Heptadecane	3.74	3.70	3.10	3.94
48.235	1-Octadecene	1.50	1.26	--	0.87
48.481	n-Octadecane	2.74	3.24	2.84	2.62
51.793	n-Nonadecane	1.04	2.53	2.27	1.85
54.910	Eicosane	2.23	1.96	1.83	1.32
57.91	Henicosane	1.74	1.44	1.34	0.88
60.918	Docosane	1.26	0.87	---	---
63.976	Tricosane	0.82	----	----	----

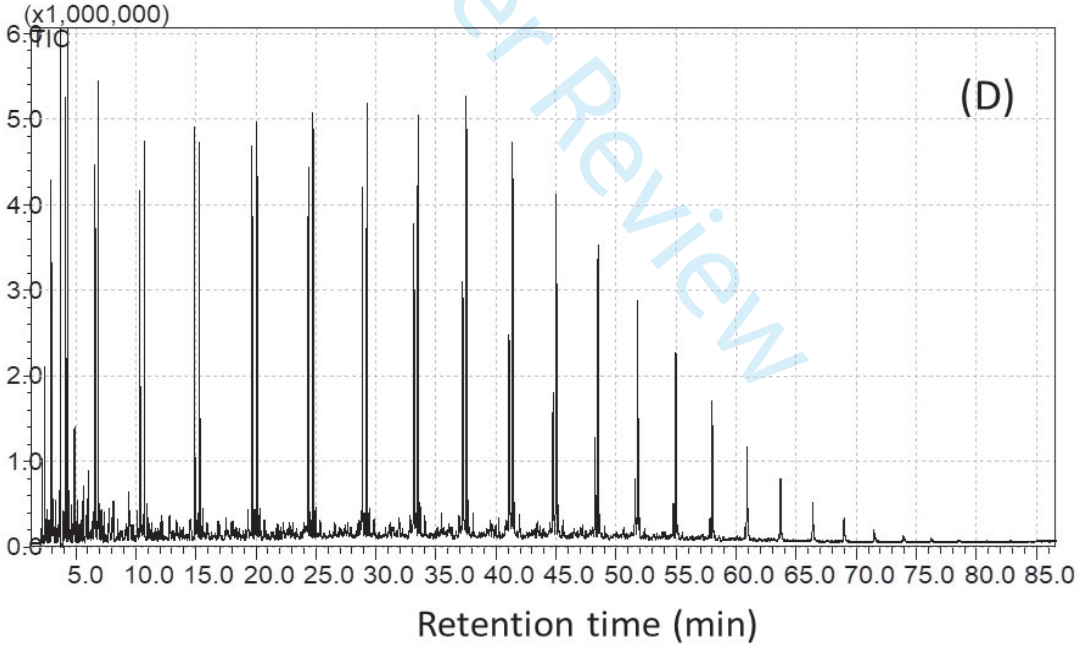
For Peer Review





For Peer Review





For Peer Review

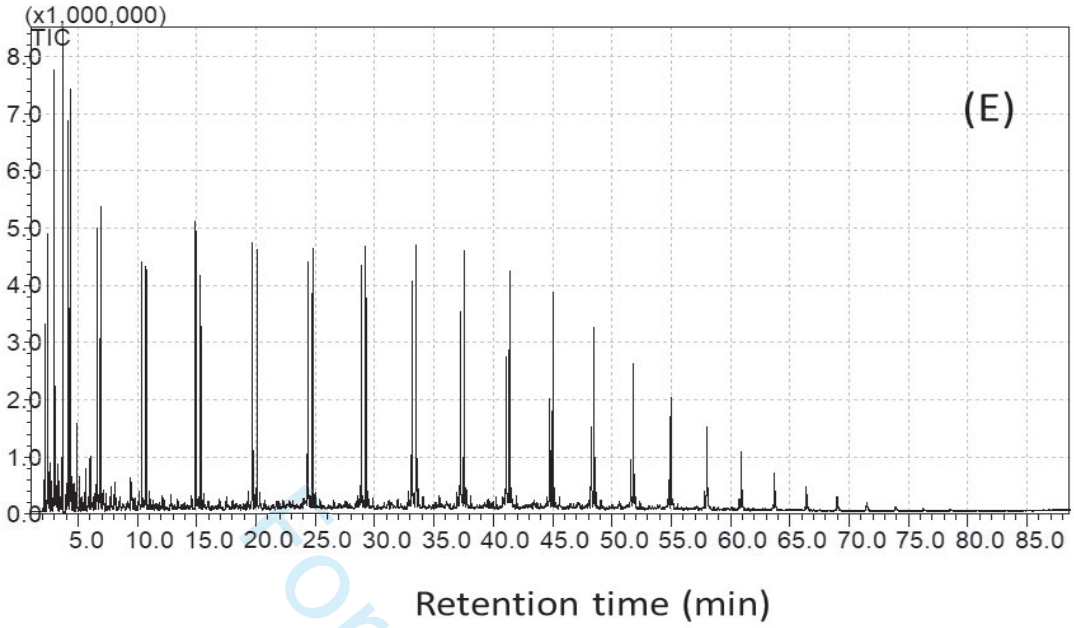


Figure S1: GC-MS spectra of oil produced by (A) FePOM, (B) 50% FePOM/Attapulgite, (C) 30% FePOM/Attapulgite, (D) 10% FePOM/Attapulgite, and (E) Attapulgite clay.

For Peer Review