Thermocatalytic Conversion of Plastics into Liquid Fuels

Subjects: Polymer Science

Contributor: Olga Lebedeva , Evgeniy Seliverstov ,

The problem of recycling polymer waste remains the main one in the context of the growth in the use of plastics. Given the non-renewability of fossil fuels, the task of processing plastic waste into liquid fuels seems to be a promising one. Thermocatalytic conversion is one of the methods that allows obtaining liquid products of the required hydrocarbon range. Clays and clay minerals can be distinguished among possible environmental-friendly, cheap and common catalysts.

secondary raw materials | plastics | fuel | catalysts | clays | clay minerals | thermocatalytic conversion

1. Introduction

The last few centuries have been marked by the rapid development of mankind. The obvious benefits that it brought were accompanied by new, serious anthropogenic challenges. One of them was the emergence in the 1950s of new synthetic materials—plastics. The main ingredient of plastic are polymers, such as polyolefins (with commercially dominant polyethylene and polypropylene) possessing the general formula $(CH_2CHR)_n$ where R is an alkyl group, polystyrene $((C_6H_5CH = CH_2)_n)$, polyvinyl chloride $((C_2H_3Cl)_n)$, etc.

One of the promising solutions is the conversion of plastic waste into liquid fuels. With a catalyst sufficiently selective to produce a mixture of hydrocarbons with an expected carbon number range, it would be possible to obtain liquid products with a composition similar to that of fuels such as gasoline and diesel. Since the production of various catalysts is often accompanied by environmental pollution, a complex preparation process, and, as a result, a high price of the final product, the catalysts must also comply with the principles of green chemistry and have a low cost.

2. Nature of Catalytic Activity of Clays

Clays belong to solid acids. They have both Lewis and Brønsted acid sites (**Figure 1**) [1].

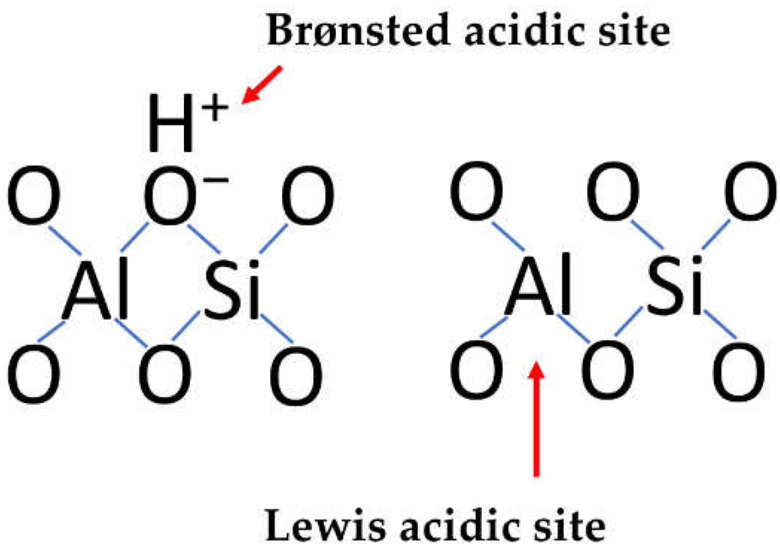

Figure 1. Acidic sites of clays.

The acidic sites are comparatively strong (H_0 typically quoted in the range from −5.6 to −8.2), though not as strong as the zeolite ones [1]. All the clays being aluminosilicates, the nature of the active sites is essentially the same for all types of clays. It is porosity that defines the specific features of different clays. Microporosity depends on the crystallographic structure of the material.

Original clays in cationic forms usually contain an insufficient number of acidic sites since the sites involve protons (**Figure 1**). Only cationic deficient samples of clays demonstrate catalytic activity in the reactions of the acid-base type. Generally, acidic activation is necessary for obtaining catalytically active clays. The conditions of acidic treatment are often crucial for the efficiency of the clay catalysts.

3. Kaolin Group Catalytic Activity

The kaolin group is represented by layered phyllosilicate minerals with the chemical composition $Al_2Si_2O_5(OH)_4$. The layers of these clay minerals consist of corner-sharing tetrahedra and edge-sharing octahedra. Tetrahedra are formed by silicon atoms, and octahedrons are constructed from aluminum atoms. The way the layers are stacked and the nature of the material between the layers distinguishes the individual minerals (kaolinite, dickite, halloysite, and nacrite, sometimes also serpentine subgroup) in the group [2]. Rocks rich in kaolinite are thus called kaolin.

Kaolin-based catalysts are the most commonly mentioned among the articles on clay catalysts for the conversion of plastics into liquid fuels due to the abundant availability of natural kaolin. All results from work on kaolin clay catalysts are presented in **Table 1**.

Table 1. Publications on the conversion of different plastics over clay minerals from kaolin group catalysts.

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
Kaolinite-containing natural clay	HDPE	478	16	Catalyst produced more alkanes than olefins in both gaseous and liquid oil products.	[3]
Kaolin and its modifications With CH_3COOH, HCl, H_3PO_4, HNO_3, and NaOH	HDPE	450	78.7	The liquid fuel consisted of petroleum products range hydrocarbons (C_{10}–C_{25}).	[4]
Kaolin	LDPE	450	79.5	The oil consists of paraffins and olefins with a predominance of C_{10}–C_{16} components.	[5]
Kaolin	**LDPE**	**600**	**about 75**	**The first addition of kaolin gives aliphatic compounds and C_6–C_{20} aromatics (90–95%).**	[6]
75% kaolinite with 25% bentonite	**LDPE**	**580**	**74.45**	**High yield of paraffins (70.62%). The percentage of aromatics was 5.27%.**	[7]
China clay (kaolinite)	LDPE	300	84	Components with a boiling point of 125–	[8]

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
				180°C were identified as alkanes, alkenes, and aromatics.	
Kaolin	**LDPE**	**450**	**99.82**	**The highest percentage component is heptane.**	[9]
Al-substituted Keggin tungstoborate/kaolin composite	**LDPE**	**295**	**84**	**During the catalytic cracking 70 mol.% of gasoline range hydrocarbons were produced.**	[10]
tungstophosphoric acid/kaolin composite	**LDPE**	**335**	**81**	**A high content of benzene-like hydrocarbons (C_{11}–C_{14}).**	[11]
Ahoko kaolin	**PP**	**450**	**79.85**	**Liquid products with properties comparable to conventional fuels (gasoline and diesel).**	[12]
Hydrochloric acid/kaolin composite	PP	470	71.9	The condensable hydrocarbons contain dominantly	[13]

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
				alkanes and alkenes in the range C_6–C_{12}.	
Commercial-grade kaolin clay	PP	450	89.5	Contains olefins, aliphatic, and aromatic hydrocarbons in the oil comparable with liquid fossil fuels.	[14]
Commercial-grade kaolin clay and kaolin treated with sulfuric acid	PP	500	92 (acid-treated), 87.5 (neat kaolin)	The oil from the neat kaolin—C_{10}–C_{18} products, from the acid-treated kaolin—mainly C_9–C_{13}.	[15]
Kaolin	PP	500	87.5	Fuel properties are identical to the different petroleum fuels.	[16]
Neat kaolin and kaolin treated with hydrochloric acid	PP	400–500	71.9	The highest yield of liquid hydrocarbons was achieved with kaolin clay treated with 3M HCl.	[17]
Kaolin	PP/vaseline (4.0 wt%)	520	52.5	The gasoline—32.77%, diesel—13.59%, residue—6.14%	[18]

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
CuO/kaolin and neat kaolin	**PS**	**450**	**96.37 (neat kaolin), 92.48 (CuO/kaolin)**	**The oil contained aromatic hydrocarbons, but from CuO/kaolin—85% $C_{10}H_8$ and ~13% C_8H_8.**	[19]
Zeolite-Y + metakaolin + aluminum hydroxide + sodium silicate all synthesized from kaolin	**HDPE + LDPE + PP + PS + PET**	**350**	**46.7**	**Catalyzed fuel samples consist of 93% gasoline and 7% diesel fraction.**	[20]
Kaolin	**Virgin HDPE, HDPE waste and mixed plastic waste**	**425**	**79**	**The catalyst was the most selective in producing diesel, which yielded 63%.**	[21]
Halloysite treated with hydrochloric acid	PS	450	90.2	Aromatic compounds of more than 99%. The main product is styrene (58.82%).	[22]

8. Khan, K.; Hussain, Z. Comparison of the Catalytic Activity of the Commercially Available Clays for the Conversion of Waste Polyethylene into Fuel Products. J. Chem. Soc. Pakistan 2011, 33, 956–959.
9. Erawati, E.; Hamid; Martenda, D. Kinetic Study on the Pyrolysis of Low-Density Polyethylene (LDPE) Waste Using Kaolin as Catalyst. IOP Conf. Ser. Mater. Sci. Eng. 2020, 778, 012071.
10. Attique, S.; Batool, M.; Yaqub, M.; Goerke, O.; Gregory, D.H.; Shah, A.T. Highly Efficient Catalytic Pyrolysis of Polyethylene Waste to Derive Fuel Products by Novel Polyoxometalate/Kaolin Composites. Waste Manag. Res. 2020, 38, 689–695.
11. Attique, S.; Batool, M.; Jalees, M.I.; Shehzad, K.; Farooq, U.; Khan, Z.; Ashraf, F.; Shah, A.T. Highly Efficient Catalytic Degradation of Low-Density Polyethylene Using a Novel Tungstophosphoric Acid/Kaolin Clay Composite Catalyst. Turkish J. Chem. 2018, 42, 684–693.

4. Smectite Group Catalytic Activity

Members of the smectite group include the dioctahedral minerals (montmorillonite, beidellite, and nontronite) and the trioctahedral minerals (hectorite, saponite, and sauconite). The basic structural unit of these clay minerals is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet [23]. The clay consisting mostly of montmorillonite is called bentonite, but in commerce, this term can be used in a more general way to refer to any swelling clay composed mostly of minerals from the smectite group.

The bentonite- and montmorillonite-based catalysts are the most commonly applied besides smectite catalysts for plastic transformation. There are a few articles devoted to the use of saponite and beidellite. All results from the work on smectite clay catalysts are presented in **Table 2**.

12. Hakeem, I.G.; Aberuagba, F.; Musa, U. Catalytic Pyrolysis of Waste Polypropylene Using Ahoko Kaolin from Nigeria. Appl. Petrochem. Res. 2018, 8, 203–210.

13. Uzair, M.A.; Waqas, A.; Khoja, A.H.; Ahmed, N. Experimental Study of Catalytic Degradation of Polypropylene by Acid-Activated Clay and Performance of Ni as a Promoter. Energy Sources Part A Recover. Util. Environ. Eff. 2016, 38, 3618–3624.

Table 2. Publications on the conversion of different plastics over clay minerals from smectite group catalysts.

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
Bentonite (50 wt%)/spent fluid catalytic cracking catalyst (FCC)	HDPE	500	100	High yields of gasoline C_5–C_{11} (50 wt%) The yield of C_{12}–C_{20} hydrocarbons—8–10 wt%.	[24]
Pillared bentonite (PILC) intercalated with Fe or Al	**HDPE and heavy gas oil (HGO)**	**500**	**>80**	**The oil from the Fe-PILC-Fe-300 catalyst was more similar to the standard diesel.**	[25]
Bentonite (Gachi clay)	LDPE	300	77	Olefin and paraffin hydrocarbons.	[26]
South Asian clay classified as bentonite andmontmorillonite impregnated with nickel NPs	**LDPE and post-consumer polybags**	**350**	**79.23 (LDPE), 76.01 (poly-bags)**	**The final products are in the range of gasoline, kerosene, and diesel.**	[27]
Bentonite thin layer loaded with MnO_2 nanoparticles (NPs)	**PP**	**750**	**Parameters were designed to get off the liquid**	**The complete decomposition of plastics with the formation of**	[28]

Catalyst in a Conical Spouted Bed. Ind. Eng. Chem. Res. 2012, 51, 14008–14017.

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
				gases (methane and hydrogen) and coke.	
Bentonite treated with 0.5M hydrochloric acid	PS	400	88.78	The obtained liquid contains styrene. Toluene and benzene were the major components.	[29]
Acid-washed bentonite clay (AWBC), Zn/AWBC, Ni/AWBC, Co/AWBC, Fe/AWBC, Mn/AWBC	PP, HDPE	300 for PP and 350 for HDPE	AWBC (PP 68.77, HDPE 70.19), Ni/AWBC (PP 92.76, HDPE 62.07), Co/AWBC (PP 82.8, HDPE 69.31), Fe/AWBC (PP 82.78, HDPE 71.34), Mn/AWBC (PP 80.4, HDPE 81.07), Zn/AWBC (PP 82.50, HDPE 91)	Co/AWBC/PP (mainly olefins and naphthenes) and Zn/AWBC/HDPE (mainly paraffins and olefins) were the most effective.	[30]
H_2SO_4-activated bentonite (synthesized)	PP + HDPE	328	79	The hydrocarbon oil.	[31]
A mixture of nature bentonite and zeolite (70:30)	PP, PET	400	78.42 (PP), 72.38 (PP + PET)	The number of C_3–C_{10} compounds increased.	[32]

37. Olivera, M.; Musso, M.; De León, A.; Volonterio, E.; Amaya, A.; Tancredi, N.; Bussi, J. Catalytic Assessment of Solid Materials for the Pyrolytic Conversion of Low-Density Polyethylene into Fuels. Heliyon 2020, 6, e05080.

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
Pelletized bentonite	**PS, PP, LDPE, HDPE**	**500**	**88.5 (PS), 90.5 (PP), 87.6 (LDPE), 88.9 (HDPE)**	**PS—95% aromatic hydrocarbons; PP, LDPE, and HDPE—aliphatic hydrocarbons; LDPE, and HDPE—diesel fuel (96% similarity); PS—gasohol 91.**	[33]
Calcium bentonite	**PP, LDPE, HDPE, PP + LDPE + HDPE**	**500**	**88.5 (PP), 82 (LDPE), 82.5 (HDPE) 81 (PP + LDPE + HDPE)**	**The oil contained only a mixture of hydrocarbons and has matching fuel properties as that of fossil fuel. Mixed plastics—C_{10}-C_{28}.**	[34]
Pillared bentonite (Al-PILC, Fe-PILC, Ti-PILC, Zr-PILC)	**HDPE + PS + PP + PET**	**300–500**	**68.2 (Al-PILC), 79.3 (Fe-PILC), 62.8 (Ti-PILC), 62.1 (Zr-PILC)**	**80.5% diesel fraction was observed in presence of Fe-PILC.**	[1]
Fe/Al pillared montmorillonite mixed with an acid Commercial bentonite as a binder	**HDPE**	**600**	**About 40**	**The catalyst gave high yields of waxes, particularly rich in diesel hydrocarbon range (C_{11}–C_{21}).**	[35]

50. Hussain, Z., Khan, K., Jan, M., Shah, J. Conversion of Low Density Polyethylene into Fuel Products Using Indian Fuller's Earth as Catalyst. J. Chem. Soc. Pak. 2010, 32, 790–793.

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
commercial acid-restructured montmorillonite and Al- and Fe/Al-pillared derivative	MDPE	300	About 70	The clay-based catalysts gave higher yields of liquid products in the C_{15}–C_{20} range. Clay catalysts produce liquid hydrocarbons in the gasoline and diesel range.	[36]
Al_2O_3-pillared montmorillonite (calcium rich)	**LDPE**	**430**	**70.2**	**Hydrocarbons from C_5 to C_{13}.**	[37]
Montmorillonite (Zenith-N) and a pillared derivative	LDPE	427	68 (montmorillonite), 75 (pillared derivative)	Clays showed enhanced liquid formation due to their mild acidity.	[38]
Al-pillared montmorillonite (Al-PILC), and regenerated samples	LDPE	360	72 (Al-PILC), 68 (regenerated sample)	These products were in the boiling point range of motor engine fuels.	[39]
Montmorillonite (Zenith-N) and a pillared derivative	LDPE	360	75 (montmorillonite), 76 (pillared derivative)	These products were in the boiling point range of gasoline.	[40]
Ionically bonding macrocyclic Zr-Zr	PP	300–400	-	A low molecular weight waxy	[41]

5 upported
a-Pac. J.
5 f Liquid
5 alyst in
5 astic
5 on
ecovery
5 n

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
complex to montmorillonite				product with paraffin wax characteristics was obtained.	
Untreated and Al-pillared montmorillonite clay	PS	400	83.2 (untreated clay), 81.6 (Al-pillared clay)	Styrene was the major product, and ethylbenzene was the second most abundant one in the liquid product.	[42]
Four different types of montmorillonites: K5, K10, K20, K30	LDPE, PP, and the municipal waste plastics	begins at 250 for mK5 (LDPE), 210–435 for mK20 (PP)	Data not presented	The catalytic degradation products contain a relatively narrow distribution of light hydrocarbons.	[43]
Organically modified montmorillonite/Co_3O_4	PP + HDPE + PS	700	59.6	The catalyst promoted the degradation of mixed plastics into light hydrocarbons and aromatics.	[44]
cloisite 15 A as a natural montmorillonite modified with a quaternary ammonium salt	**Industrial grade of HDPE, which was a copolymer with 1-hexene (1.5**	**473.7**	**Data not presented**	**It was found that the nano clay reduces the temperature at a maximum degradation rate.**	[45]

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
	wt%) as comonomer				
Commercial acid-restructured saponite and Al- and Fe/Al-pillared derivatives	MDPE	300	About 70	The clay-based catalysts gave higher yields of liquid products in the C_{15}–C_{20} range. Clay catalysts produce liquid hydrocarbons in the gasoline and diesel range.	[36]
Saponite, with a small number of impurities, mainly sepiolite and a pillared derivative	LDPE	427	83 (saponite), 82 (coked pillared derivative)	Clays showed enhanced liquid formation due to their mild acidity.	[38]
Al-pillared saponite and regenerated samples	LDPE	360	72 (pillared saponite), 67 (regenerated sample)	These products were in the boiling point range of motor engine fuels.	[39]
Saponite and a pillared derivative	LDPE	360	68 (saponite), 72 (pillared derivative)	These products were in the boiling point range of gasoline.	[40]
Commercial acid-restructured beidellite	MDPE	300	About 70	The clay-based catalysts gave higher yields of	[36]

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
and Al- and Fe/Al-pillared derivatives				liquid products in the C_{15}–C_{20} range. The catalysts produce liquid hydrocarbons in the gasoline and diesel range.	

5. Other Clay Minerals' Catalytic Activity

The variety of clay minerals is not limited to the above-mentioned two groups. Only a few examples of studying the catalytic activity of other clay minerals (sepiolite, vermiculite, talc, and pyrophyllite) in relation to plastics were found (**Table 3**).

Table 3. Publications on the conversion of different plastics over sepiolite, talc, pyrophyllite, and vermiculite catalysts.

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
Commercial sepiolite	PE, PP, PS, EVA	432.65 (PE), 401.65 (PP), 449.75 (PS), 459.85 (EVA)	Data not presented	Clay reduces the decomposition temperatures of PE and PP. However, steric effects associated with the PS and EVA substituents nullify this catalytic behavior.	[46]
Tetraethyl silicate modified vermiculite, Co, and Ni	**PP + PE**	**300-480**	**80.6 (organic vermiculite), 73.2 (Co/verm), 70.7 (Ni/verm), 73.9 (Co/Ni/verm)**	**The obtained liquid is mainly composed of C_9–C_{12} and C_{13}–C_{20}.**	[47]

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
intercalated vermiculite					
Talc (French chalk)	LDPE	300	91	Components with a boiling point of 125–180°C were identified as alkanes, alkenes, and aromatics.	[8]
Talc (plastic filler)	**PP**	**620**	**About 23**	**The liquid product contained a higher aromatic content (57.9%) and a lower n-alkene content (5.8%).**	[48]
Pyrophyllite treated with hydrochloric acid	PS	450	88.3	The catalysts showed selectivity to aromatics over 99%. Styrene (63.40%) is the major product, and ethylbenzene is the second-most abundant one (6.93%).	[22]

6. Catalytic Activity of Mixed Natural Clays

Some works were focused on uncharacterized mixed clays from different fields (**Table 4**).

Table 4. Publications on the conversion of different plastics over clays from different fields.

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
Acid-activated fire clay	**HDPE**	**450**	**41.4**	**The identified compounds were mainly paraffins and**	[49]

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
(Pradeep Enterprises, Ajmeri Gate, Delhi)				**olefins with a carbon number range of C_6–C_{18}.**	
Indian Fuller's earth (Multan clay)	LDPE	300	58.33	The obtained liquid contained olefin, paraffin, and aromatic hydrocarbons. Light naphtha—15%, heavy naphtha—35%, middle distillate—60%.	[50]
Fuller's earth	LDPE	300	91	Components with a boiling point of 125-180°C were identified as alkanes, alkenes, and aromatics.	[8]
Natural clay mineral (Indonesia) with $LaFeO_3$ NPs	**PP**	**460–480**	**88.8 (5th cycle)**	**The liquid fraction: alkanes (44.70%), alkenes (34.84%), cyclo-alkanes (9.87%), cyclo-alkenes (3.07), branched-chain alkanes (2.42%), branched-chain alkenes (0.88%).**	[51]
natural clay with kaolinite, hematite, smectite, quartz	**PS**	**410**	**86.68**	**Fuel properties of the liquid fraction obtained showed a good resemblance with gasoline and diesel oil.**	[52]
Red clay (Auburn, Alabama, USA)	**PS and LDPE (co-pyrolysis**	**500, 600, 700, 800**	**data not presented**	**The carbon yield of a lignin-derived compound, guaiacol, increased during co-pyrolysis of lignin with**	[53]

Catalyst	Plastic	Temperature, °C	Highest Liquid Yield, wt%	Specific Results	Reference
	with a lignin)			**LDPE, and PS with red clay as a catalyst.**	
Shwedaung clay, Mabisan clay	HDPE + LDPE + PS + PP + PET	210-380	65.81 (Shwedaung clay), 67.06 (Mabisan clay)	Fuel can be used internal combustion engine after distillation. Char can be used as solid fuel.	[54]
Fe-restructured clay (Fe-RC)	**PE + PP + PS + PVC + PET**	**450**	**83.73**	**High selectivity for the C_9–C_{12} and C_{13}–C_{19} oil fractions, which are the major constituents of kerosene and diesel fuel.**	[55]
Romanian natural clays: Vadu Crişului clay and Lugoj clay	PS + PET + PVC	420	62.18 (Vadu Crişului clay), 54.98 (Lugoj clay)	The liquid products contained monoaromatic compounds such as styrene, toluene, ethylbenzene, or alpha-methylstyrene.	[56]