

Catalytic pyrolysis of LDPE plastic wastes over mortar cement catalyst

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Abstract. A CaO based catalyst synthesized from mortar previously used in construction was chosen for pyrolysis of LDPE plastic waste. The samples were calcined at temperatures of 500 and 800 °C for comparison purpose. After calcination, two mixed oxides were obtained, denoted as catalyst A and B. The chemical composition of the metal oxide catalysts and the liquid products of the pyrolysis were characterized by X-ray Fluorescence (XRF) and Simulated Distillation - Gas Chromatography (SD-GC), respectively. The XRF analysis indicated that the catalyst, reformed from the mortar cement, consisted of CaO, silica (silicon dioxide, SiO₂) and alumina (aluminium (III) oxide, Al₂O₃) as the main constituents, though, the composition of each compound differed because of the influence of calcination temperature. Catalyst A had 41.96% of CaO, 4.27% of Al₂O₃ and 30.82% of SiO₂ when the catalyst B had 37.04% of CaO, 2.38% of Al₂O₃ and 37.31% of SiO₂. The amount of CaO in the catalyst B was found to be less in catalyst A. The catalyst A gave higher percentage yield of naphtha oil (48±1.14%v/v), compared to catalyst B (21±1.26%v/v). The performance of this catalyst (A) towards the pyrolysis of plastic wastes was compared to commercial grade ZSM-5 and FCC catalysts. It was found that the catalyst A, CaO based catalyst, reformed from the mortar cement, gave the highest yield of naphtha oil (48±1.14%v/v) compared to ZSM-5 (26±1.52%v/v) and FCC (16±1.09%v/v). The optimum operating temperature for the pyrolysis was found at 410 °C (in the temperature range 370 °C to 450 °C) and the optimum catalyst (A) composition was 0.3 %w/w of mortar cement catalyst in LDPE. This optimum condition gave 86.67± 0 %w/w of liquid, 12.49± 0.24 %w/w of gas and 0.84± 0.24 %w/w of solid. The catalyst A showed the best performance amongst all the catalysts towards the pyrolysis process of plastic wastes.

1. Introduction

The total plastic wastes volume in 2011 was reported to be 1.84 million tons/day in Thailand. [1]. The plastic wastes are forecast to grow to around 2.6 million tons/years by 2016. Currently, plastic wastes are disposed of by combustion, landfill, recycle, reuse and pyrolysis. In Thailand, less than 500 million tons/years of municipal plastic waste was reused and recycled in 2011, 61% of it was openly dumped, 37% went to landfilling and 2% was used in municipal incineration projects.

Pyrolysis is the thermochemical decomposition of organic materials at high temperature without oxygen. The pyrolysis can be carried out with or without catalyst. Plastic wastes were reported to be pyrolysed to liquid fuels under high ranges of temperature (350 °C to 400 °C) [2] over various catalysts such as Y-zeolite or zeolite ZSM-5 catalyst [3], CaC₂ catalyst [4], CaO [5], HZSM-5 [6]. The catalyst properties (pore size, acidity, basicity and types) and reaction parameters (operating temperature, retention time and quantity of the catalyst) are reported to influence the types the liquid hydrocarbon compounds produced [7].

Zeolite Socony Mobil (ZSM-5) was reported to be a promising catalyst for plastic wastes conversion to fuels [3, 8-9]. Fluid Catalytic Cracking (FCC) catalyst is also well-known for petroleum production processes. The FCC catalyst basically has the same chemical formula as the ZSM-5 but with different composition, 40.17 % wt SiO₂, 46.15 %wt Al₂O₃, 0.22 %wt Na₂O and 0.35 %wt CaO [10]. From previous work [10], the yield of naphtha oil produced via the pyrolysis of LDPE over the FCC catalyst was reported to be relatively low [10] (16±1.09%v/v). Recent work by Z. Tingyu and et al, have reported that the key compound that helps catalyzing the pyrolysis

reaction is CaO [5]. In this work, mortar cement was chosen, as a CaCO_3 rich-source, to be a raw material for producing CaO catalyst substitute.

In this work, samples of mortar were removed from local buildings. This mortar is composed of sand (SiO_2 , in quartz form), lime (CaCO_3 and Ca(OH)_2), and water. This research focuses on use of waste mortar as a potential CaO based-catalyst for pyrolysis process of plastic wastes to liquid hydrocarbons.

2. Materials and Methods

2.1 Materials

The CaO from mortar cement catalyst, prepared at the Laboratory of chemistry department, Chandrakasem Rajabhat University was calcined at 500 and 800 °C and grounded. The commercial grade ZSM-5 and FCC catalysts were supplied from Xusen, China. Some of ZSM-5 and FCC properties are displayed in Table 1. 99.99% nitrogen gas was used as a carrier and introduced to the reactor at 1 liter.min⁻¹.

Table 1 Characteristics of the ZSM-5 and FCC catalysts

Catalyst property	ZSM-5	FCC
Particle size (μm)	≤ 6 μm	0-40 μm (14.8%), 0-149 μm (85.2)
Pore size (nm)	2-3	-
Pore volume (ml/g)	≥ 0.17	0.34
Surface area (m ² /g)	≥ 340	298

2.2 Methods

2.2.1 Pyrolysis reactor

The pyrolysis reactor's design and fabrication were described elsewhere [10]. The electrical furnace can produce a maximum temperature of 800 °C. The reactor was 322 mm in length and 20 mm in diameter. Thermocouples were inserted into three different locations of the reactor as shown below.

2.2.2 Preparation and characterization of mortar catalyst

The mortar samples were calcined at 500 °C and 800 °C to give CaO based catalysts named as catalyst A and B, respectively. The ground mortar catalysts chemical composition and morphology were characterized by X-ray fluorescence (XRF) and Scanning Electron Microscope (SEM) to investigate the catalyst's chemical composition and morphology.

2.2.3 Determining optimum catalyst quantity and operating conditions for naphtha yield?

30 g of low density polyethylene (LDPE) was used as feedstock and mixed with catalyst of weight ratios at 0.1, 0.3, 0.5 and 1 %w/w. Nitrogen carrier gas was introduced into the reactor at 1 Liters min⁻¹. The reaction was carried out at temperatures of 370, 390, 410 and 450 °C under atmospheric pressure for 3 hours. The liquid and condensable gaseous-products were collected in a glass vessel in a cooling bath (containing 70% ethylene glycol) at -20 °C. The products were then analyzed by Simulate Distillation-Gas Chromatography.

3. Results and discussions

3.1 Morphology and characteristic of mortar, ZSM-5 and FCC catalysts

The mortar generally consists of 1 part cement, 4 parts of rough sand, and 1.5 parts of lime and 10 liters of clean water [11]. 50 g of Mortar cement was calcined at 500 °C and 800 °C then pounded to produce fine particles. The morphology of the particles were observed by SEM techniques and shown in Figure 1. Figure 2 shows the SEM of catalyst calcined at 500 °C. The pore size of the mortar was measured as 116.85 nm. The chemical composition of the prepared mortar catalysts particles defined as catalysts A and B (calcined at 500 and 800 °C, respectively), were analyzed by X-ray Fluorescence (XRF). The composition of the catalysts was tabulated in Table 2. Catalyst B has less CaO than the catalyst A due to the decomposition of CaO which occurred at 800 °C [12].

The naphtha oil obtained from pyrolysis process catalysed by catalyst A gave a yield of 48±1.14%v/v. This is possibly because the polarity of the active site of calcium oxide can affect the p-electron cloud's stability of condensed aromatic compounds, and calcium oxide itself has an active cracking site on both inner and outer surfaces [5]. The amount of CaO in catalyst A and B are

quite similar, but the naphtha oil received from catalyst B was only $21 \pm 1.26\%v/v$. However, the level of SO_3 found in the catalyst B was quite high ($11.15\%v/v$). Therefore, it is possible that the SO_3 reacted with the CaO producing $CaSO_4$ [13]. This obviously reduced the amount of the reactive CaO resulting in less amount of the naphtha oil produced.

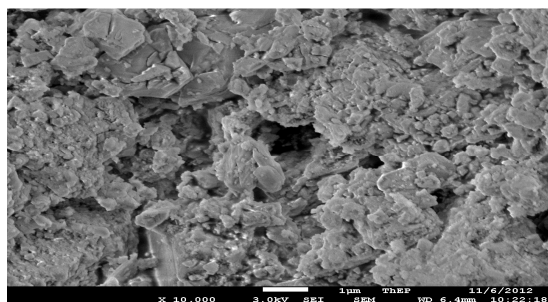


Fig. 1 Characteristic of mortar particles

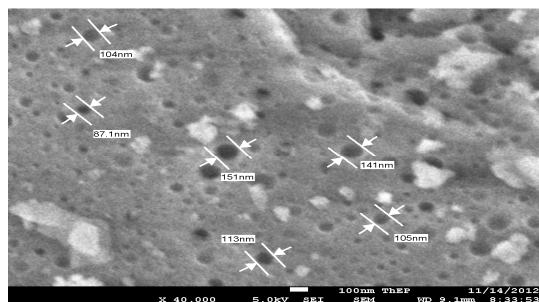


Fig. 2 Pore size of mortar catalyst at 500 °C

Table 2 Chemical Compositions of vary catalysts

Percent compositions					Percent compositions				
Compound	Mortar		ZSM-5	FCC	Compound	Mortar		ZSM-5	FCC
	500	800				500	800		
SiO ₂	30.82	37.31	96.23	40.1	MnO ₂	0.04	0.03	0	0
Al ₂ O ₃	4.27	2.38	3.41	46.1	Fe ₂ O ₃	2.15	1.64	0.14	0.74
CaO	41.96	37.04	0.04	0.35	ZnO	0.02	0	0	0
MgO	0.67	0	0	0	SrO	0.01	0.01	0	0
Na ₂ O	0.29	0	0.05	0.22	ZrO ₂	0.01	0.01	0.003	0
P ₂ O ₅	1.06	0	0	0.36	SnO ₂	0	0	0	0.04
SO ₃	1.63	11.15	0.04	2.61	La ₂ O ₃	0	0	0	3.07
Cl	0.12	0	0.03	1.31	Ce ₂ O ₃	0	0	0	4.33
K ₂ O	2.16	0.43	0.03	0.38	TiO ₂	0.19	0.21	0.034	0.30

3.2 Condition of pyrolysis with mortar catalyst

Quantity of the liquid and gaseous products (by weights) produced via the pyrolysis over catalyst A, at different weight of mortar cement, was categorized in Table 3 at 410 °C for 2 hours under N₂ atmosphere. 0.3% weight of catalyst (catalyst to feed) was suitable for the process as this condition produced the greatest amount of liquid and gas products. The less catalyst used will help reducing cost of production and also reduce the contamination of the produced fuel [14].

Table 3. Percent of products at vary percent weight of mortar cement catalyst at 410 °C for 2 hours

Plastic wastes	Type of catalyst	%weight of catalyst	Percent of products (by weights)		
			gas	liquid	solid
LDPE	A	0.1	50.81±2.26	48.44±2.12	0.75±0.01
		0.3	12.49±0.24	86.67±0.00	0.84±0.24
		0.5	57.24±3.21	42.22±3.21	0.54±0.10
		1	8.83 ± 1.00	90.00±1.00	1.17±0.07

Table 4 shows the percentage of the liquid and gaseous products (by weights) produced through the pyrolysis of LDPE over catalyst A, at different temperatures of pyrolysis. The reaction occurring under 410 °C gave the greatest quantity of liquid product ($86.67 \pm 0.00\%w/w$) as the liquid hydrocarbons started to be cracked to smaller molecules or lighter hydrocarbons [15]. At temperatures higher than 410 °C, the amounts of liquid products were decreased as they were converted to lighter hydrocarbons appearing in gas phase.

Table 4. Percent of products at vary temperature with mortar cement catalyst

Plastic waste	Type of catalyst	%weight of catalyst	Pyrolysis temperature (°C)	Percent of products (by weights)		
				gas	liquid	Solid
LDPE	A	0.3	370	36.58±0.46	32.22±0.29	31.2±0.30
			390	47.67±2.88	48.89±3.21	3.44±0.73
			410	12.49±0.24	86.67±0.00	0.84±0.24
			430	65.45±3.73	33.89±3.75	0.66±0.03
			450	63.77±2.22	35.56±2.25	0.67±0.04

Table 5 shows the yield of liquid fuel obtained from pyrolysis process catalysed by catalyst A was similar to the yield of liquid fuel with the catalyst B due to their similarity of the CaO content. The quantity of CaO is believed to have a strong effect on the catalyst's performance.

Table 5. Percent of products using catalyst A and B

Plastic waste	Type of catalyst	%weight of catalyst	Temperature (°C)	Percent of products (by weights)		
				gas	liquid	solid
LDPE	Mortar cement	0.3	500 (A)	12.49 ± 0.24	86.67 ± 0	0.84 ± 0.24
			800 (B)	21.16 ± 1.00	77.77 ± 1.15	1.07 ± 0.17

Table 6 shows percent of products which were produced from pyrolysis over different types of catalyst. Catalyst A showed the best performance towards the pyrolysis process amongst ZSM-5 and FCC because it has higher level of CaO. Also, the different degree of CaO level may affect the catalyst's alkalinity which possibly causes the difference in liquid product selectivity [16].

Table 6. Comparison of percent of products at 410 °C using various types of catalyst

Plastic Waste	Type of Catalyst	% weight of catalyst	Percent of products (by weights)		
			Gas	Liquid	Solid
LDPE	A	1	8.83 ± 1.00	90.00 ± 1	1.17 ± 0.07
	ZSM-5		30.37 ± 4.08	66.73 ± 4.07	2.9 ± 1.22
	FCC		20.73 ± 1.15	73.33 ± 5.42	5.94 ± 2.95

3.3 Characterization of liquid fuel

Table 7 shows compositions of liquid fuels in pyrolysis processes using FCC catalyst, ZSM-5 catalyst and catalysts A and B. The catalyst A gave the highest yield of naphtha oil due to it having the largest amount of CaO which effected on the numbers of the catalyst's acid site. The lack of acid sites caused lower performance of the catalyst. In general, the catalyst's performance depends on the amount of acid sites, pore size and shape of catalyst [6].

Table 7. Compositions of liquid fuels in pyrolysis processes using FCC catalyst, ZSM-5 catalyst and catalysts A and B

Fuel Type	Range of distillation temperature	Percent of products (by volumes)			
		Mortar		ZSM-5	FCC
		at 500 °C (A)	at 800 °C (B)		
naphtha	< 200 °C	48±1.14	21±1.26	26±1.52	16±1.09
kerosene	200-250 °C	22±1.3	15±1.32	6.5±0.76	7±1.6
light gas oil	250-300 °C	14±0.54	19±1.02	20.5±0.5	22±2.03
heavy gas oil	300-370 °C	11±0.83	32±1.74	22±2.07	29±0.75
Residue (tar+catalyst)	> 370 °C	5± 1.48	13±0.74	25±1.5	26±1.72

The composition of the liquid product obtained from the pyrolysis process over catalyst A was determined using SD-GC. The result agreed with table 7 confirming that the liquid product from the process consists of naphtha oil, kerosene oil, light gas oil and heavy gas oil. Naphtha oil was found to be the main compound of the liquid product.

4. Summary

The optimum condition for pyrolysis of LDPE was found to be at 410 °C under atmospheric pressure using 0.3% wt of the catalyst (to feed) produced from mortar calcined at 500 °C (named as catalyst A) giving $48 \pm 1.14\%$ of naphtha oil. Catalyst A has higher quantity of CaO as it was calcined at lower temperature (compared to Catalyst B, calcined at 800 °C). Catalyst A has more CaO content compared with ZSM-5 and FCC. CaO caused reduction of the catalyst's acidity, therefore, reducing the ability of the catalyst to crack hydrocarbons. This inhibits conversion of liquid product to gas product resulting in higher amount of naphtha oil.

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