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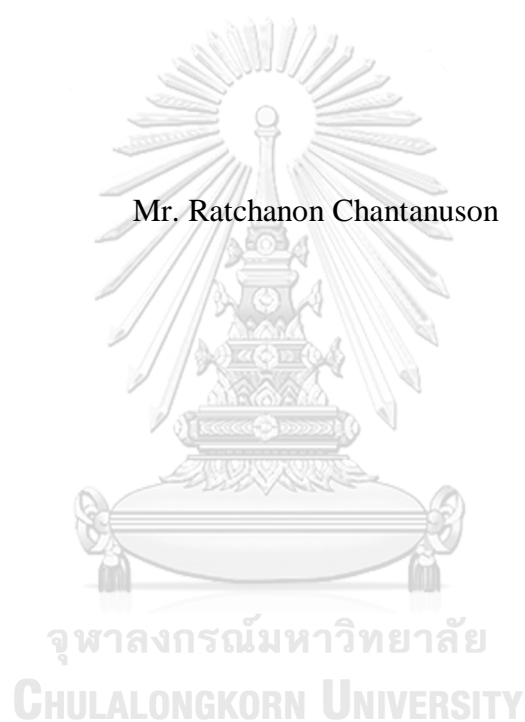
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A study of catalyst type and dispersion on pyrolysis of high density polyethylene

Mr. Ratchanon Chantanuson



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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การศึกษาผลของชนิดและการกระจายตัวของตัวเร่งปฏิกิริยาต่อการแยกสลายด้วยความร้อนของพอลิเอทิลีนความหนาแน่นสูงทำการทดลองในระบบปฏิกรณ์แบบกะและแบบกึ่งกะ โดยระบบการแยกผลิตภัณฑ์ในระบบแบบกึ่งกะจะเป็นการแยกสารในขณะที่เก็บผลิตภัณฑ์ทันที ระบบปฏิกรณ์แบบกะจะเก็บผลิตภัณฑ์ทั้งหมดหลังจากการระบายความร้อน น้ำมันที่ได้จากระบบแบบกึ่งกะมีปริมาณของสารไฮโดรคาร์บอนสายสั้นมากกว่าในระบบปฏิกรณ์แบบกะ เนื่องจากความดันที่เพิ่มขึ้นและความรุนแรงสูงในระบบปฏิกรณ์แบบกะอาจทำให้เกิดปฏิกิริยาข้างเคียงขึ้น ตัวเร่งปฏิกิริยาที่ใช้ในการศึกษามี 2 ชนิด คือ ตัวเร่งปฏิกิริยา Cat A เป็นตัวเร่งปฏิกิริยาที่มีความเป็นกรดมีพื้นที่ผิว 200 ตารางเมตรต่อกรัมและรูพรุนขนาด 20 อังสตรอม ตัวเร่งปฏิกิริยาซีโอไลต์ชนิด HZSM-5 มีความเป็นกรดโดยรวมมากกว่า มีพื้นที่ผิว 550 ตารางเมตรต่อกรัมและรูพรุนขนาด 7 อังสตรอม โดยตัวเร่งปฏิกิริยาซีโอไลต์ชนิด HZSM-5 จะมีอุณหภูมิในการทำปฏิกิริยาต่ำที่สุดที่ประมาณ 400 องศาเซลเซียสและมีปริมาณของผลิตภัณฑ์ที่เป็นแก๊สมากที่สุดเนื่องจากดูดพลังงานไปใช้ในการแยกสลายพันธะไฮโดรคาร์บอน ตัวเร่งปฏิกิริยา Cat A ได้ผลิตภัณฑ์หลักเป็นแนฟทาถ้าทำปฏิกิริยาโดยไม่มีตัวเร่งปฏิกิริยาจะได้ผลิตภัณฑ์ที่มีไฮโดรคาร์บอนตัวหนัก เช่น แวกซ์ และดีเซล เป็นส่วนประกอบจำนวนมากว่าการใช้ตัวเร่งปฏิกิริยา เนื่องจากเกิดการแยกสลายน้อยกว่า อุณหภูมิที่ทำปฏิกิริยาการแยกสลายด้วยความร้อนโดยไม่มีตัวเร่งปฏิกิริยาและใช้ Cat A เป็นตัวเร่งจะมีค่าใกล้เคียงกันที่ 430 องศาเซลเซียส เนื่องจากมีอัตราการแยกสลายที่ต่ำกว่า โดยตัวเร่งปฏิกิริยาซีโอไลต์ชนิด HZSM-5 จะเป็นตัวเร่งปฏิกิริยาที่มีความเป็นกรดสูงทำให้เกิดอัตราการแยกสลายมากและผลิตผลิตภัณฑ์ที่เป็นแก๊สมาก การกระจายตัวของตัวเร่งปฏิกิริยาโดยการผสมเข้าไปในเนื้อพลาสติกในขณะที่ขึ้นรูปได้ผลของของอัตราการทำปฏิกิริยาของตัวเร่งปฏิกิริยาสูงที่สุด โดยจะมากกว่าการใช้การปั่นกวนในขณะที่ทำปฏิกิริยาเพราะสถานะกึ่งของแข็งคล้ายขี้ผึ้งก่อนที่จะเกิดน้ำมันในช่วงแรกของการทำปฏิกิริยาจะทำให้การกระจายตัวของตัวเร่งปฏิกิริยาขากขึ้น อย่างไรก็ตามเมื่อเพิ่มผลของการกระจายตัวของตัวเร่งปฏิกิริยาในขณะที่ขึ้นรูปจะทำให้ผลของการแยกสลายดีขึ้นทั้งจากในการใช้ตัวเร่งปฏิกิริยาซีโอไลต์ชนิด HZSM-5 และ ตัวเร่งปฏิกิริยา Cat A

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RATCHANON CHANTANUSON: A study of catalyst type and dispersion on pyrolysis of high density polyethylene. ADVISOR: ASST. PROF. APINAN SOOTTITANTAWAT, D.Eng., pp.

The study of catalyst type and dispersion on pyrolysis of high density polyethylene (HDPE) was investigated in batch and semi-batch reactor system. The separation system in semi-batch was rapidly separated between oil and gas products while in batch system was separated after cooling down process. The obtained oil products in semi-batch system had higher in short-chain hydrocarbon. Because the increased pressure and the high severity in batch system led to occur side reactions. Two types of catalyst were studied, Cat A was acid catalyst with 200 m²/g surface area and 20 Å average pore diameter and HZSM-5 zeolite was stronger acid catalyst with 550 m²/g surface area and 7 Å average pore diameter. The catalytic pyrolysis of HZSM-5 zeolite had lower reaction temperature around 400 °C and produced higher gas yield. These lower temperatures come from high consumed heat for cracking HDPE to gas products. Cat A catalyst was obtained naphtha as main product. The thermal pyrolysis of HDPE was obtained higher in heavy hydrocarbon products such as wax and diesel from lower rate of cracking reaction. The thermal pyrolysis and catalytic pyrolysis of Cat A had the reaction temperature around 430 °C because lower rate of cracking reaction. The higher acidity of HZSM-5 led to higher rate of cracking reaction and produce higher gas yield products than Cat A. For dispersion of catalyst in HDPE, the extruded plastic with catalyst shows the highest activity of catalyst than mixing with impeller because waxy state before oil formation in pyrolysis of HDPE was difficult to make the dispersion. The increased dispersion of catalyst was higher rate of cracking reaction. This result was obtained in both Cat A and HZSM-5 zeolite.

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CHAPTER 1 INTRODUCTION

1.1 Motivation for this research

Municipal solid waste (MSW) is waste in a solid form that produced in daily life from households and non-hazardous solid waste from commercial, industrial and institutional establishments including hospitals, markets, yard and street. In 2015, the amounts of generated waste in Thailand were around 26.19 million tons. The trend in waste generation is increasing each year. Rapid expansion of industry, urbanization and increasing population have intensely increased the amount of MSW generated in Thailand. However, the rate of material recovery from MSW in Thailand is still low, only 18.4% of MSW in 2014. MSW management is a major concern in Thailand. The composition of MSW in Thailand consists of kitchen waste or organic waste (51%), plastic and foam (22%), paper (13%), and glass (3%). (Pharino 2017) The amount of plastic wastes produced is growing year by year. There are six main plastics occurring in MSW, high density polyethylene (HDPE); low density polyethylene (LDPE); Polypropylene (PP); polyvinyl chloride (PVC); polystyrene (PS) and polyethylene terephthalate (PET). Moreover, the polyethylene plastics, HDPE and LDPE, were above 40% of the total plastic content of MSW. The waste increasing from the expanding use of plastics is enormous. Only a small percentage is recycled while the large majority of waste management is landfilled or incinerated. (Mastral, Esperanza et al. 2002)

The recycled methods for generate energy or value-added products such as pyrolysis, anaerobic digestion, incineration and refuse derived fuel have been developed as shown in table 1. Landfilling requires large space for using. Incineration may lead to release of toxic and greenhouse gases and completely destroys the organic matter content of wastes. Pyrolysis is an alternative process for material recycling. This method can recycle a lot of plastic wastes and produce oil fuel and petrochemical products. The advantages of pyrolysis process are recovery 80% energy from waste, reduction land requirements for landfilled, products have high calorific values, liquid products easily separated from vapor phase and reduction of waste volume 50 - 90%. The limitations are low yields of liquid products, coke formation, byproducts cleaning, corrosion of metal tubes used in pyrolysis and high operating and maintenance cost. (Ouda, Raza et al. 2016) This process consumes large amounts of energy due to the low thermal conductivity of polyolefins with the endothermic nature of thermal pyrolysis. (Olazar, Lopez et al. 2009)

Table 1 Advantages and disadvantages of waste management methods. (Ouda, Raza et al. 2016, Sadef, Nizami et al. 2016)

Method	Advantages	Disadvantages
Landfilling	<ul style="list-style-type: none"> ▪ Least cost/cheap option ▪ No skilled labor requirements ▪ Marshy land can be converted into useful land 	<ul style="list-style-type: none"> ▪ High space requirement ▪ Ground and groundwater contamination ▪ High transportation costs

Anaerobic digestion	<ul style="list-style-type: none"> ▪ Natural resources are returned to ground ▪ Low solid product ▪ High rate anaerobic composting with energy ▪ Nutrient rich digestate as an organic fertilizer ▪ Cost effective technology 	<ul style="list-style-type: none"> ▪ Greenhouse gases emissions ▪ Odor problems ▪ Space requirements ▪ Nonattractive at large scale ▪ Susceptibility to shocks and overloads ▪ Contain impurities
Refuse derived fuel (RDF)	<ul style="list-style-type: none"> ▪ RDF pellets have high calorific value ▪ Waste size reduction ▪ Convenient RDF pellets transportation 	<ul style="list-style-type: none"> ▪ Air pollution from power plants ▪ Ash formation and handling in power plant with RDF ▪ High net unit cost per ton ▪ Required waste separation ▪ Air and waterborne pollution ▪ Cancer forming chemical (dioxins) production ▪ High investment ▪ Social deprecation
Incineration	<ul style="list-style-type: none"> ▪ Waste volume reduction up to 80% ▪ Waste mass reduction up to 70% ▪ Larger waste amounts consumed ▪ Fast treatment 	<ul style="list-style-type: none"> ▪ High solid waste (slag) production ▪ Low liquid products yield ▪ Pyrolytic water production from organic matter ▪ Coke production ▪ By-products cleaning ▪ Corrosion of metal tubes in pyrolysis system ▪ High operating and maintenance cost
Pyrolysis	<ul style="list-style-type: none"> ▪ Recovery up to 80% energy from waste ▪ Reduces land requirements ▪ High calorific products ▪ Liquid products separation in vapor phase ▪ Volume Reduction up to 50-90% 	

Waxes and char residues were produced in pyrolysis process that is not considered economically interesting and is usually disposed off by landfilling. The pyrolysis of some type of wastes have a positive effect on the immobilization of heavy metals in solid residues. The specific surface area and the pore structure of char may be an effect for restraining metal leaching. The major metals content in the pyrolysis solid residues are Chromium (Cr), Nickel(Ni) and Zinc (Zn). (Bernardo, Lapa et al. 2009, Bernardo, Lapa et al. 2010) The landfilled of solid residues may contaminate the metals to soil and groundwater.

Therefore, catalytic pyrolysis was developed to improve efficiency and decrease the demerits of pyrolysis process. The use of catalyst can modify the process to produce a narrow distribution of hydrocarbons with higher valuable products and reduce the energy consumption for the process. The selection of catalyst in catalytic pyrolysis depends on raw materials and the desired products such as liquid oil, waxes and gases and their quality. In this thesis, HDPE were used in catalytic pyrolysis process of two different types of catalysts. HZSM-5 zeolite is the commercial catalyst which was used in many plastic waste pyrolysis process but it is expensive and higher acidity. (Sebestyén, Barta-Rajnai et al. 2017) CatA were used to compare because it cheaper, lower acidity and larger pore size than HZSM-5 zeolite. The strong acid solid catalyst and larger pore size lead to high yield of aromatic hydrocarbon and also when using higher catalyst/raw material ratio or longer residence times. The pore size influenced selectivity and Si/Al ratio influenced the number of catalytically active sites on the catalyst surface. (Miguel, Aguado et al. 2006) The higher pore size allows larger molecules to enter the catalyst and undergo catalytic reactions. (Bagri and Williams 2002) The lower pore size resulted in a lower production of aromatic compounds and the lower silica/alumina ratio, which has higher surface activity, resulted higher aromatic hydrocarbon content.(Williams and Brindle 2003) Preliminary studies have the results of products of these catalysts that are very effective catalysts for plastics cracking and lead to produce more gas and oil products and less of waxes and char residues compare with the others.

1.2 Objective

This thesis aims to investigate the effect of two acidic catalyst type and dispersion of catalyst in batch and semi-batch reactor on the conversion/selectivity and the product distribution in catalytic pyrolysis of HDPE.

1.3 Scope of this research

To achieve desired objective, the following scope of experimental work in catalytic pyrolysis of HDPE with two different types of catalysts (HZSM-5 zeolite and cat A) would be considered. Four operating variables will be investigated their effects on the conversion/selectivity and the product distribution.

- 1) Effect of catalysts which were HZSM-5 zeolite (pore size 7A) and Cat A (pore size 20A).
- 2) Effect of catalyst blending into HDPE while plastic molding process and pure HDPE adding catalyst before pyrolysis process with or without mixing.

CHAPTER 2 FUNDAMENTAL THEORY AND LITERATURE REVIEW

To investigate catalytic pyrolysis of HDPE with two different types of catalysts: HZSM-5 zeolite and Cat A, the knowledge and literature reviews are important. Therefore, literature reviews and knowledge of HDPE, pyrolysis products, HZSM-5 zeolite and Cat A are explained in this chapter.

2.1 High density polyethylene (HDPE)

Polyethylene is one of the world's most popular plastics. It has many of type that is generally classified by its density and branching. The most common and widely used polyethylene is Low Density Polyethylene (LDPE) and High-Density Polyethylene (HDPE). HDPE is much more crystalline, has a much higher density, and is often used in completely different circumstances than LDPE. HDPE has a lower degree of branching. The mostly linear molecules pack together well, so intermolecular forces are stronger than LDPE which has highly branched polymers. It is frequently used as a plastic for milk cartons, laundry detergent, water pipes, garbage bins and cutting boards. For the physical properties of HDPE, the density is 0.944 - 0.965 g/cm³, melting point is around 130 °C and tensile strength is 0.20 - 0.40 N/mm². The chemical formula is (C₂H₄)_n. (Product Data Sheet & General Processing Conditions of HDPE)

2.2 Pyrolysis products

The pyrolysis products were gases, oil and waxes. The waxes were obtained when the reactor is cooled down, are rich in aliphatic hydrocarbons up to C₃₀ and char of catalyst. The oil and gases were taken out by gas outlet valve and rapidly cooled down by cooling unit for prevention side reactions on the products. The main hydrocarbons in gas were ethylene, methane and propylene, the remaining products being oils with C₅₊ and aromatic hydrocarbon content. The results obtained showed the effect of operating parameters on the production and composition of gases, oil and waxes. The H₂, CH₄, N₂ and C₂ to C₄ were compounds on the gas product. The gas and oil product were analyzed by gas chromatography. (Mastral, Esperanza et al. 2002) The cracking reaction of HDPE was highly endothermic reaction. The heat of reaction for cracking HDPE to ethylene was around 108 kJ/mole of ethylene. From this reason, the pyrolysis reaction will consume a lot of energy for cracking reaction. (Roberts 1950)

2.3 HZSM-5 zeolite

The cation present in the zeolite structure was hydrogen (H-ZSM-5). HZSM-5 increases the volatility of the liquid products and enhances the formation of aromatic hydrocarbons. Moreover, HZSM-5 has very low rate of deactivation and is suitable for reuse. (Sebestyén, Barta-Rajnai et al. 2017) It widely uses in commercial pyrolysis process. The catalyst had average grain diameter 300 μm.

2.4 Cat A

Cat A is cheaper than HZSM-5 zeolite. The property of cat A is it had lower acidity and surface area but bigger pore size than HZSM-5 zeolite. The pore size is significant in determining the size of the reactants and products, which can enter and leave the active sites of the catalyst.

2.5 Literature reviews

2.5.1 Thermal pyrolysis

There were several researches represented that pyrolysis of plastic wastes to valuable products. Onwudili, et al. reported effects of temperature and residence time on composition of products from the thermal pyrolysis under nitrogen atmosphere of LDPE, polystyrene (PS) and their mixtures. LDPE, PS and mixtures (LDPE:PS = 7:3) were thermally degraded to oil at 425°C, 350°C and 400°C respectively and the formation of char and hydrocarbon gas increased when temperature was higher than these temperatures. The increasing residence time led to increase the proportion of light and aromatic compounds. (Onwudili, Insura et al. 2009) Conesa, et al. reported the result of thermal pyrolysis of HDPE in fluidized bed reactor. The yield of total gas obtained increased in the range 500°C - 800°C from 5.7% to 96.5%. At 800°C, the yield of total gas obtained was 94.5%, decreased slightly, with the main component of ethylene (37%), benzene (24%) and methane (20%). (Conesa, Font et al. 1994) Mastral, et al. reported the similar result from thermal pyrolysis of HDPE in a fluidized bed reactor. The highest gas yield was obtained at 780°C, 86.4 wt.% of gas and 9.6 wt.% of oil. (Mastral, Esperanza et al. 2002)

2.5.2 Catalytic pyrolysis

2.5.2.1 Effect of polymer type

For the effect of different polymer type of pyrolysis process, Marcilla, et al. studied the catalytic decomposition of PE over a solid catalyst (MCM-41). Three samples of LLDPE, LDPE and HDPE were used in experiments which have different branching degree (HDPE < LLDPE < LDPE). The result shown that no significant differences in the thermal decomposition process when catalyst is used. The decomposition temperature decreased 60-79°C when about 9% of catalyst MCM-41 is added. The catalyst had an affects to the decomposition temperature of LLDPE less than LDPE and HDPE. (Marcilla, Gómez et al. 2002) Kayacan, et al. studied thermal decomposition kinetic of raw and waste LDPE and HDPE using thermogravimetric analyzer. First-order decomposition reaction was assumed, the apparent activation energy and the kinetic parameters of HDPE were larger than the LDPE. The decomposition temperature of the samples increases, when the heating rate increases. (Kayacan and Doğan 2008) López, et al. investigated catalytic pyrolysis of three real plastic waste (film, paper and glass rich sample) in ZSM-5 zeolite. The result obtained catalytic pyrolysis with ZSM-5 that is a very effective catalyst for polyolefin rich samples cracking and increasing the C5-C9 fraction in pyrolysis oil and C3-C4 fraction rich gases. Table 3 show the yields highly vary depending on the sample pyrolysed. Film rich sample contained large amount of polyolefin that affected to obtain more liquid organic and gases than the others. Paper rich sample had a lot of moisture that affect to obtain large amount of aqueous phase in liquid products. (López, de Marco et al. 2011) Sebestyén, et al. studied thermo/HZSM-5 zeolite catalytic pyrolysis of biomass and plastic mixtures (PE, PP and PET). As the results, the HZSM-5 catalyst significantly decreased the decomposition temperature of hydrocarbon polymers but the catalyst effect was blocked when 50% cellulose or 10% lignin were mixed in the plastic waste. (Sebestyén, Barta-Rajnai et al. 2017) Miandad, et al. investigated catalytic pyrolysis of different types of plastic. Polystyrene (PS), polypropylene (PP),

polyethylene (PE) and their mixtures (PS/PE(1:1), PS/PP(1:1), PP/PE(1:1), PS/PP/PE(2:1:1) and PS/PP/PE/PET(2:1:1:1)) were used to catalytic pyrolysis in small pilot scale reactor at 450°C for 45 min. PS plastic waste had the highest liquid oil product yield compared with the other pure plastic waste as shown in figure 1. The liquid oil products mostly contained of aromatic hydrocarbons with a few aliphatic hydrocarbon compounds. The types of plastic had an effect in types and amounts of compounds obtained in liquid oils such as styrene, ethylbenzene, benzene, azulene, naphthalene, and toluene. (Miandad, Barakat et al. 2017)

Table 3 Composition of the samples and product yields.

Composition of samples (wt%)				
		Film rich	Paper rich	Glass rich
Mixed plastics		92.3	43.46	59.98
paper		2.8	33.25	4.19
glass		0.01	0.6	16.18
others		4.89	22.69	19.65
Pyrolysis yield (wt%)				
Liquids	Organic phase	41.5	25.5	39.2
	Aqueous phase	0	17.1	3.3
Gases		49.9	29.4	13.8
Solid	Inorganics	2.1	11.2	30.8
	Char	6.5	16.9	12.9

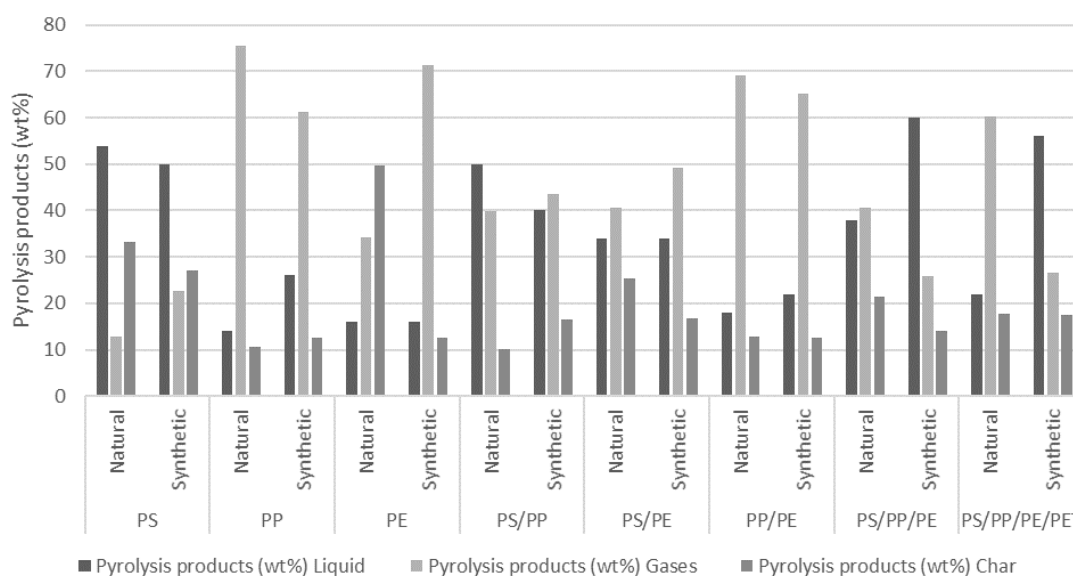


Figure 1 Products yield produced from catalytic pyrolysis of plastics with natural and synthetic zeolite catalysts. (Miandad, Barakat et al. 2017)

2.5.2.2 Effect of catalyst type

For the pyrolysis catalyst, table 4 shows characteristics of pyrolysis catalyst that usually uses in pyrolysis process. Zeolites are an important nonporous material for the chemical industry as heterogeneous catalysts with shape/size-selective character in various reactions due to its unique shape selectivity, solid acidity, ion exchangeability, pore size, thermal stability and structural network. (Yilmaz and Müller 2009) Ng, et al. explored conversion of polyethylene to transportation fuels by thermal pyrolysis (open - close system) in a tubing-bomb reactor and catalytic cracking (Y type USY zeolite) in a fixed-bed reactor. Products distribution of gases and naphtha were higher in the closed system. In contrast, the open system produced more gas oil. Waxes product from thermal pyrolysis were catalytically cracked at 470°C and 510°C in a fixed-bed reactor. The results were obtained high yield of improved quality gasoline and small amount of coke. (Ng, Seoud et al. 1995) Sharratt, et al. investigated catalytic pyrolysis of HDPE over silicalite/HZSM-5 catalyst in a laboratory fluidized-bed reactor. The silicalite contained very few or no active sites and gave lower conversion of polymer to volatile hydrocarbons than HZSM-5 under the same conditions. As the results, the used of HZSM-5 catalyst could reduce the required reaction temperature, improve the yield of volatile products, and provide selectivity in the product distributions. (Sharratt, Lin et al. 1997) Bagri, et al. investigated effect of Y-zeolite/zeolite ZSM-5 catalytic of the pyrolysis gases derived from the pyrolysis of LDPE. The Y-zeolite had a larger pore size and higher surface area compared to the ZSM-5 catalyst. The higher pore size allows larger molecules to enter the catalyst and undergo catalytic reactions. A fixed bed reactor was in 2 parts (a pyrolysis reactor and a catalyst reactor). LDPE was pyrolyzed in first reactor and the pyrolysis gases passed to a secondary reactor containing Y-zeolite or zeolite ZSM-5 catalyst. The Y-zeolite produced greater concentration of aromatic hydrocarbons in the derived oils than the zeolite ZSM-5 but the zeolite ZSM-5 gave higher gases content as shown in table 5. (Bagri and Williams

2002) Williams, et al. studied pyrolysis of scrap tires in a semi-continuous fluidized bed reactor that was connected series with a fixed bed of zeolite catalyst. Y- type and ZSM-5 zeolite catalysts, different pore size and surface activity, were examined at constant temperature 500 °C. The two catalysts produced similar concentration of single ring aromatic compounds in pyrolysis oil. (Williams and Brindle 2003) The another work of Williams, et al. was pyrolysis of scrap tyres in a fixed bed reactor that was connected with catalytic reactor. Three types of zeolite catalyst that different surface acidity and pore size were investigated to obtain maximise the concentration of single ring aromatic compounds. Three zeolite catalysts were used, Y-zeolite (CBV-400) of larger pore size (7.8 Å) and high acidity, Y-zeolite (CBV-780) of larger pore size (7.8 Å) and lower acidity and zeolite ZSM-5 of smaller pore size (5.6 Å) and lower acidity. The lower pore size resulted in a lower production of aromatic compounds and the lower silica/alumina ratio, therefore higher surface activity, resulted higher aromatic hydrocarbon content as shown table 6. (Williams and Brindle 2003) Miguel, et al investigated the effect of acid solid catalyst in the conversion of tyre rubber into hydrocarbon products. Five catalysts were compared aluminum contents, pore size and acidity, including three zeolites (standard ZSM-5, nanocrystalline n-ZSM-5 and beta) and two mesostructured materials (Al-MCM-41 and Al-SBA-15). All zeolitic catalysts showed a marked selectivity towards the formation of single ring aromatic species and higher concentration when using stronger acid catalysts. Mesostructured catalysts shown a strong aromatisation capacity and an intense alkylation effect on the resulting aromatic rings, which resulted in the formation of a much wider range of aromatic products as shown in table 7. This behaviour was related with their weaker acidity and larger pore sizes, which posed no barrier to the formation of larger molecular size products. The yield of aromatic hydrocarbons was higher when using catalysts with stronger acid properties and larger pore sizes and also when using higher catalyst/raw material ratio or longer residence times. The pore size influenced selectivity and Si/Al ratio influenced the number of catalytically active sites on the catalyst surface. (Miguel, Aguado et al. 2006) Shirazi, et al. synthesized ZSM-5 zeolite with different Si/Al molar ratios that had different morphologies and particle sizes. The results shown that the average ZSM-5 crystal size and surface area increased but total acidity decreased as Si/Al molar ration increased. (Shirazi, Jamshidi et al. 2008) López, et al. investigated the influence of ZSM-5 zeolite and Red Mud in the pyrolysis of mixed plastics (40 wt% polyethylene, 35 wt% polypropilene, 18 wt% polystyrene, 4 wt% polyethylene terephthalate and 3 wt% polyvinyl chloride). ZSM-5 zeolite had weak and strong acid sites, higher BET surface area and acidity than Red Mud. As the results, ZSM-5 zeolite generated higher yield of gases and a greater proportion of aromatics in the liquids than without catalyst and needs lower temperatures than Red Mud as shown in table 8. (López, De Marco et al. 2011) Rehan, et al. studied the quality and applications of liquid oil produced by thermal and zeolite catalytic pyrolysis of polystyrene (PS) plastic waste by using a small pilot scale pyrolysis reactor. The zeolite catalytic pyrolysis produced higher gases than thermal pyrolysis, but liquid oil yield decreased. The synthetic and natural zeolite were used in this study. For catalytic pyrolysis, the lowest liquid oil yield and highest gas production in catalytic pyrolysis with synthetic zeolite can be due to its microporous structure and high BET surface area can lead to an increase in gases production and decrease in liquid oil yields. The natural zeolite has lower BET surface area and microporous volume as compared to synthetic zeolite, thus increased the char

production. Moreover, the synthetic catalyst had higher acidity than natural zeolite, thus it increased the gases production with a decrease in liquid oil yields. The product oil needed to remove of acid, solid residues and contaminants before using as oil fuel. (Rehan, Miandad et al. 2016) Miandad, et al. investigated catalytic pyrolysis of plastic wastes that used natural/synthetic zeolite. The experiment was used catalyst/raw material ratio about 0.1 and pyrolysis at 450°C and 75 min. The catalytic pyrolysis with both natural and synthetic zeolite catalysts produced low amounts of liquid oil, whereas the gases yields were high. The synthetic zeolite pyrolysis produced higher gases yields than natural zeolite in all plastic waste samples as shown in figure 1. The higher yield of gases with synthetic zeolite catalyst could be attributed to its higher catalytic efficiency because of its higher BET surface area and acidity as compared to natural zeolite catalyst. (Miandad, Barakat et al. 2017)

Table 4 Characteristics of pyrolysis catalysts from literature.

Catalyst	Si/Al molar ratio	Acidity NH ₃ desorption (meq g ⁻¹)	BET surface area (m ² g ⁻¹)	Pore size (Å)	Reference	
Zeolite	ZSM-5	50	n/a	300	5.5	Bagri, et al. 2002
	Y-zeolite	11	n/a	440	7.4	Bagri, et al. 2002
	ZSM-5	40	n/a	n/a	5.6	Williams, et al. 2003
	Y-CBV-400	5.4	n/a	n/a	7.8	Williams, et al. 2003
	Y-CBV-780	40	n/a	n/a	7.8	Williams, et al. 2003
	ZSM-5	30	0.538	404	5	Miguel, et al. 2006
	nano-ZSM-5	31	0.53	409	5	Miguel, et al. 2006
	Beta	35	0.453	563	7	Miguel, et al. 2006
Mesostructured	Al-MCM-41	40	0.331	1168	22.6	Miguel, et al. 2006
	Al-SBA-15	52	0.24	496	43.8	Miguel, et al. 2006
Red mud	-	n/a	0.094	27.5	n/a	Lopez, et al. 2011
Zeolite	ZSM-5	50	0.176	412	n/a	Lopez, et al. 2011
	natural	9.2	n/a	3.21	8.3	Miandad, et al. 2017
	synthetic	5.1	n/a	900	24.5	Miandad, et al. 2017

Table 5 Product distribution of catalytic pyrolysis of LDPE in fixed bed reactor at 500 °C.(Bagri and Williams 2002)

Parameter	no catalyst	Y-zeolite	ZSM-5
oil yield (wt%)	95	80	75
gas yield (wt%)	5	10	20
char yield (wt%)	0	10	5
Oil product (wt%)			
toluene	0.01	7.93	0.22
ethylbenzene	0.01	8.13	0.55
xylene	0.03	3.1	0.37
other single ring aromatics	0.1	4	2.87
Total aromatic	0.34	25.9	6.01
Gas product (wt%)			
butene	n/a	0.5	0.5
propene	n/a	2	2.5
ethene	n/a	1	2.5
butane	n/a	1	1
propane	n/a	2	3
ethane	n/a	1	1
methane	n/a	1	1

Table 6 Product distribution of catalytic pyrolysis of scrap tyres in fixed bed reactor at 500 °C.(Williams and Brindle 2003)

Parameter	no catalyst	ZSM-5	CBV-400	CBV-780
oil yield (wt%)	55.8	38	35	35
gas yield (wt%)	6.1	24	27	27
char yield (wt%)	38.1	38	38	38
Oil product (wt%)				
benzene	0.2	3	5.2	4
toluene	1.1	15	24.3	18
m/p-xylene	1.3	9	20.2	16.7
o-xylene	0.2	2.6	7	6
Total yield	2.8	29.6	56.7	44.7

Table 7 Semi-quantitative analysis of products resulting from the catalytic conversion of tyre rubber.(Miguel, Aguado et al. 2006)

Parameter	ZSM-5	Nano-ZSM-5	Beta zeolite	MCM-41	SBA-15
Conversion (%)	47	53.6	45.8	n/a	n/a
Oil product					
benzene	7	7.4	10.3	0.7	0.7
toluene	16.6	19.8	17.9	4.1	6.1
m/p-xylene	16.5	16.9	11.8	5.2	7.5
o-xylene	5.2	5.4	3.7	1.9	2.7
Total yield	45.3	49.5	43.7	11.9	17

Table 8 Product distribution of catalytic pyrolysis of plastic wastes in unstirred reactor at 500 °C.(López, De Marco et al. 2011)

Parameter	no catalyst	ZSM-5	Red mud
oil yield (wt%)	65.2	39.8	57
gas yield (wt%)	34	58.4	41.3
char yield (wt%)	0.8	1.8	1.7
Oil product (%area in oil)			

toluene	8.1	17.5	14.2
dimethyl-heptane	5.9	0.8	2.1
ethylbenzene	5	9.6	9
xylene	3	13.8	4.2
styrene	48.4	27.9	42.3
Total aromatic	73.9	98.4	89.6
Gas product (wt%)			
H ₂	0.4	1	0.8
CO	0.7	0.7	1.2
CO ₂	2.9	1.9	7.5
methane	8.3	10.6	14.1
ethane	10	8.6	12.4
ethene	12.2	11.1	17.3
C ₃ -C ₄	46.7	50.7	41.5
C ₅ -C ₆	18.7	15.5	5.3

2.5.3 Mechanism of pyrolysis process

For HDPE pyrolysis mechanism, Conesa, et al. suggested a mechanism which involved steps of formation and free radicals and abstraction of hydrogen by radicals and mechanism to explain the process of thermal degradation of olefins and other polymers. This mechanism involves several steps such as initiation, propagation or free-radical transfer, and termination. Regarding a free radical formed in the initiation or in any other steps, one of two competing reactions may follow propagation (unzipping) to yield monomers and free-radical transfer involving an abstraction of hydrogen from a polymer chain and resulting in the formation of one saturated end, one unsaturated end, and a new free radical. (Conesa, Font et al. 1994) Onwudili, et al. suggested the modification kinetic mechanisms for plastic pyrolysis by studied effects of temperature and residence time of LDPE, PS and their mixtures as shown in figure 2. (Onwudili, Insura et al. 2009) Ceamanos, et al. studied experiments of the thermal decomposition of HDPE in inert atmosphere with isothermal and dynamic experiments and suggested mechanism for thermal decomposition and weight loss of HDPE as shown in figure 3. Reaction step 1 and 6 were the reversible reaction from the random scission. The HDPE (P) was reacted by the random scission to short radical chains (Rp, Rp'). Reaction step 2 and 5, The β -scission generates ethene (G1) and either alkenes (G2) and a shorter primary radical (Rp). Reaction step 3 and 4, the primary radicals react to generate mainly secondary radicals (Rs) and alkanes (G3) by intramolecular hydrogen transfer.

Comparing the rates of these three steps, the β -scission step, much slower than the hydrogen transfer, is the rate-limiting step. (Ceamanos, Mastral et al. 2002) Marcilla, et al. studied kinetic of catalytic decomposition of polyethylene over a solid acid catalyst (MCM-41). The result was a decrease in the thermal decomposition temperature when catalyst MCM-41 is added to the PE. The catalytic thermal decomposition of PE can be modelled considering two ways that involve three reactions as shown in figure 4 by PE: the polyethylene, C: the catalyst, PEC: an intermediate in the reaction, and G1 and G2: the volatiles formed through pathways W1 and W2, respectively. Letter "a" represents the ratio grams of catalyst per gram of PE necessary to obtain the complex PEC. (Marcilla, Gómez et al. 2002)

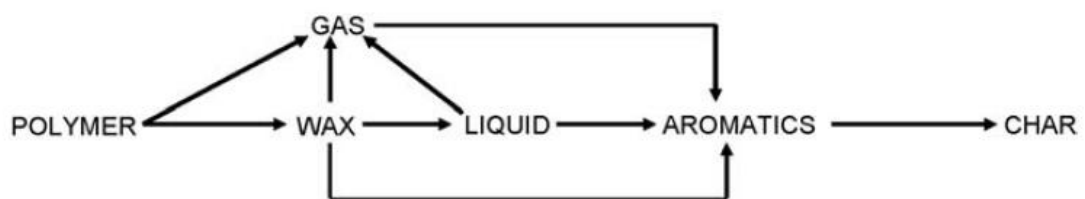


Figure 2 Kinetic scheme of kinetic of plastic pyrolysis process.

(Onwudili, Insura et al. 2009)

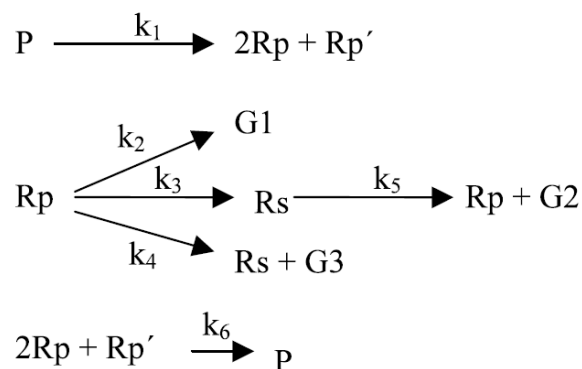


Figure 3 Mechanism for thermal decomposition and weight loss of HDPE.

(Ceamanos, Mastral et al. 2002)

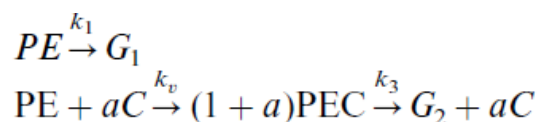


Figure 4 Mechanism for catalytic thermal decomposition of PE.

(Marcilla, Gómez et al. 2002)

2.5.4 Temperature effect

For the temperature range of this thesis, the compositions of the pyrolysis products pure low-density polyethylene (LDPE) have been investigated over a

temperature range from 300°C to 500°C. The pyrolysis experiments were carried out in a closed batch reactor under inert nitrogen atmosphere to study the effects of reaction temperature and residence time. LDPE was thermally degraded to oil at 425 °C. (Onwudili, Insura et al. 2009) The thermal degradation of HDPE is higher than LDPE. López, et al. obtained the results of ZSM-5 zeolite catalytic pyrolysis of plastic wastes. The conversion to gas and liquid was very high at 440°C -500°C (López, De Marco et al. 2011) Ng, et al. studied conversion of HDPE to fuels using pyrolysis and catalytic cracking. The results were found thermal decomposition of HDPE was 450°C and optimum temperature for distillate product was 470°C - 490°C. (Ng, Seoud et al. 1995) Kayacan, et al. studied thermal decomposition kinetics of LDPE and HDPE using thermogravimetric analyzer (TGA). The results were the decomposition temperature range from 387°C to 577°C for LDPE and 422°C to 567°C for HDPE. HDPE samples decomposed later than the LDPE samples. The activation energy values were found for raw HDPE between 401- 470 kJ/ mol and for waste HDPE between 396- 493 kJ/mol.(Kayacan and Doğan 2008)



CHAPTER 3 EXPERIMENTAL

According to literature reviews which related to catalytic pyrolysis of HDPE with catalysts HZSM-5 zeolite and catA. This chapter describes the data of raw materials and chemicals, pyrolysis system, experimental procedures and products characterization.

3.1 Raw materials and chemicals

The plastic used in the experiments was high density polyethylene (HDPE), obtained from Inno Plus, Thailand. The HDPE was virgin plastics of 1 – 2 mm average diameter pellets. Zeolite HZSM-5 and catA were used and obtained from Global R&D co., ltd, Thailand. The experiments used waste plastic by extruded HDPE and catalysts by using twin-screw extruder, CHAREON TUT co., ltd, Thailand. The conditions for extruded plastic samples were at the temperature of 180°C and 60 rpm screw speed. The blended HDPE with catalyst samples were extruded in this process. Then, the extruded plastics were cut to the same size as virgin plastics by pelletizer, CHAREON TUT co., ltd, Thailand.

3.2 Pyrolysis system

3.2.1 Batch reactor

The reactor operated in this work was stainless steel autoclave reactor which is shown in figure 5. The reactor was an 80 mL reactor made of 316 stainless steel. The reaction vessel was slowly shaken using motor device for improving heat and mass distribution in reactor. The reactor was obtained from HIRO co., ltd. The electric heater (220 V, 500 W) contacted the sides of the batch reactor. The internal temperature of the reactor was detected by a thermocouple. The reactor was equipped with a pressure gauge to measure its pressure during experiments. Nitrogen gas (99.99%) was used as reaction atmosphere for all experiments in pyrolysis condition. The experiments were carried out with an ambient initial nitrogen pressure. Since experimental work was carried out in a batch reactor, the reactions produced gases and oil products in vapor phase and increased the internal pressure of the reactor. Residence time was start at zero when the set pyrolysis temperature was reached. The average heating time was 30 min per experiment. At the end of the reaction, the heater was switched off and the reactor was rapidly cooled by air until the temperature inside the vessel reached to room temperature. Then, oil and solid were taken out from the reactor. The oil and solid were separated with filter paper and oil product were kept for testing with analyzers. The gases product was kept with GC needle after cooling down the reactor and opening the gas valve. 4 operating variables are investigated their effects on the product distribution; effect of type of catalysts, amount of plastic pellets (5.15 g and 15.45 g), effect of pyrolysis temperature (430°C, 450°C and 500°C) and effect of reaction time (10 min, 30 min, 60 min and 120 min). All of experiments used about 3 wt% of catalyst blended with HDPE as raw material.

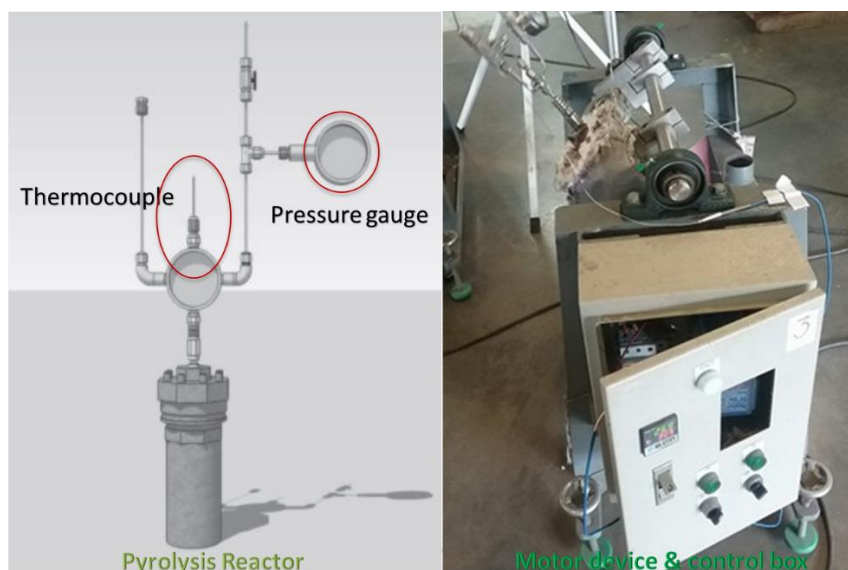


Figure 5 Illustration of pyrolysis batch reactor and motor device (Sawasraksa, VITIDSANT et al. 2013)

3.2.2 Semi-batch reactor

The reactor utilized in this work was stainless steel stirred reactor with graphite liner, a schematic diagram and illustration of which is shown in figure 6, 7. The reactor was a 3 L stirred pressure reactor made of 304 stainless steel. Inner diameter, outer diameter and height of the reactor are 108, 124 and 325 mm respectively. The 4-pitch blade impeller with 45° impeller Ø 36.3 x OD 10 x ID 8 mm thickness 2 mm and shaft Ø 7.94 x 307.40 mm made of 316L stainless steel. The reaction vessel was stirred using magnetic drive with wetted parts of 316 stainless steel. The electric motor was Mitsubishi model SF-JRV (1/2 Hp, 4P, 220/380 V). The reactor and instruments were obtained from Global R&D co., ltd, Thailand. A stirrer shaft with 4-pitch blades at the base was attached to an inner magnetic drive rotor powered through an outer magnetic drive rotor. The reactor was heated using electric heater (220 V, 25 A, 5000 W), which contacted the sides and bottom of the reaction vessel. The internal temperature of the heater and the reactor were monitored by K type thermocouples from Siam RTD.P. Heater Supply ltd. The reactor vessel was fitted with a gas inlet valve which served for filled inert gas, a gas outlet valve which served for sampling. The reactor was equipped with a pressure gauge to measure its internal pressure during experiments. Raw materials were prepared by being dried at 80 °C overnight to remove moisture and cooled to room temperature before pyrolysis process. About 500 ± 0.1 g of sample was used in each experiment that include among of catalyst for 3 wt% of pure HDPE. The amount of sample was determined by volume of reactor that sample was over the impeller during reaction. The reactor was filled with the sample and closed cap with graphite liner. After that, the reactor was filled with N_2 for ensuring the inert pyrolysis condition. Nitrogen gas (99.99%) was used as reaction atmosphere for all experiments to ensure inert pyrolysis condition. The experiments were carried out with an initial nitrogen pressure of 0.25 MPa. The reactor pressure was higher than ambient pressure to prevent contamination from outside the system. The considered pressure was used the other catalytic cracking experiments for determining the operating pressure of this experiments. (López, De Marco et al. 2011, Miandad, Barakat et al. 2017, Uttamaparakrom, Reubroycharoen et al. 2017) The reactor was heated with electric

heater until reach the reaction temperature, the pyrolysis gases and oil were taken out at that temperature for the residence times of the experiment by using gas outlet valve. The gases and oil product were connected with cooling down unit and flash drum to phase separation of the product and kept the product to test with analyzers. Since experimental work was carried out in a semi-batch reactor, the reactions produced gases and oil products in vapor phase and increased the internal pressure of the reactor. The vapor of product passed to gas outlet valve that was at ambient pressure due to increasing pressure. Therefore, the pressure in a reactor was constant at initial pressure. Residence time was set to zero as soon as the set pyrolysis temperature was reached, and the pyrolysis gases and oil were taken out at that temperature for the specific residence times of the experiment by gas outlet valve to flash drum. The gas products were rapidly cooled using condenser to prevent oil products evaporation. The condenser was used cooling water at 15°C. At the end of the reaction, the heater switched off, all of pyrolysis gases and oil were taken out from the reactor and reactor rapidly cooled by air until the temperature inside the vessel reached to room temperature. After that, the waxes were kept from inside reactor that left. The reactor temperature was calibrated by using pure nitrogen. The reactor and heater temperature were constantly different around 150°C for every calibrations after the reactor heated for 60 min. The reaction temperatures that shown in the experiments were the calibrated reactor temperature with pure nitrogen. The mixing condition used around 400 rpm of stirrer motor for mixing because melted HDPE was highly viscous.

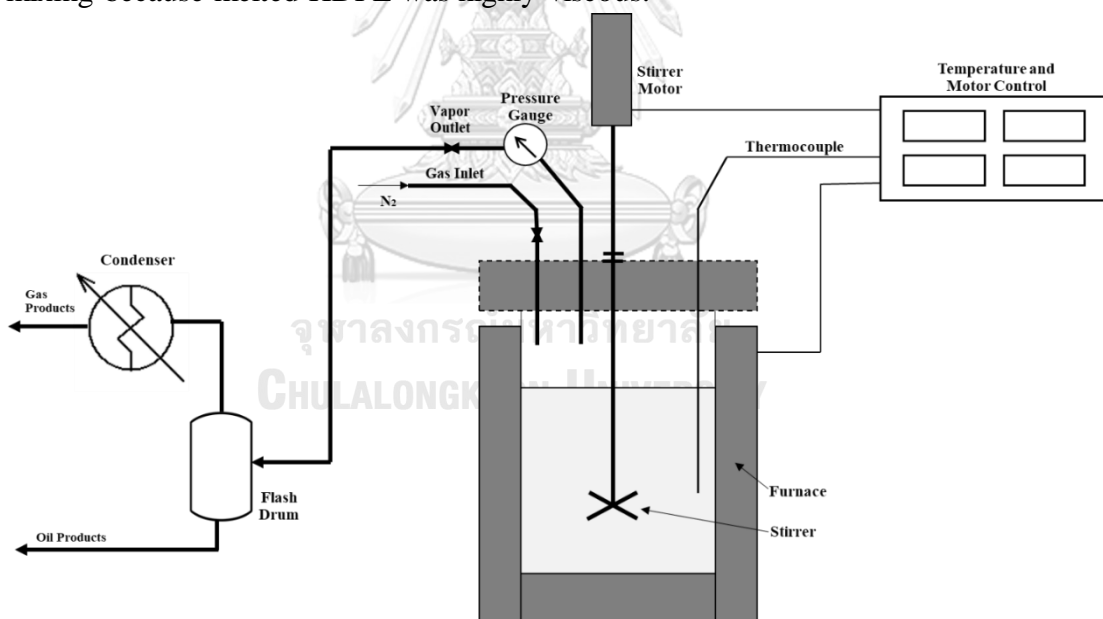


Figure 6 Pyrolysis semi-batch reactor scheme



Figure 7 Illustration of pyrolysis semi-batch reactor instruments and control device

3.3 Product characterization

The percentage of yield liquid, yield gas, and conversion were defined as:

$$\% \text{ yield liquid} = \frac{\text{weight of liquid}}{\text{weight of initial plastic}} \times 100$$

$$\% \text{ yield gas} = \frac{\text{weight of initial plastic} - \text{weight of solid} - \text{weight of liquid}}{\text{weight of initial plastic}} \times 100$$

$$\% \text{ conversion} = \frac{\text{weight of initial plastic} - \text{weight of solid}}{\text{weight of initial plastic}} \times 100$$

3.4.1 Gas analysis

The gas products which were collected at each specific residence times and temperatures were analyzed on line using a Shimadzu 2014 GC system with thermal conductivity and flame ionization detectors (GC- TCD/ FID) . A Restek Rt-Al BOND/Na₂SO₄ capillary column (30 m × 0.53 mm × 10 μm) was used to qualify nitrogen and gaseous hydrocarbons from C1 to C4. Helium was used as carrier gas with linear velocity constant at 45 cm/sec, total flow 33.7 mL/min, and pressure 41.6 kPa. The oven temperature was set at 150 °C held isothermally for 30 min. The detectors were operated at 200 °C.

3.4.2 Oil analysis

The liquid products were analyzed with Shimadzu 2014 GC system with flame ionization detectors (GC-FID) to identify individual compounds. The liquid products were analyzed directly with gas chromatography. The liquid products were collected at each specific residence times and temperatures. A Agilent DB-1 capillary column (60

m × 0.25 mm × 1 μm) was used to qualify the liquid products. The oil consisted of mainly paraffins and olefins carbon atoms C5-C44. The carrier gas used was helium and this was set to a flow rate of 3 ml min⁻¹. The temperature programmed of the oven was 60 °C for 1 min followed by a ramp rate of 10 °Cmin⁻¹ to 200 °C and heated up to 320 °C by a ramp rate of 20 °Cmin⁻¹, at which point the oven was held isothermally for 19 min to ensure elution of all low volatility material. The injection temperature was operated constantly at 350 °C and the FID was operated at 320 °C.

3.4.3 Solid analysis

The solid or wax products were analyzed with thermogravimetric analyzer (TGA) to define characteristic of decomposition temperature. The samples about 5 mg were placed on the sample holder and heated up in nitrogen atmosphere in each experiment. The nitrogen (99.99%) flow rate was constant at 100 mL/min. The sample was heated to the temperature at 750 °C with heating rate 10 °C/min.



CHAPTER 4 RESULTS AND DISCUSSION

This chapter discusses the results and data of catalytic pyrolysis of different pyrolysis system and experimental procedures by products characterization.

4.1 Catalyst characterization

The acidity of the catalysts was determined by NH₃-TPD. In NH₃-TPD curves, catalysts generally have two desorption peaks. The low-temperature peak at below 300 °C and the high-temperature peak at 300-800 °C correspond to weak and strong acid sites of Bronsted and Lewis type sites, respectively. (Lónyi and Valyon 2001, Shirazi, Jamshidi et al. 2008) The number of total acid sites was determined by pH of the catalysts with titration method. The titration technique involved an aqueous ion-exchange step. Catalyst 0.2 g was added to 10 mL of a 3.42 mol/L aqueous solution of NaCl under stirring. After 30 h of ion exchange at room temperature between the catalyst H⁺ ions and the Na⁺ ions in solution, the liquid was filtered off and titrated with a 0.05 mol/L aqueous NaOH solution to determine the number of exchangeable acid sites. (López, Goodwin et al. 2007) The specific surface area of catalysts was measured by BET methods with nitrogen adsorption isotherms at 77 K. Table 9 shows the characteristics of the catalysts. The elemental properties of catalysts were analyzed by Energy Dispersive X-Ray and shown in table 10. The main components of both catalysts were Silicon (Si) and Aluminum (Al). HZSM-5 and Cat A have Si/Al molar ratio as 8.0 and 7.1, respectively. Si/Al molar ratio of catalyst affected acidity, BET surface area and crystal size of HZSM-5 zeolite catalyst. The increase of Si/Al molar ratio leads to the increase of the BET surface area and crystal size, except the acidity that become decreased. (Shirazi, Jamshidi et al. 2008) Si/Al ratio influenced the number of active sites on the catalyst surface. (Miguel, Aguado et al. 2006)

Table 9 Properties of the catalysts used.

Property	HZSM-5	Cat A
NH ₃ - TPD desorption peak size at low temperature (below 300°C) (ml/g at STP) - weak sites	>30.2	>43.1
NH ₃ - TPD desorption peak size at high temperature (300-800 °C) (ml/g at STP) - strong sites	>33.5	<8.7
H ⁺ /g-adsorbent (μmol)	>1,000	>500
pH	1.3	3.3
BET surface area (m ² /g)	550	202
Pore size (Å)	7	20
Catalyst size (μm)	300	300

Table 10 Elemental and elemental-oxide analysis of cat A & HZSM-5 by Energy Dispersive X-Ray Analysis (EDX)

Composition (wt%)	Cat A	HZSM-5	Composition (wt%)	Cat A	HZSM-5
Element			Element-Oxide		
Si	69.404	85.565	SiO ₂	92.010	98.768
Al	10.071	11.132	SO ₃	3.233	1.180
Ca	5.985	0.190	Fe ₂ O ₃	2.130	-
S	4.094	2.890	CaO	1.636	-
Zn	0.114	0.114	TiO ₂	0.425	-
Fe	6.961	-	K ₂ O	0.214	-
Ba	0.638	-	BaO	0.151	-
Zr	0.337	-	MnO	0.077	-
Mn	0.292	-	ZrO ₂	0.073	-
Sr	0.171	-	SrO	0.034	-
Ti	1.068	-	ZnO	0.010	-
K	0.864	-	NbO	0.007	-
Cu	-	0.110	Eu ₂ O ₃	-	0.052

Note: EDX results were analyzed by Shimadzu EDX Spectrometer model EDX720 with power 50 kV, 100 μ A, and collimator 3mm.

4.2 Solid analysis with thermogravimetric analyzer (TGA)

The wax product which was obtained in pyrolysis reaction at 400 °C was analyzed with TGA to compare the decomposition temperature with HDPE and HDPE blended with catalyst. The wax is a mixture of long chain molecular hydrocarbon. It is solid at room temperature and begins to melt at temperature around 60 °C. The wax product started to decompose at temperature lower than the others. The results of HDPE blended with Cat A started to decompose at temperature lower than the pure and HDPE blended with HZSM-5 as shown in figure 8. Pure HDPE and HDPE blended with HZSM-5 had the same characteristic of decomposition. The results of TGA show that there are no significant differences in the characteristic of decomposition process of HDPE and HDPE with solid acid catalyst from the other author. (Marcilla, Gómez et al. 2002, Kayacan and Doğan 2008)

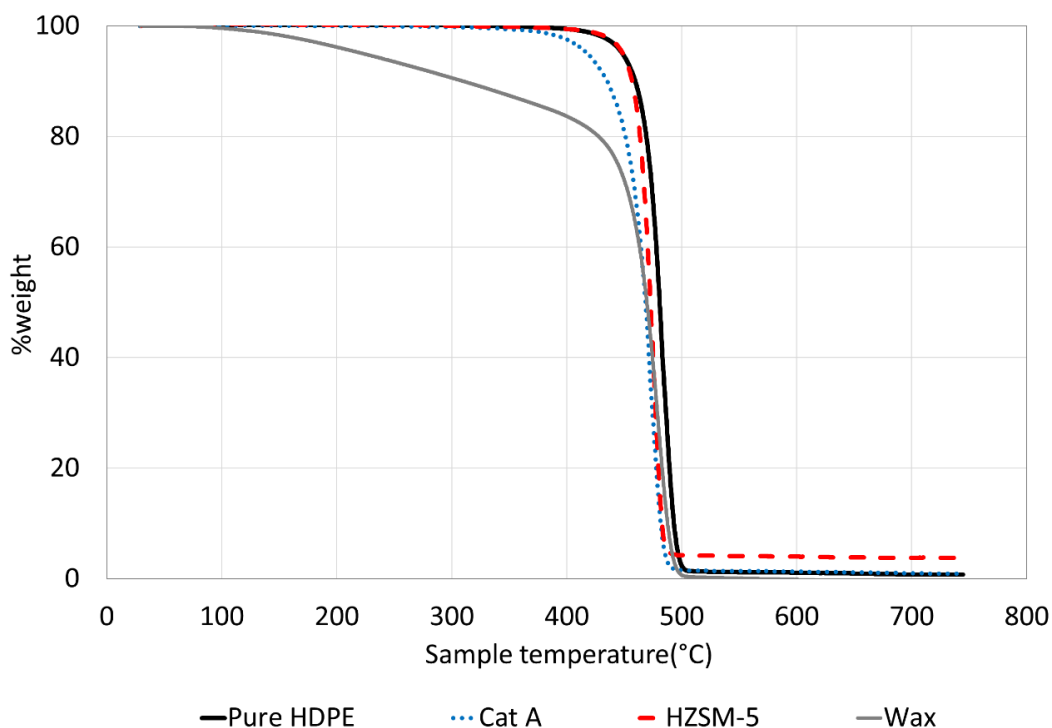


Figure 8 Effect of catalyst on decomposition temperature of HDPE and decomposition temperature of wax product.

4.3 Batch pyrolysis system

4.3.1 Effect of types of catalyst on conversion and product distribution

Two types of catalyst were used to pyrolyze of HDPE at 430°C for 2 h. and were compared to the percentage yield of pyrolysis products and the conversion. The yield gas product and conversion were higher in Cat A comparing to HZSM-5 at 430°C pyrolysis temperature as shown in figure 9. The conversion and gas yield were higher in Cat A even the lower surface acidity. That might be from the large average pore size which the large molecule of reactant was easy to access the active site of Cat A or from the side reactions in batch reactor. The porosity and acidity of catalyst had an influence to the cracking ability of catalyst that was also reported by other authors. The large pore size resulted in a higher production of aromatic hydrocarbon and also when using strong acid catalyst. (Williams and Brindle 2003, Miguel, Aguado et al. 2006, Hernández, Gómez et al. 2007, López, De Marco et al. 2011) The carbon range of oil products for both catalyst shows in figure 10. Both of types of catalyst condition had the similar result of carbon range of oil products. However, the condition with Cat A had a little higher concentration of light carbon chain.

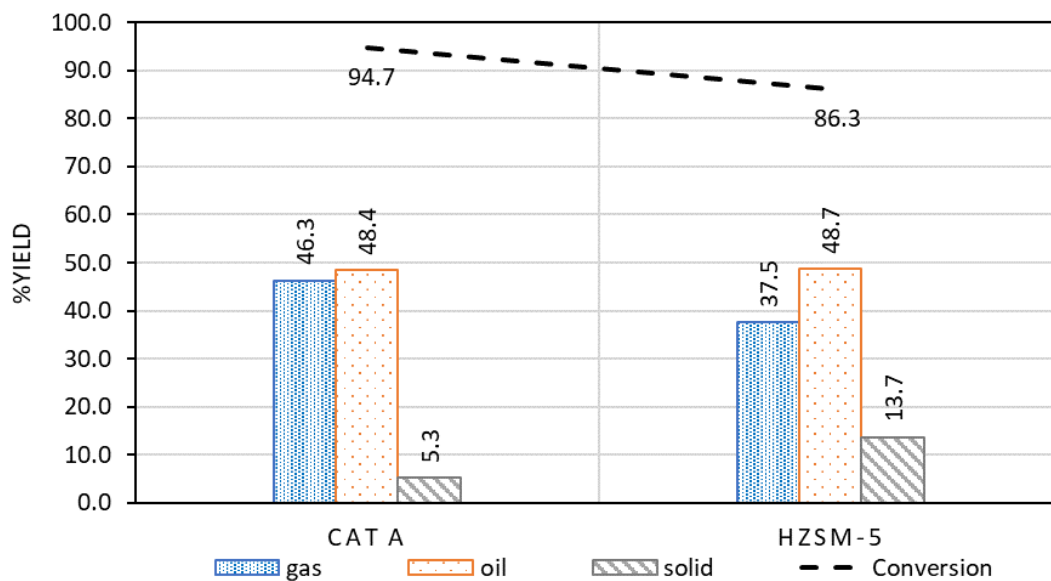


Figure 9 Effect of types of catalyst on conversion and product distribution (430°C, 2h., 15.45 g conditions)

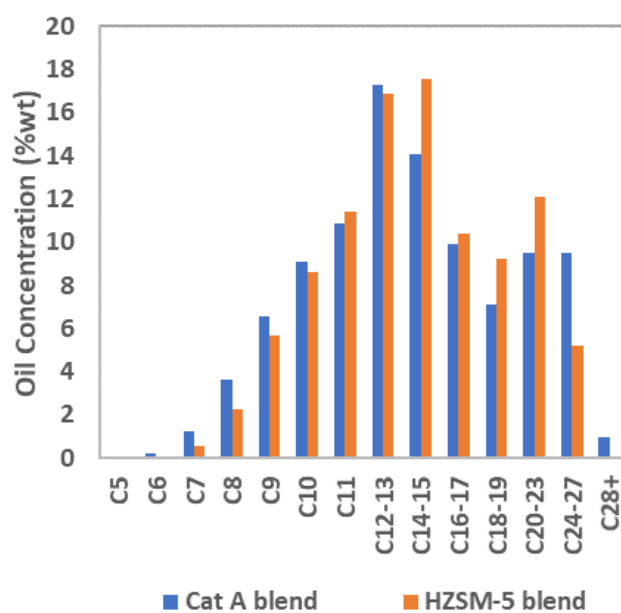


Figure 10 Effect of type of catalyst on oil products composition (430°C, 2h., 15.45 g conditions).

4.3.2 Effect of amount of plastic pellets on conversion and product distribution

The different amount of plastic pellets showed the percentage yield of pyrolysis products of HDPE with Cat A obtained at 430°C for 2 h. in figure 11. The amount of plastic pellets was initial raw material in the reactor when reacting to the products (especially gas products) increased the pressure inside the reactor from the initial pressure until the end of the reaction. The amount of 15.45 g plastic pellets produced more products that led to high pressure in the reactor. High pressure in the reactor increased the side reactions to occur. The side reactions could react with the

high sensitivity reactant such as double bond and triple bond molecule which easily react with hydrogen by hydrogenation or with other reactant. (Ng, Seoud et al. 1995) The result in figure 11 supported this proposal that the lower amount of plastic pellets in the reactor, which reduced the final pressure in the reactor, showed the higher catalytic conversion at the same reaction time.

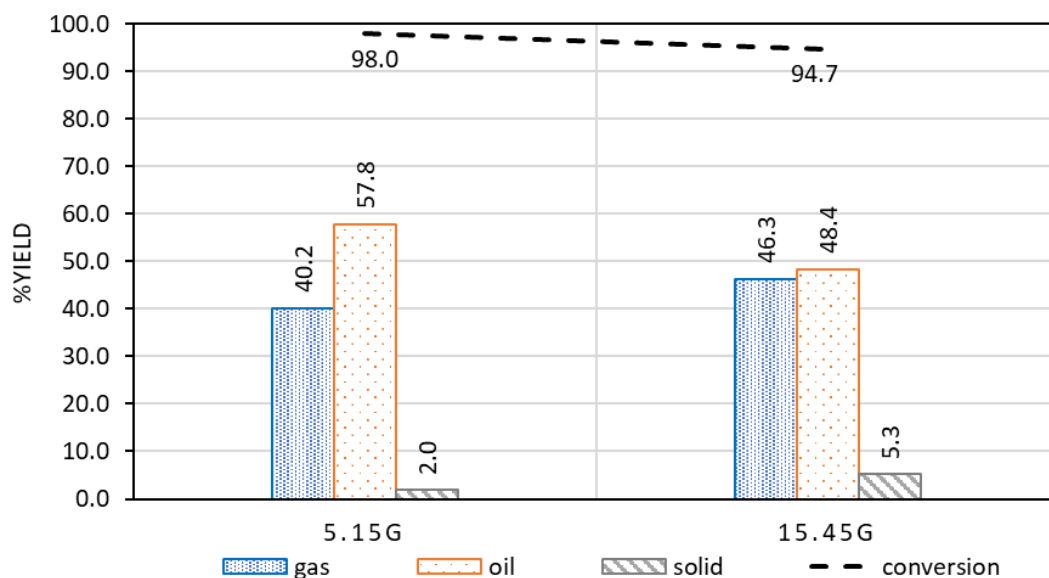


Figure 11 Effect of amount of plastic pellets on conversion and product distribution (Cat A, 430°C, 2h. conditions)

4.3.3 Effect of temperature and time on conversion and product distribution

The longer of reaction time showed, the higher reaction conversion with the increasing of gas product yield as shown in figure 12. The increased of gas products come from the higher heat supplied for cracking that was cracked both solid and liquid. The range of temperature between 430°C and 500°C was selected for experiments. The temperature that is lower than 430°C was not good temperature enough to decompose the all of the samples that still was unconverted HDPE even with catalyst condition. Figure 13 shows that the higher temperature presented the liquid yield was decreased and the gas yield was increased. This behavior was similarly reported by other authors. (Hernández, Gómez et al. 2007, López, De Marco et al. 2011) The higher cracking reaction of C-C bonds took place at higher temperature that was given by the rise of lighter hydrocarbon or shorter hydrocarbon chain. For the increase of formation of gas and oil product at high temperature, also lead to char production. The reaction pathways of char formation were the same as kinetic scheme of kinetic of plastic pyrolysis process which were proposed by Onwudili, et al. The formation of gas and solid were occurred at high temperature with the same time from liquid oil cracking. (Onwudili, Insura et al. 2009)

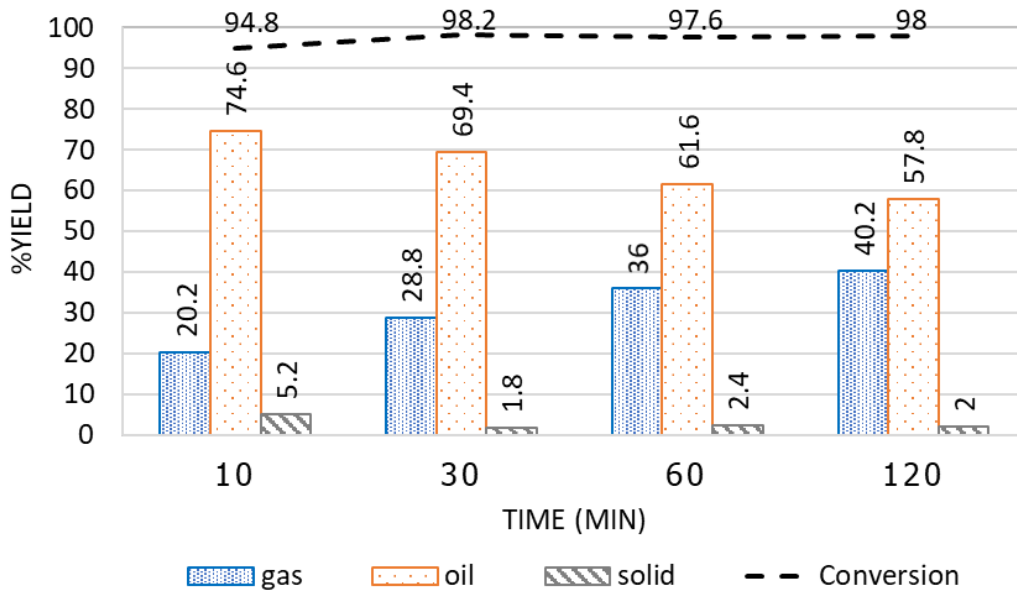


Figure 12 Effect of time on conversion and product distribution
(Cat A, 430°C, 5.15g conditions)

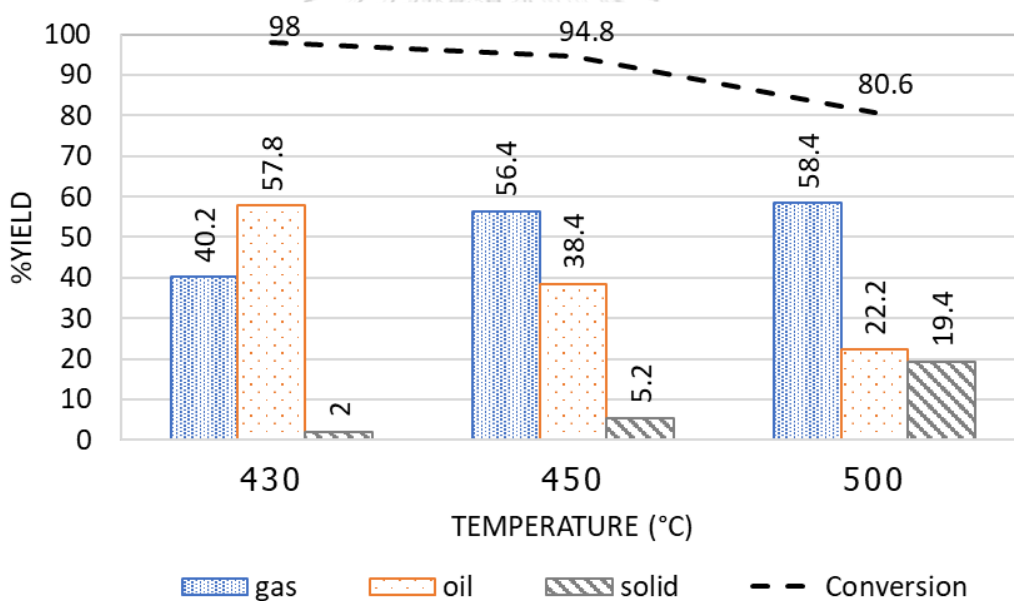


Figure 13 Effect of temperature on conversion and product distribution
(Cat A, 2h., 5.15g conditions)

4.3.4 Products composition of pyrolysis reaction

The products were being grouped by range of number of carbon atoms per molecule for easier to understand the behaviour of the reactions as shown in table 11. The main components of pyrolysis products were methane and hydrogen in gas products. Oxygen and carbon dioxide that were detected came from initial ambience. Tar, diesel, naphtha and kerosene were observed in oil products. The conditions of

figure 14 were long residence time that may lead to produce lighter hydrocarbon in gas and oil products than the other shorter reaction time condition. The shorter reaction time condition may produce heavier or longer hydrocarbon because the shortness in reaction time was low energy for cracking reaction. The components in gas products were left only non-sensitivity reactant which were methane and hydrogen. The high sensitivity reactant could react and was in the higher carbon form.

Table 11 Product hydrocarbon range grouping by number of carbon atoms. (Eneh 2011)

No. of carbon atoms per molecule	Component	Boiling range (°C)
C1-C4	Gas	<30
C5-C11	Naphtha	30-150
C12-C15	Kerosene	150-300
C16-C23	Diesel	300-400
C24-C30	Wax	>400
C40+	Tar	>400

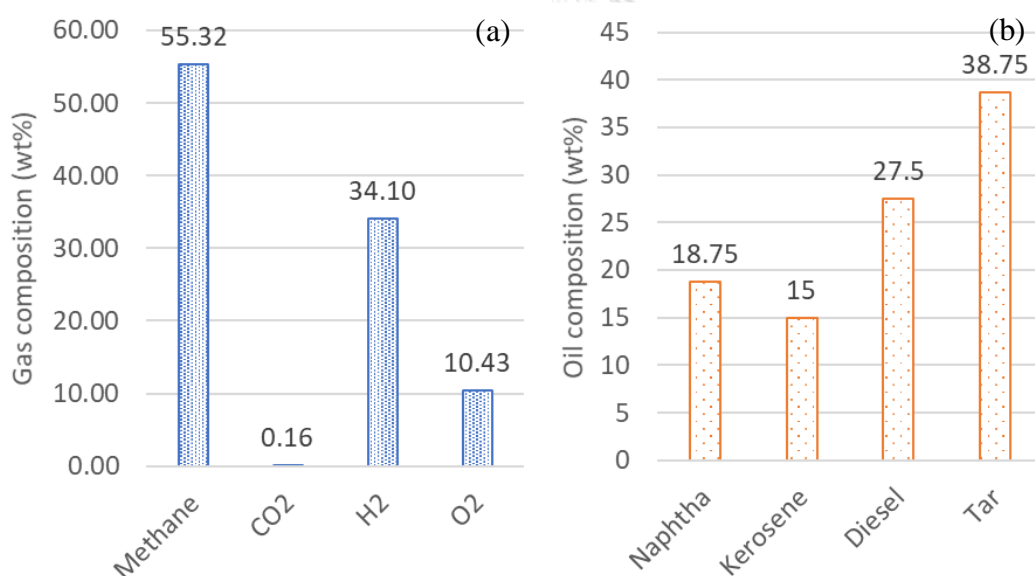


Figure 14 Gas (a) and oil (b) product composition (Cat A, 450°C, 2h., 5.15 g conditions).

Catalytic cracking of HDPE in a 80 mL batch reactor resulted in production of hydrocarbon. There are many effects that influenced to product distribution and conversion of HDPE. The experiments were investigated with catalyst blended with HDPE at 3 wt%. The two different surfaces of the acidity of catalysts namely Cat A and HZSM-5 were studied. The Cat A has weak and strong acid sites with 200 m²/g surface area and 20 Å average pore diameter. The HZSM-5 has higher in strong acid sites with 550 m²/g surface area and 7 Å average pore diameter. The cracking reaction is higher in Cat A even the lower surface acidity. That might be from the large average

pore size which the large molecule of reactant was easy to access the active site of Cat A. The lower amount of plastic pellets in the reactor showed the higher catalytic conversion and yield of oil product at the same reaction time. The longer of reaction time showed, the higher reaction conversion with the increasing of gas product yield. The higher of reaction temperature showed, the higher gas product yield but lower in reaction conversion. The higher temperature led to produce solid product that might be from generated of char by cracking reaction. The higher cracking reaction of C-C bonds taken place at higher temperature that gave the rise of lighter hydrocarbon or shorter hydrocarbon chain. The best condition to obtain oil product with great conversion was to use Cat A, 5.15g, 10 min, 430°C that was obtained 74.6 % yield of oil and 94.8 % conversion. The main components of pyrolysis products were methane and hydrogen in gas product. Oxygen and carbon dioxide that were detected came from initial ambience. Tar, diesel, naphtha and kerosene were observed in oil product. Long cooling time in batch reactor provided opportunity for secondary reactions to occur. The semi-batch operation was suggested for this research, that will get higher quality of pyrolysis oil because the product oil and solid were separated while running reaction for prevention side-reaction before taking the samples.

4.4 Comparison of batch and semi-batch system

The comparison of batch and semi-batch system, the batch system was used a 80 mL autoclave reactor with a single filled raw material and opened products while the semi-batch system was used a 3 L stirred pressure reactor with continuous collecting products. The conversion and product yield of both system that operated in the same condition show in figure 15. In batch system, conversion, gas and oil products yield had higher than semi-batch system. The batch system had higher heat for cracking reaction because the heat loss from product collecting in semi-batch even heating with the same conditions since the solid products in semi-batch were wax that still unconverted to char or oil product. The gas products in batch system were found only methane and hydrogen as might be from occurrence of reaction of unsaturated hydrocarbon. The oil products composition in semi-batch system had higher in short-chain hydrocarbon (naphtha) as shown in figure 16. The separate system in semi-batch was a rapidly separation between oil and gas products while in batch system was separated after cooling down process. Moreover, the increase pressure in batch system led to occur side reactions in the process. (Onwudili, Insura et al. 2009) From the studied of Ng, the results of open system obtained more and better oil products than in close system and the high severity of reaction occurred side reactions. (Ng, Seoud et al. 1995) The side reactions were saturation, isomerization, cyclization, aromatization, alkylation, and polymerization. The side reactions scheme shows in figure 17. These reactions could be found in batch pyrolysis reaction of HDPE that have high reactive products such as double bond and triple bond hydrocarbon, high pressure, and long time for cooling down process.

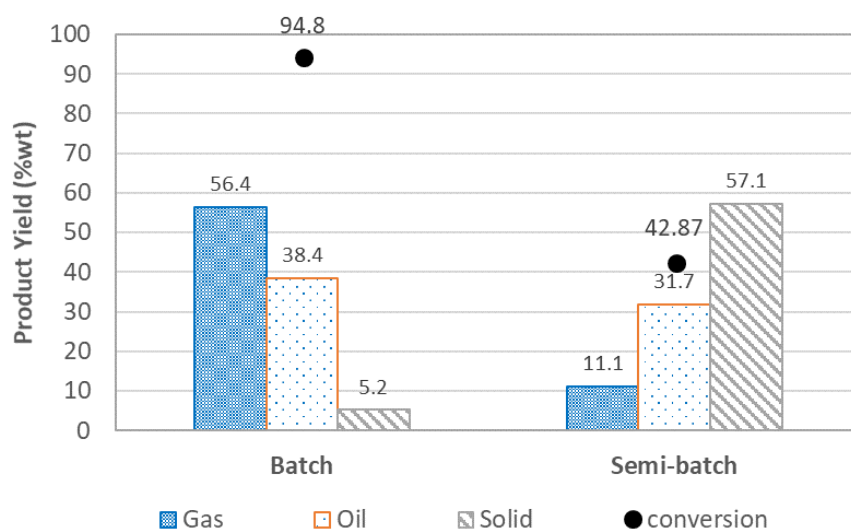


Figure 15 Effect of operating system on conversion and products yield.
(Cat A, 450°C, 2h. conditions)

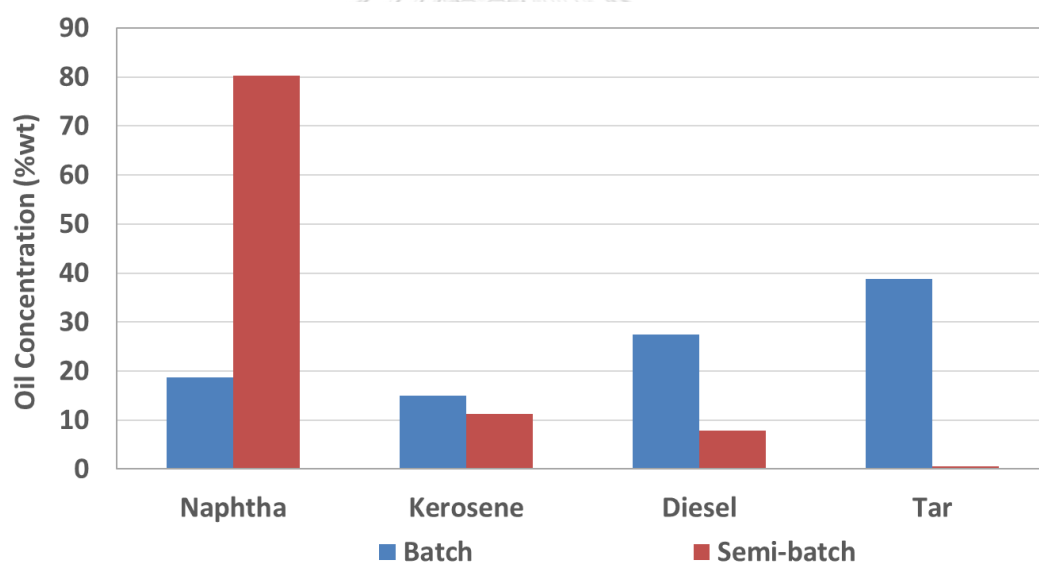


Figure 16 Effect of operating system on oil product distribution.
(Cat A, 450°C, 2h. conditions)

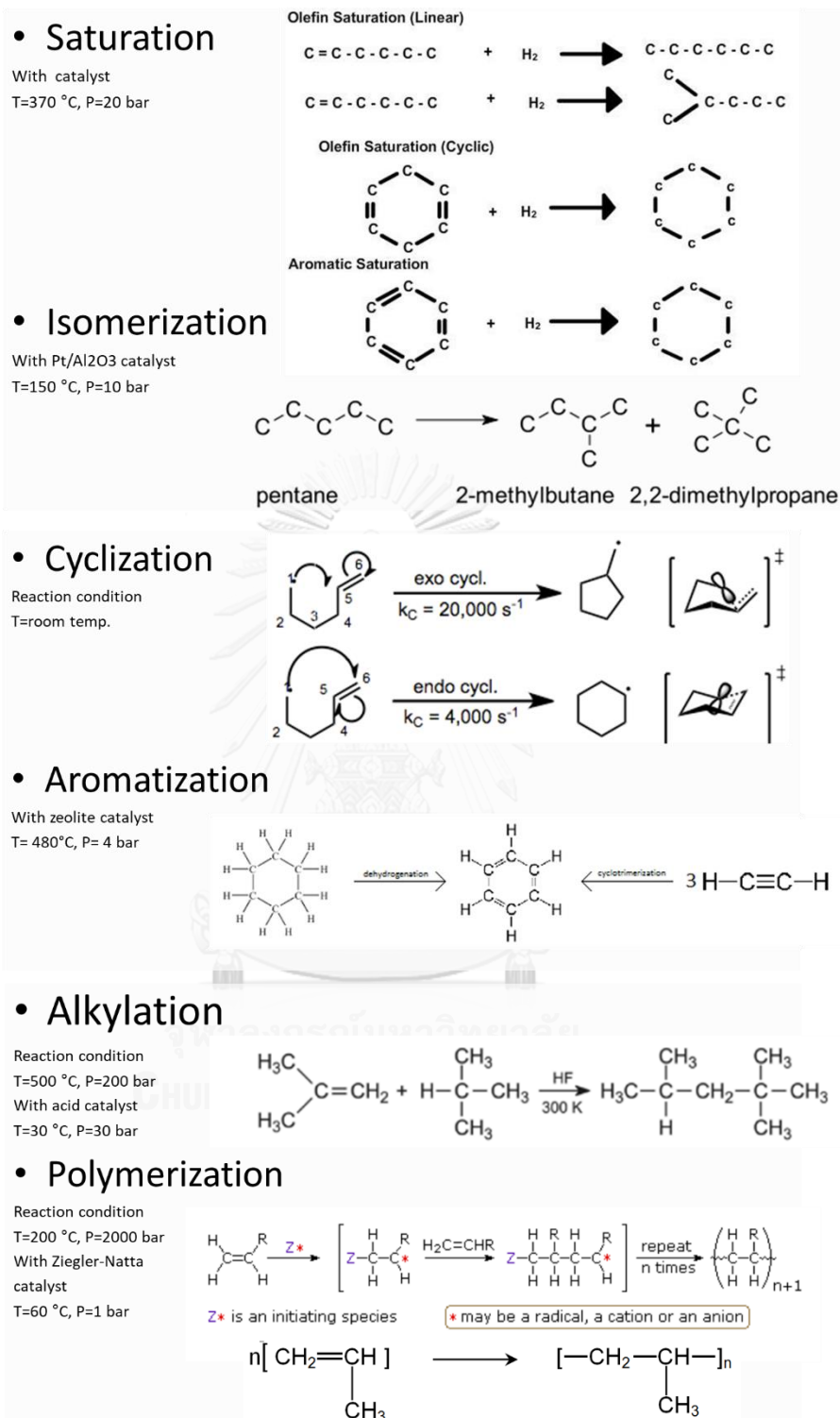


Figure 17 Side reaction schemes and reaction conditions of pyrolysis reaction.
(Beckwith and Schiesser 1985, Ng, Seoud et al. 1995)

4.5 Semi-batch pyrolysis system

4.5.1 Effect of calibration temperature and residence time on reaction temperature and products rate

The two types of acidic catalyst blended with HDPE and pure HDPE had studied in this section. The calibration temperature of each experiment was used hydrogen atmosphere to calibrate reactor temperature. The heater temperature was set higher temperature than the reactor around 150 °C. The heating time of each experiment used approximately 50 minutes to reach the setting temperature. The characteristic of heating was the same in every experiment as shown in figure 18,20,22(a). In each experiment, the setting reactor temperature had the same heat rate for reacting. The setting temperature at 450 °C and 500 °C were constant at nearby reaction temperature until 180 minutes reaction because the pyrolysis reaction consumed heat to cracking reaction. The pyrolysis reaction is highly endothermic reaction that consumed a lot of heat to crack the substance. Therefore, the reactor temperature was constant. The results of setting temperature at 450 °C and 500 °C had wax products that still unconverted to oil products from incomplete reaction. For setting temperature at 600 °C and 650 °C, the reactions temperature was monitored, and it completed before 180 minutes reaction. The temperature was nearly constant at lower than calibration temperature because the heat was consumed for cracking reactions. When the temperature was higher and approached the calibrated temperature, it could approximate to complete the reaction. The increasing temperature came from lower substances in the reactor as it generated to gas and oil products. That supported by lower slope of products rate as shown in figure 18,20,22(b,c). When lower substances and reactions in the reactor, the cumulative heat will increase the reactor temperature. In each setting reaction temperature had the same of heat rate for the reaction because of the setting of furnace temperature. The products rate was higher at higher setting temperature. Both oil and gas products rate at 600 °C and 650 °C were higher than at 450 °C and 500 °C that can approximate by using slope of products yield in figure 18,20,22(b,c). It was generally that higher temperature was obtained high products rate. (Onwudili, Insura et al. 2009, López, De Marco et al. 2011)The products rate in each experiment was highest at the time before reaction temperature ramping. So, the reaction rate was the highest at the temperature reaction before increasing to calibration temperature. This result supported the proposal of complete reaction by using temperature monitored.

The pyrolysis products distribution was analyzed and show in figure 19, 21, 23. The main product is naphtha that was mainly obtained products from every experiment. Almost all products, which obtained at 450 °C and 500 °C, were light hydrocarbon products. That could be from low severity reaction so plastic and catalyst had longer time for cracking. The cumulate heat in reactor at long reaction time could evaporate middle chain hydrocarbons such as diesel that has boiling point at 300 °C - 400 °C and come out with light products. The results in figure 19, 21, 23 show that the heavy hydrocarbon was generated at temperature 650 °C and lower followed by the lower temperature with the rate of products that was lower at lower temperature.

4.5.1.1 Effect from temperature of Cat A.

The reaction temperature of Cat A condition was around 440 °C as shown figure 18(a). The highest yield of naphtha was obtained at 600 °C which was 45.76

wt%. The temperature at 450 °C was the lowest yield of heavy hydrocarbon as shown in figure 19.

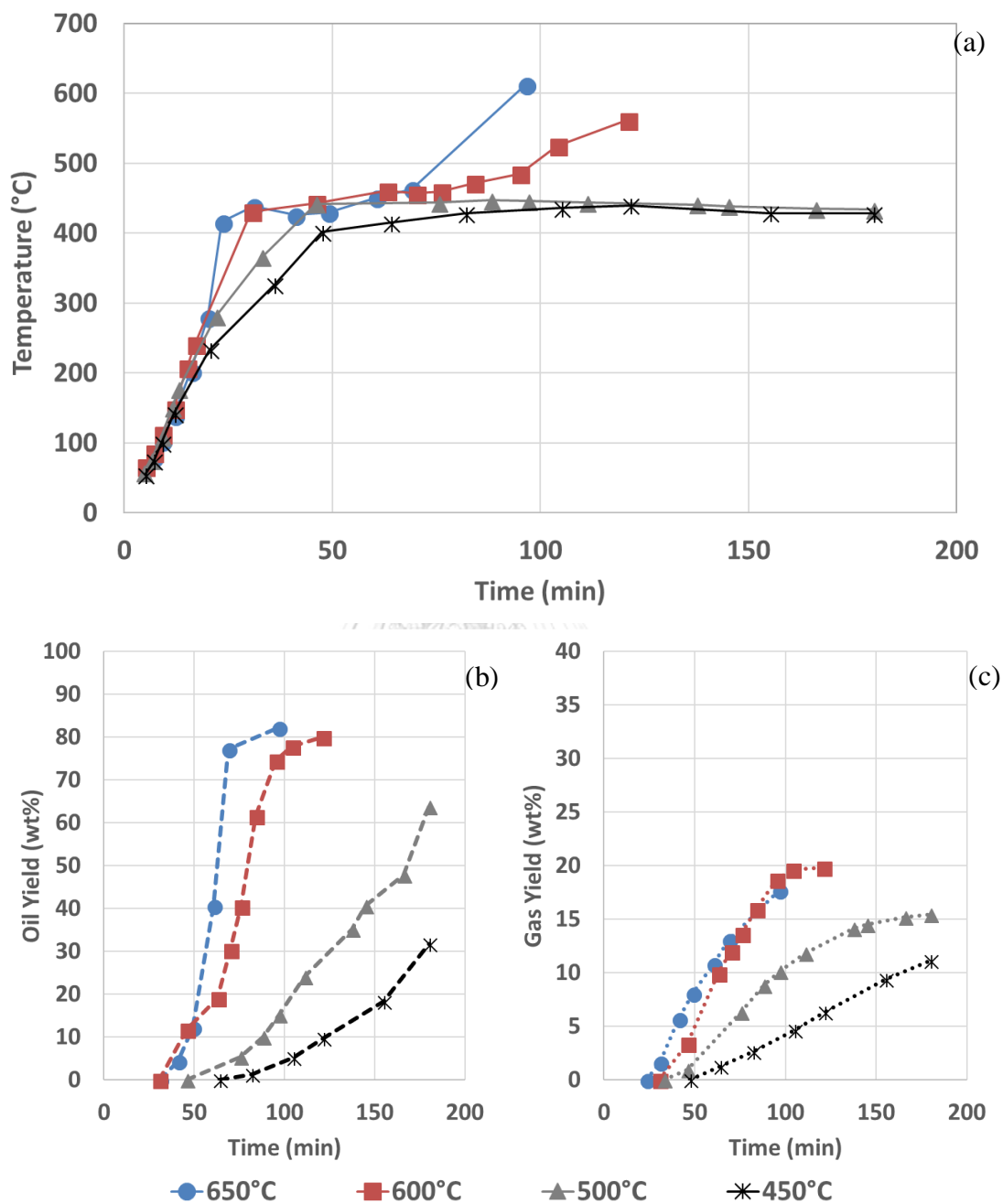


Figure 18 Effect of temperature of Cat A on reaction temperature (a), oil products yield (b), and gas products yield (c).

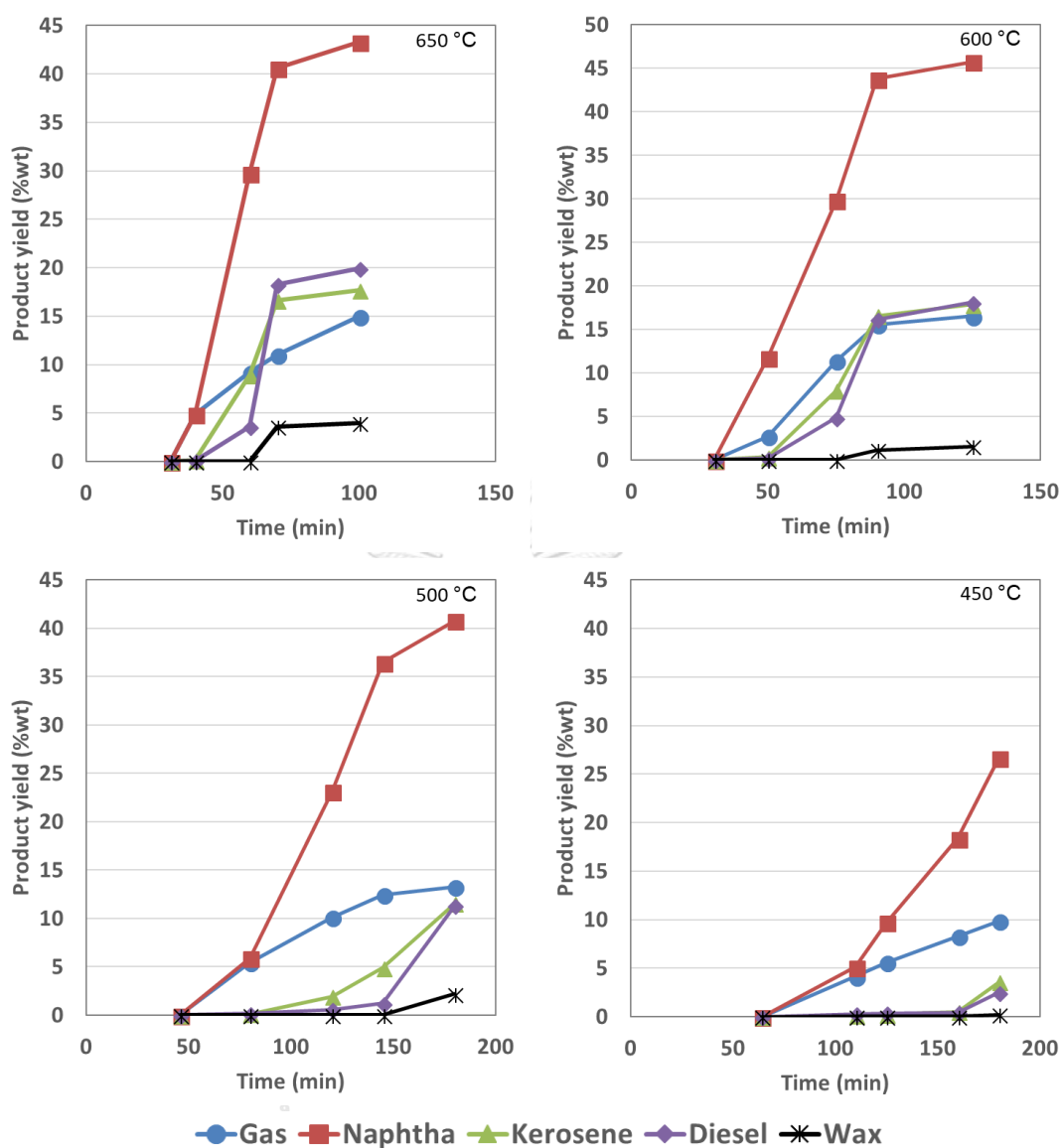


Figure 19 Effect of reaction temperature of Cat A on cumulative of products distribution.

4.5.1.2 Effect from temperature of HZSM-5.

The reaction temperature of HZSM-5 condition was around 400 °C as shown figure 20(a). The highest yield of gas product was obtained at 650 °C which was 30.93 wt% and the highest naphtha was obtained at 600 °C. The gas products and heavy oil were increased with the increased temperature as shown in figure 21.

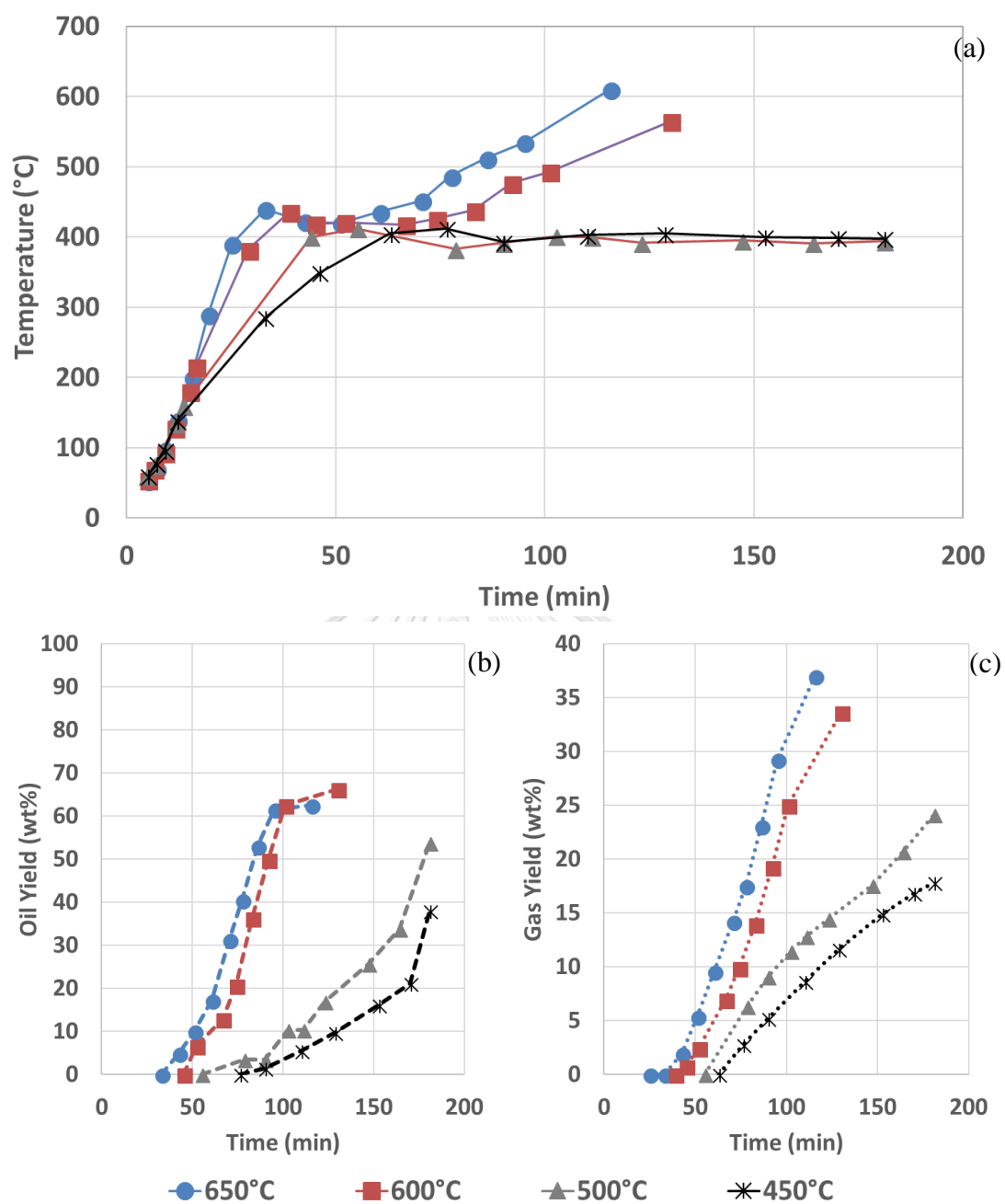


Figure 20 Effect of temperature of HZSM-5 on reaction temperature (a), oil products yield (b), and gas products yield (c).

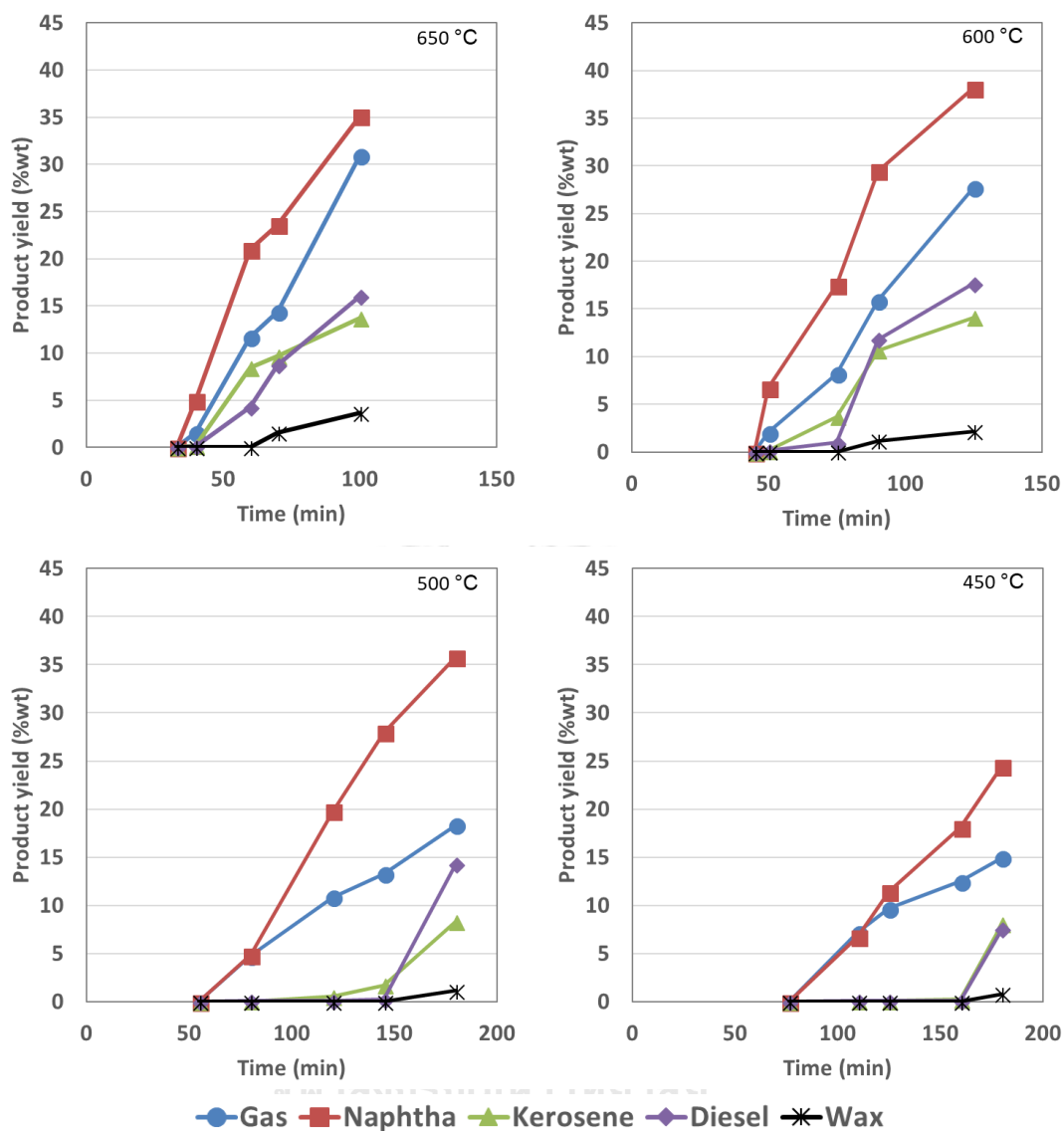


Figure 21 Effect of reaction temperature of HZSM-5 on cumulative of products distribution.

4.5.1.3 Effect from temperature of pure HDPE.

The reaction temperature of HZSM-5 condition was around 440 °C as shown figure 22(a). The highest yield of naphtha was obtained at 650 °C which was 38.85 wt%. Pure HDPE condition was obtained higher in heavy oil such as diesel the other conditions at every temperature as shown in figure 23.

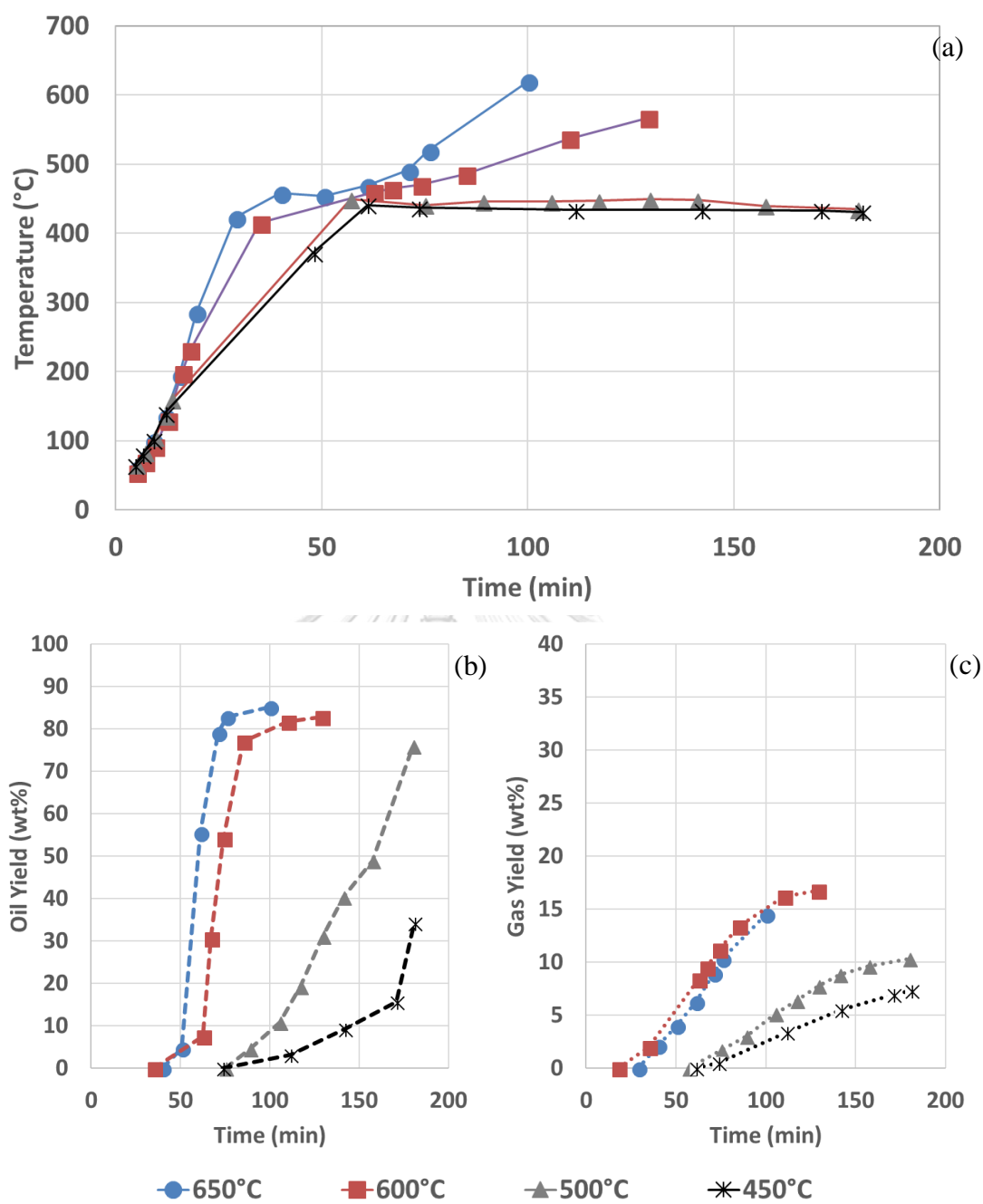


Figure 22 Effect of temperature of pure HDPE on reaction temperature (a), oil products yield (b), and gas products yield (c).

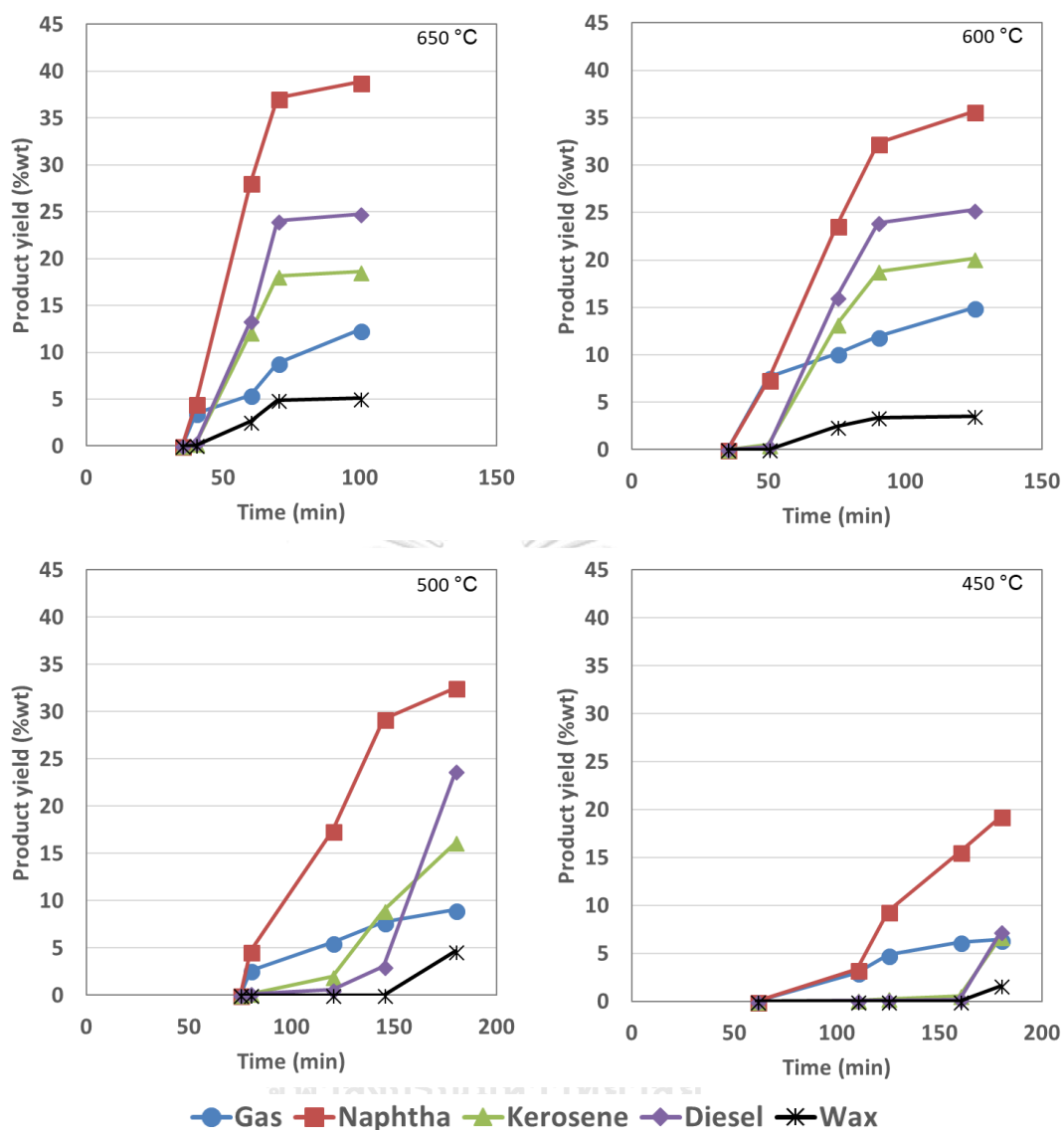


Figure 23 Effect of reaction temperature of pure HDPE on cumulative of products distribution.

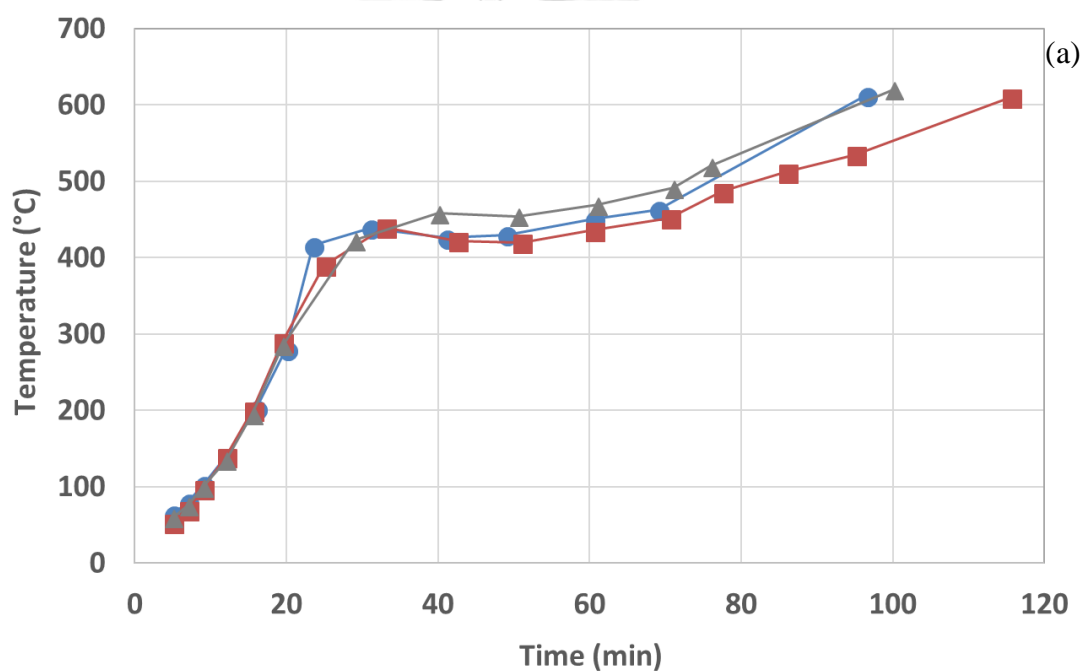
4.5.2 Effect of types of catalyst on pyrolysis reaction.

4.5.2.1 Effect on reaction temperature and products rate.

The blended HDPE with about 3 wt% of catalyst were used to study in this section. HZSM-5 had strong effect on reaction temperature that had lower in reaction temperature as shown in figure 24(a). While Cat A and pure HDPE had the similar characteristic of reaction temperature. HZSM-5 reaction temperature was lower than Cat A and pure HDPE reaction temperature around 30-40 °C. These lower temperatures might be form heat loss from cracking HDPE to light oil and gas products. The results of gas rate of HZSM-5 show in figure 24(b) that higher than another. However, Cat A had effect on reaction time that faster reaction than HZSM-5 and pure HDPE conditions as shown in figure 24(a). The condition at 650 °C was the complete of pyrolysis reaction that were monitored using temperature in the reactor. The pyrolysis of HDPE reaction temperature was around 400-450 °C that the same as the other author reported. (Bagri

and Williams 2002, Onwudili, Insura et al. 2009, López, De Marco et al. 2011) Cat A condition was faster in reaction time that means it consumed lower heat for cracking reaction and produced lower in gas products. While HZSM-5 and pure HDPE were used longer reaction time that was higher heat consumed.

The pure HDPE condition obtained the highest oil products yield as shown in figure 24(b). The oil products yield was reduced when the catalysts were used. It was higher in pure HDPE, Cat A, and HZSM-5 condition, respectively. In contrast of gas products yield, HZSM-5 condition was the highest gas products yield as shown in figure 24(c). The gas production was influenced from cracking ability of catalyst. HZSM-5 has higher acidity than Cat A that will produce higher gas products rate. HZSM-5 had been studied in a many author because it has high acidity catalyst and suitable for cracking reaction. The high acidity of HZSM-5 has highly effect on cracking reaction of polymer to smaller hydrocarbons. (Bagri and Williams 2002, Williams and Brindle 2003, López, De Marco et al. 2011)



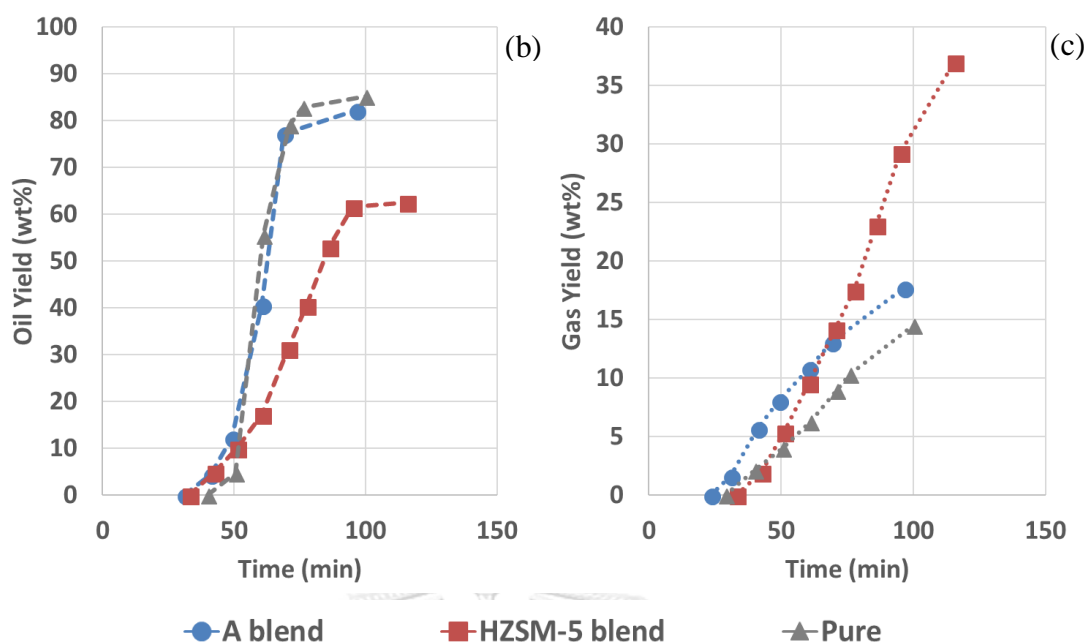


Figure 24 Effect of catalysts on reaction temperature (a), and oil products yield (b), gas products yield (c).

4.5.2.2 Effect on conversion and products yield.

The conversion and products yield of catalytic pyrolysis process show in table 12. The products at 600°C and 650°C were collected by the last product at different time that depended on pyrolysis complete time. The residence time of each experiment was shown in this section. There were no differences in solid product obtained at complete reaction. The results show that HZSM-5 blend condition obtained the highest gas yield in every experiment. The pure HDPE obtained the highest oil yield and Cat A blend obtained in the middle rank of gas and oil yield. The generated of gas from HZSM-5 come from the high acidity of catalyst that lead to produce gas product. (López, De Marco et al. 2011) The oil yield was reduced with the increased of gas in the presence of catalyst. This result also reported in other studied. (Williams and Brindle 2003)

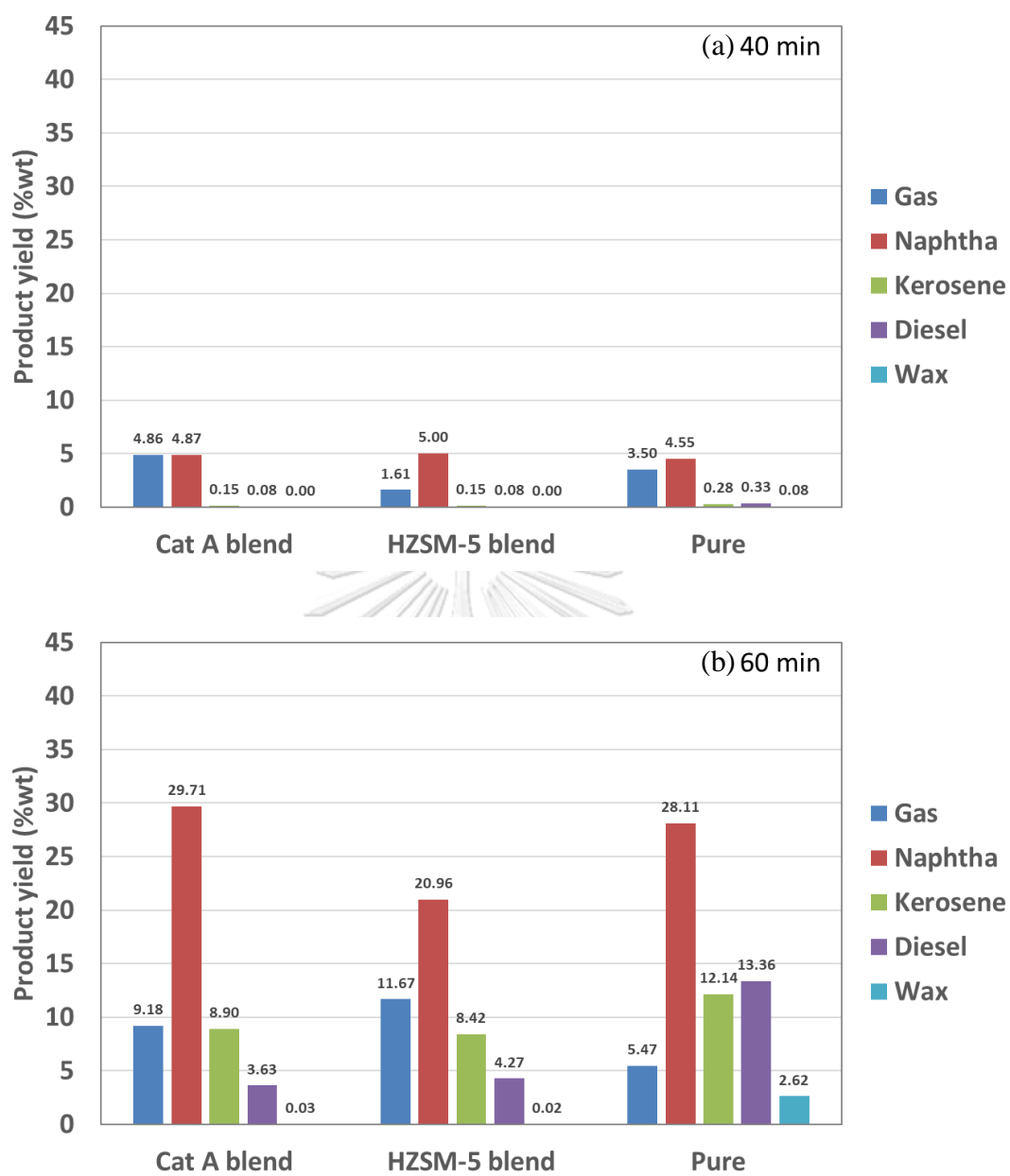
Table 12 Effect of temperature on conversion and product yield.

Condition	Yield (wt%)			Conversion	Reaction Time (min)
	Gas	Oil	Solid		
650 °C calibration temperature					
Cat A	17.7	82.2	0.1	99.90	96.5
HZSM-5	37.0	62.4	0.6	99.42	115.5
Pure	14.5	85.2	0.3	99.7	100

600 °C calibration temperature					
Cat A	19.8	80	0.2	99.81	121
HZSM-5	33.6	66.2	0.2	99.81	130
Pure	16.8	82.9	0.4	99.62	129
500 °C calibration temperature					
Cat A	15.4	63.7	20.9	79.13	180
HZSM-5	24.1	53.8	22.1	77.90	180
Pure	10.3	75.9	13.8	86.16	180
450 °C calibration temperature					
Cat A	11.1	31.7	57.1	42.87	180
HZSM-5	17.8	38.0	44.2	55.81	180
Pure	7.3	34.1	58.6	41.42	180

4.5.2.3 Effect on products distribution.

The effect of type of catalyst on cumulative of products distribution was investigated with the same condition at 650 °C. The results of products distribution show in figure 25. Both of catalyst were obtained lighter hydrocarbon than pure HDPE. HZSM-5 blend was obtained the highest yield of gas product around 30.93%wt and Cat A blend had the highest yield of light hydrocarbon (naphtha) around 43.33%wt. The high acidity of HZSM-5 led to produce high gas yield products. HZSM-5 had higher cracking reaction than Cat A from higher acidity. That similar result was reported from another author. from López, et al. studied ZSM-5 zeolite and compared with lower acidity catalyst. The obtained results were the greater of oil and gas products when higher acidity catalyst was used. Williams, et al. studied the pore size and acidity of zeolite catalyst in pyrolysis of scrap tyres. The obtained results were the pore size of catalyst which influenced products distribution and selectivity and acidity which was active sites of catalyst surface. Miguel, et al. investigated effect of pore size and acidity of catalyst. The pore size of catalyst had influence to range of products. (Williams and Brindle 2003, Miguel, Aguado et al. 2006, Hernández, Gómez et al. 2007, López, De Marco et al. 2011)



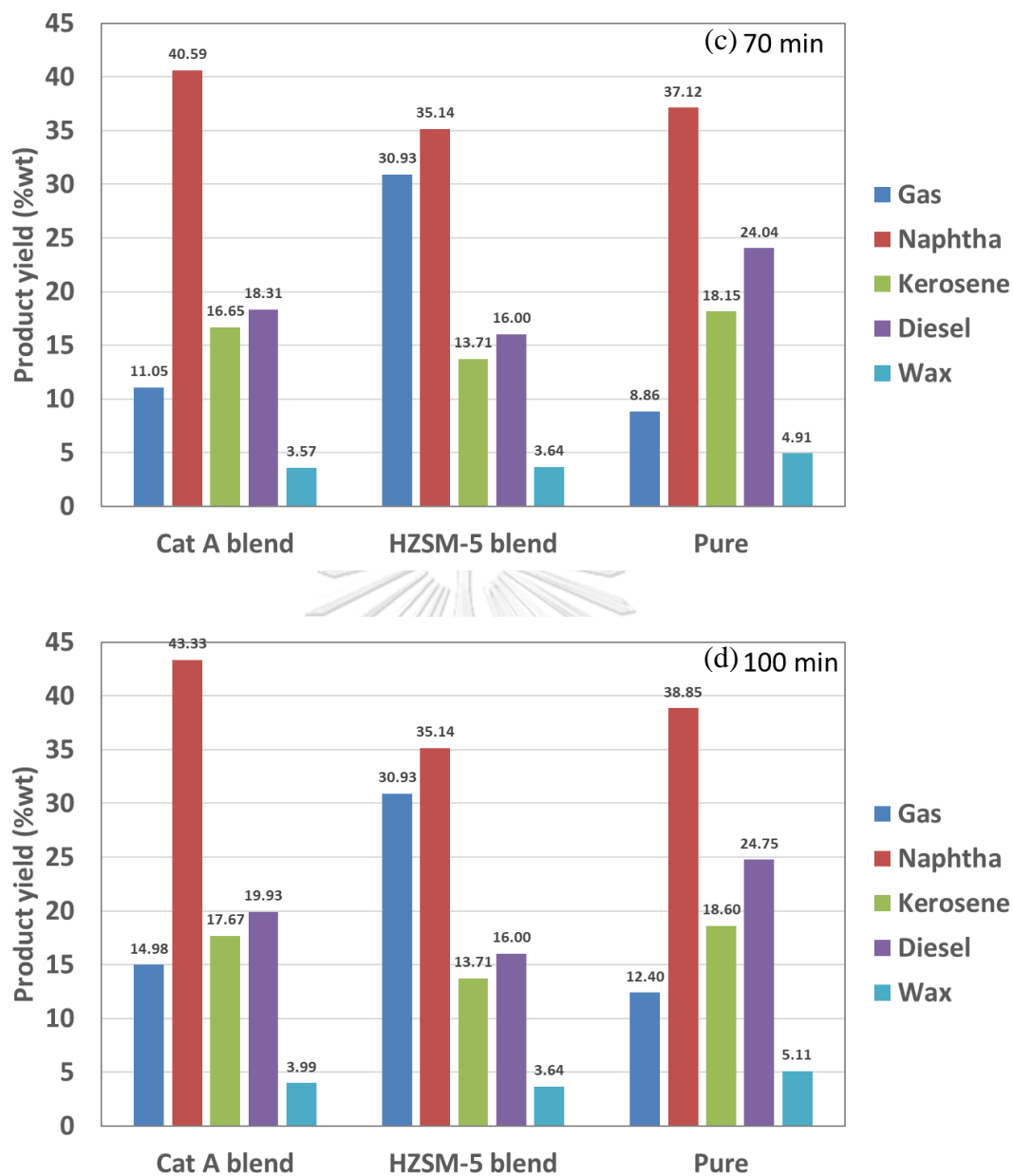


Figure 25 Effect of type catalysts on cumulative of products distribution at 650 °C for 40min(a), 60min(b), 70min(c), 100min(d).

4.5.3 Effect of catalyst dispersion on conversion and product distribution

4.5.3.1 Effect on conversion and product yield

The conversion and product yield of Cat A and HZSM-5 show in figure 26, 27. The difference of dispersion of catalyst in HDPE was studied by using the conditions of Cat A and HZSM-5: HDPE and catalyst were not mixing; Cat A mixing and HZSM-5 mixing: HDPE and catalyst were mixing with rotor around 400 rpm; Cat A blend and HZSM-5 blend: HDPE and catalyst were blended with extruder. The other conditions were the similar such as temperature at 650 °C, pressure at 2.5 bar and reaction time. The effect of catalyst dispersion of cat A show in figure 26. There were not significant different from catalyst dispersion of Cat A on conversion and product

yield. However, the catalyst dispersion of HZSM-5 had strong effect on conversion and gas products yield. At the same conversion, HZSM-5 blend had higher gas product yield at 37% gas. Therefore, the HZSM-5 blend condition was higher in cracking reaction than the other dispersion.

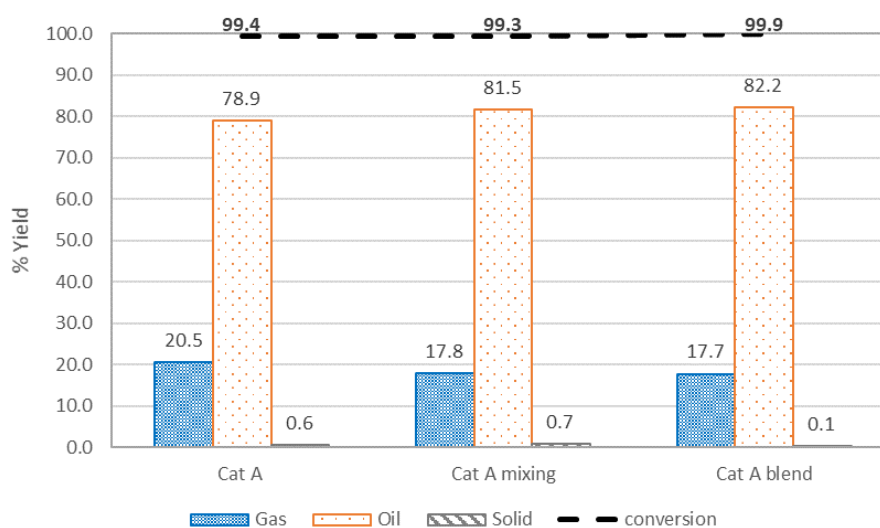


Figure 26 Effect of catalysts dispersion on selectivity and conversion of Cat A at 650 °C.

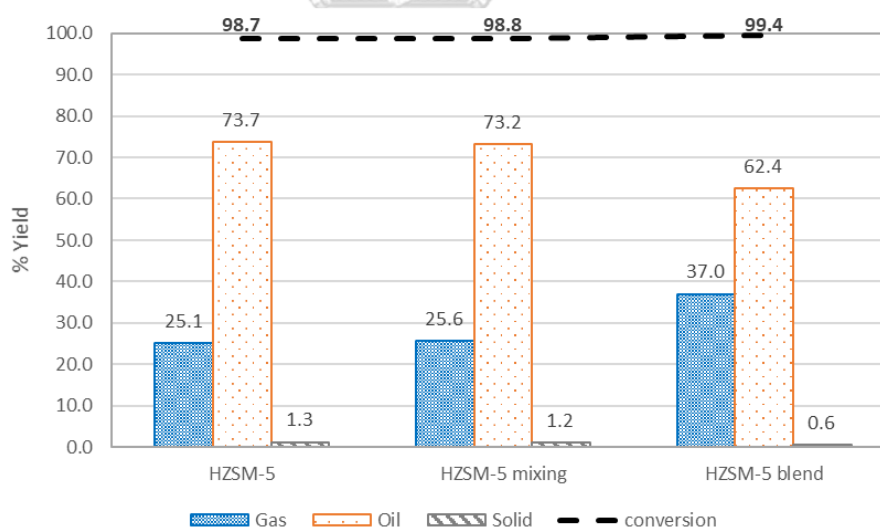


Figure 27 Effect of catalysts dispersion on selectivity and conversion of HZSM-5 zeolite at 650 °C.

4.5.3.2 Effect on products distribution

The results in figure 28, 29 show the cumulative of products distribution of Cat A and HZSM-5 dispersion. The results of Cat A blend had the highest yield of light hydrocarbon compared with other dispersion. Naphtha was the main component of light hydrocarbon in Cat A products distribution that the highest around 43.33 %wt for Cat A blend. The results of HZSM-5 blend had the highest yield of gas products. HZSM-5 mixing condition obtained the highest yield of naphtha around 47.99 %wt. However, the higher of gas yield in HZSM-5 blend than HZSM-5 mixing means the higher of cracking reaction that was occurred in HZSM-5 blend condition. The catalyst blended with HDPE had better results of catalyst activity. These results were better than the mixing condition because waxy state before oil formation in pyrolysis of HDPE as shown in figure 32 was semi-solid state. (Onwudili, Insura, & Williams, 2009) That was difficult to make the dispersion by mixing. So, the blended condition could be effective that the other condition. Figure 30 show the concentration of products distribution of oil products from Cat A that separately reported by sampling time. The results of 40 min and 60 min in mixing and blend Cat A had higher concentration of light hydrocarbon oil than no mixing condition. But when the 70 min and 100 min were reached, the results of 70 min and 100 min condition were similar results in concentration of oil product. These results were also happened in the HZSM-5 condition that show in figure 31. The effect of catalyst dispersion had strong effect when the substance was in wax stage at short reaction time. But when reaction time was longer, the substance was in liquid stage and the effect of catalyst dispersion was depreciated.

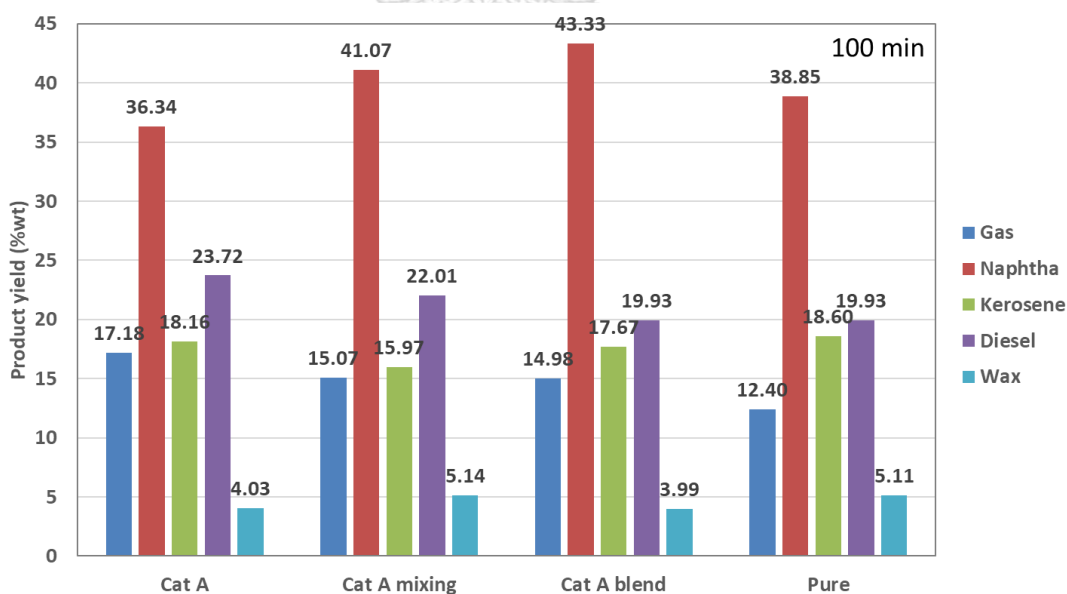


Figure 28 Effect of catalyst dispersion on cumulative of products distribution of Cat A and pure HDPE at 650 °C for 100 min.

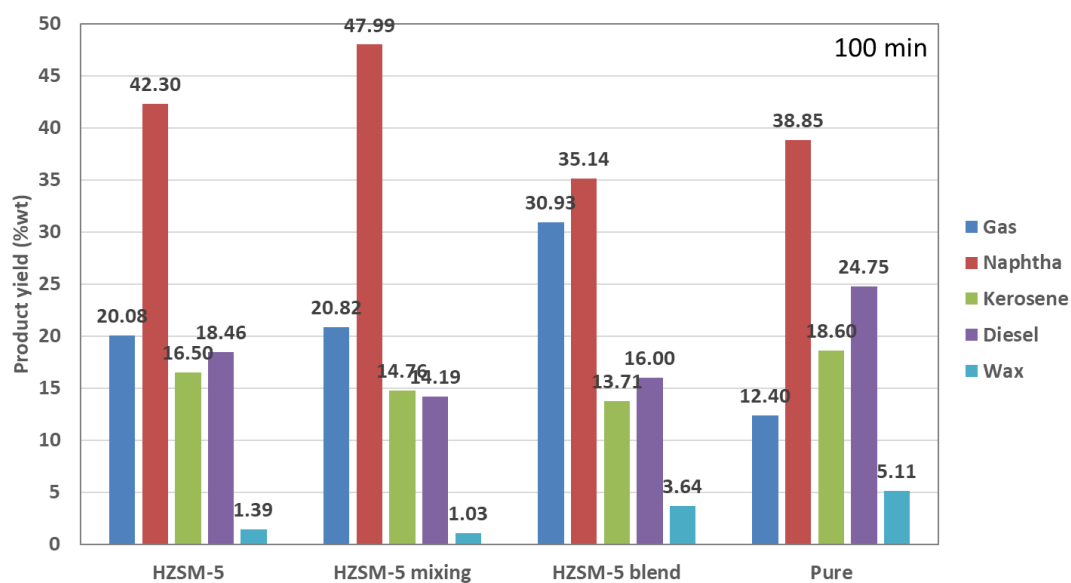
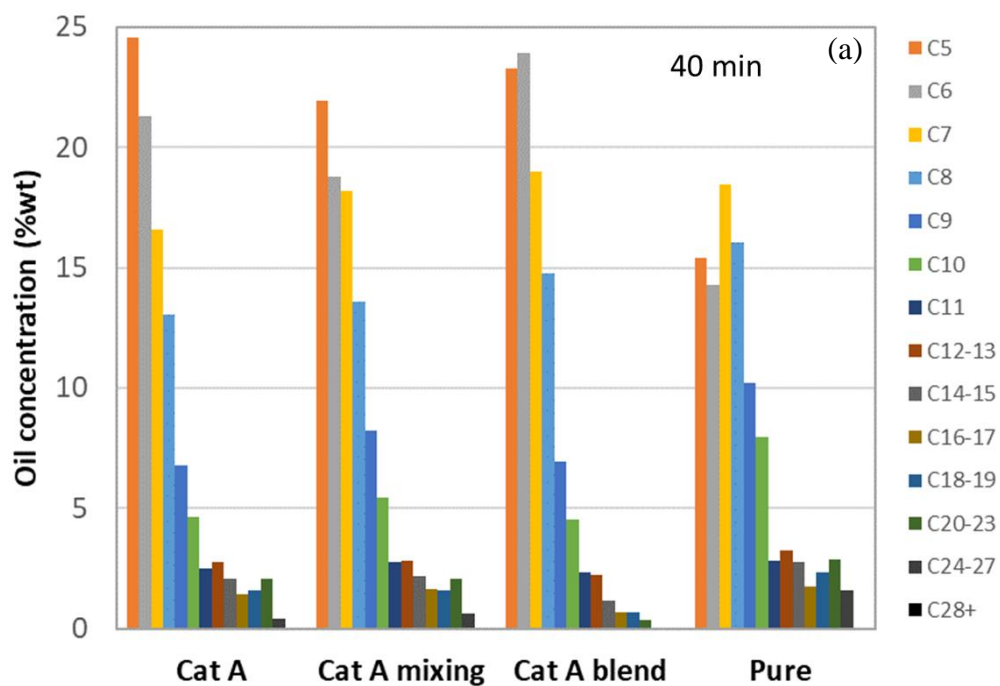
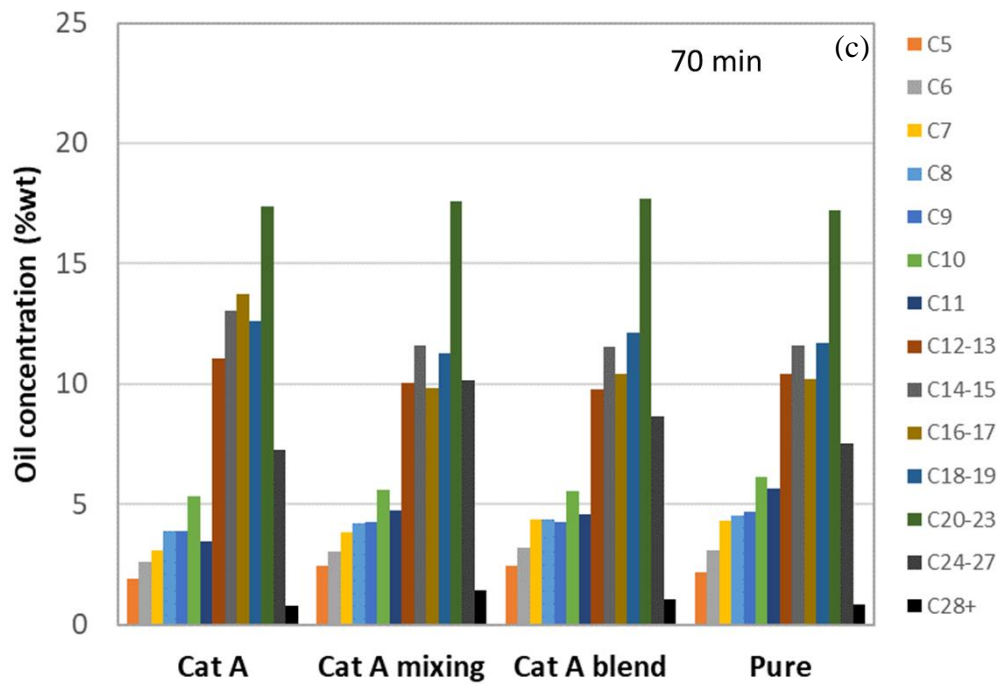
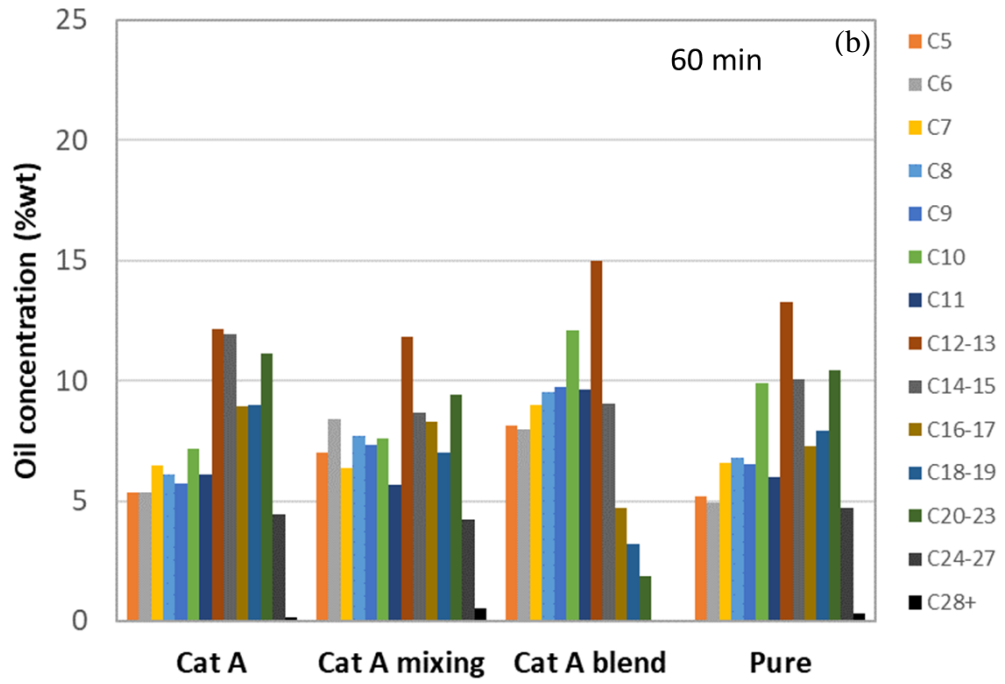


Figure 29 Effect of catalyst dispersion on cumulative of products distribution of Cat A and pure HDPE at 650 °C for 100min.





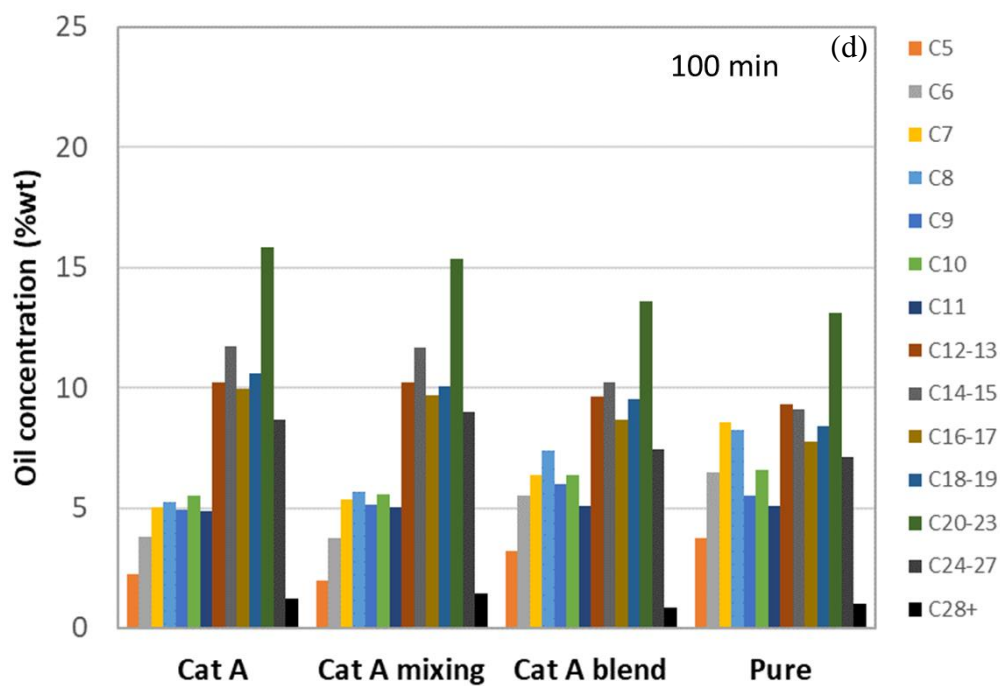
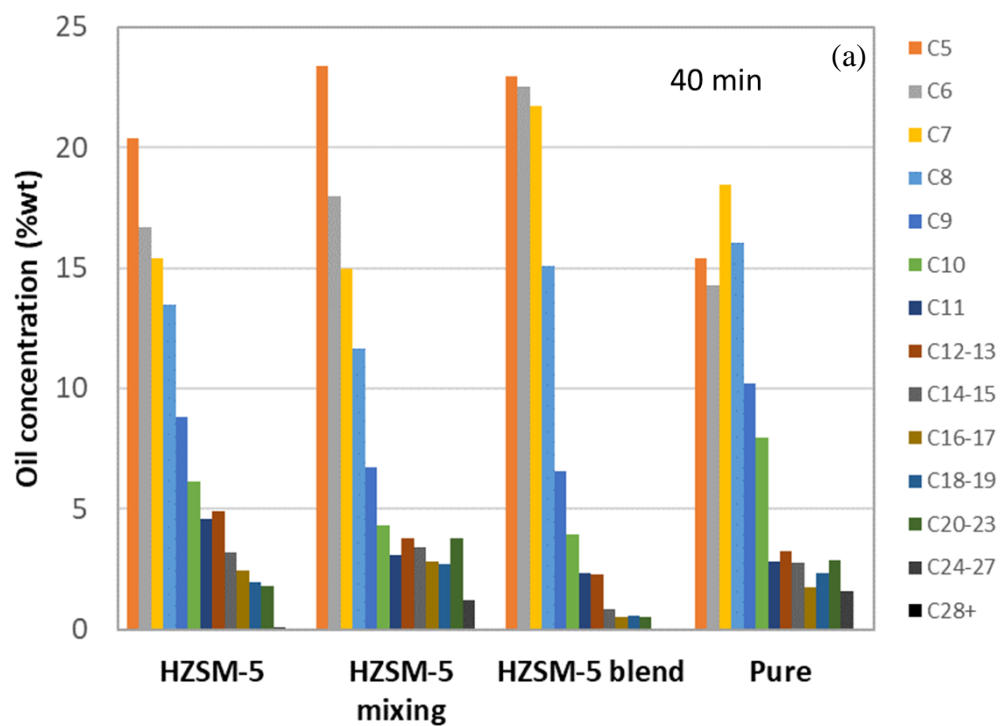
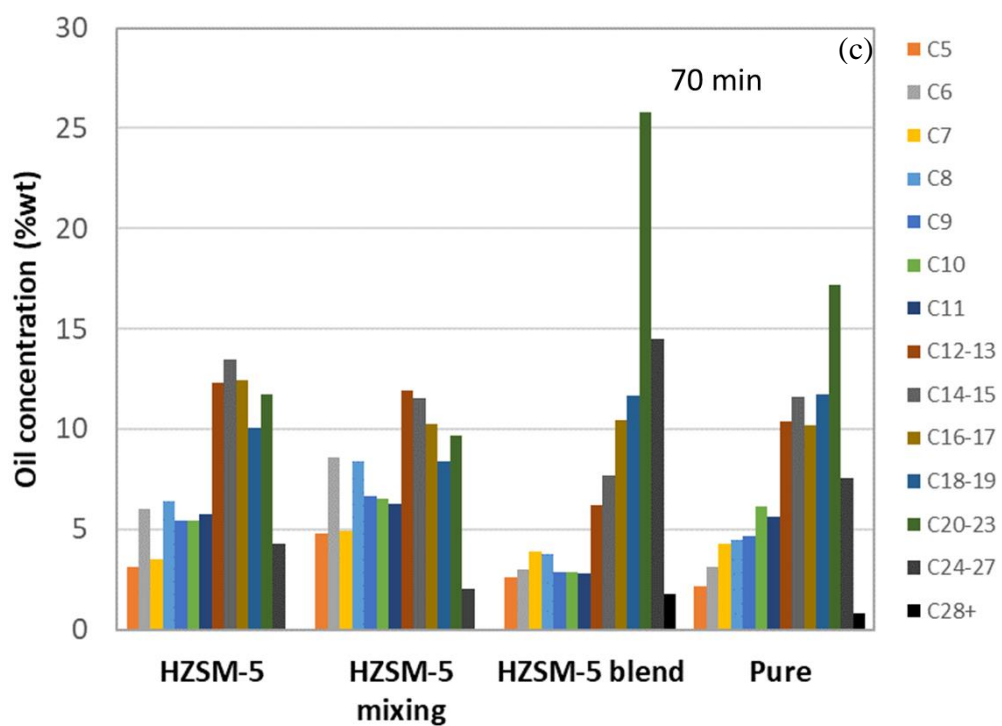
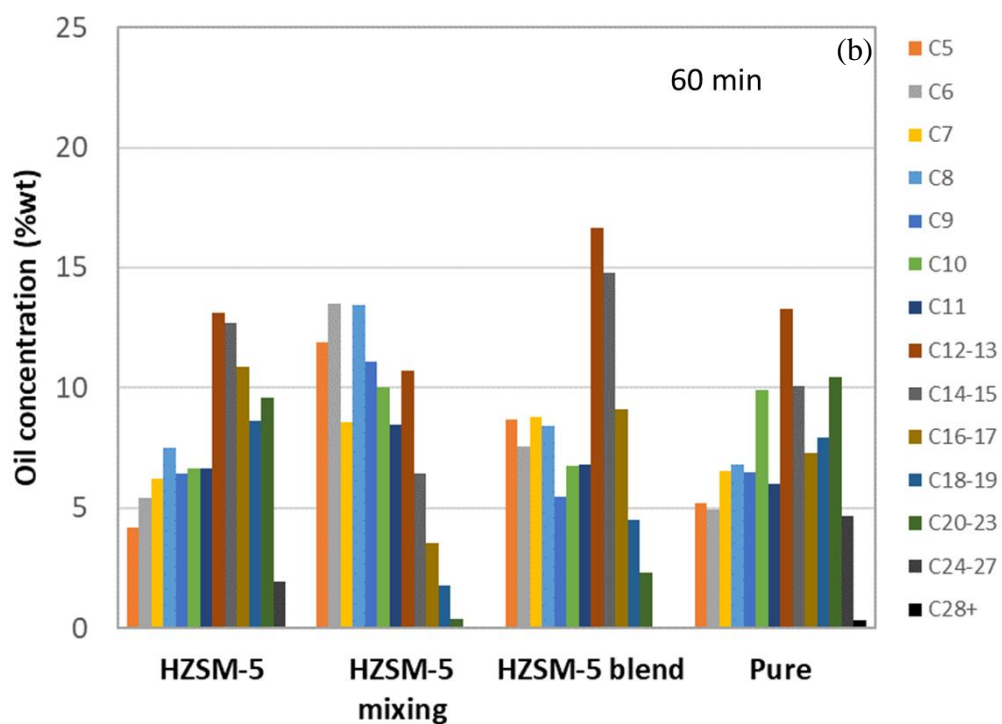


Figure 30 Effect of catalyst dispersion on oil products distribution of Cat A and pure HDPE at 650 °C for 40 min (a), 60 min (b), 70 min (c), 100 min (d).





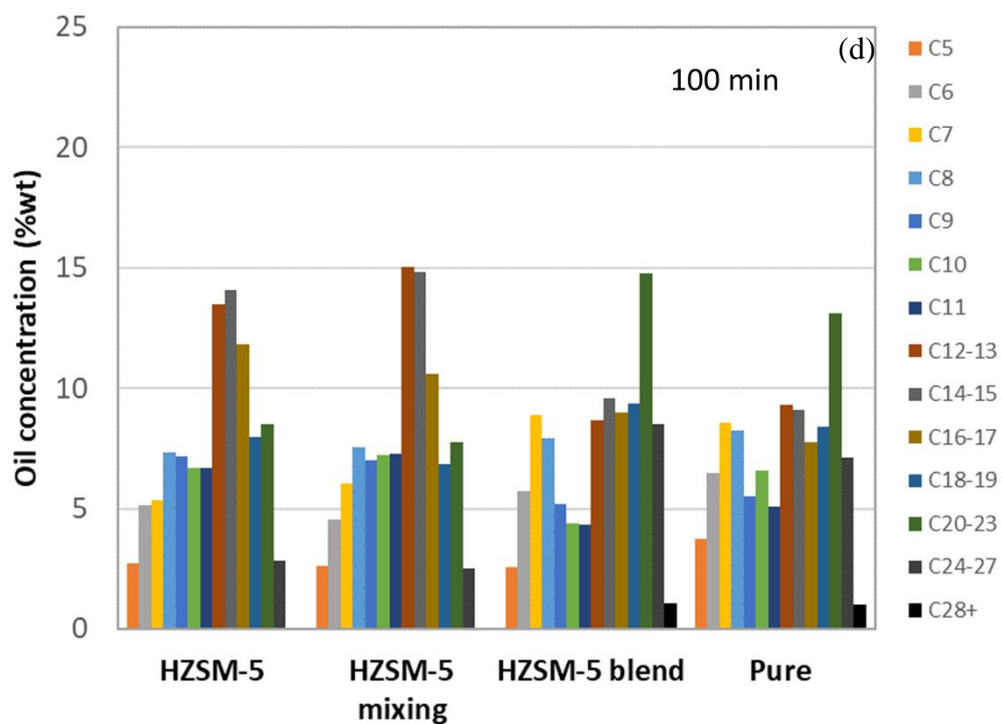


Figure 31 Effect of catalyst dispersion on oil products distribution of HZSM-5 and pure HDPE at 650 °C for 40 min (a), 60 min (b), 70 min (c), 100 min (d).

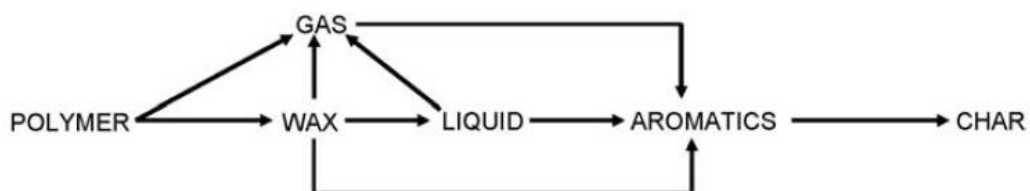


Figure 32 Kinetic scheme of plastic pyrolysis process.
(Onwudili, Insura, & Williams, 2009)

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study of catalyst type and dispersion on pyrolysis of HDPE was investigated in batch and semi-batch reactor system. The batch system was used a 80 mL autoclave reactor with a single filled raw material and opened products while the semi-batch system was used a 3 L stirred pressure reactor with continuous collecting products. The separate system in semi-batch was rapidly separated between oil and gas products while in batch system was separated after cooling down process. The obtained result of oil products composition in semi-batch system had higher in short-chain hydrocarbon. Because the increase of pressure and the high severity in batch system led to occur side reactions such as saturation, isomerization, cyclization, aromatization, alkylation, and polymerization. The semi-batch was suggested for pyrolysis reaction of HDPE to produce light hydrocarbon.

The two different surfaces of acidities of catalysts namely Cat A and HZSM-5 was studied. The Cat A has weak and strong acid sites with 200 m²/g surface area and 20 Å average pore diameter. The HZSM-5 was higher in strong acid sites with 550 m²/g surface area and 7 Å average pore diameter. HZSM-5 decreased reaction temperature around 30-40 °C when about 3% catalyst was added. These lower temperatures come from high consumed heat for cracking HDPE to gas products that had higher gas products rate. Cat A was used lower heat consumption to complete pyrolysis reaction. Moreover, both of catalysts were obtained lighter hydrocarbon than pure HDPE. HZSM-5 blend was obtained the highest yield of gas product around 30.93% wt and Cat A blend had the highest yield of light hydrocarbon (naphtha) around 43.33% wt. The higher acidity of HZSM-5 led to higher rate of cracking reaction and produce higher gas yield products than Cat A.

The difference of dispersion of catalyst in HDPE was studied by using the conditions of HDPE and catalyst were not mixing, HDPE and catalyst were mixing with rotor around 400 rpm, HDPE and catalyst were blended with extruder. The results of Cat A blend had the highest yield of light hydrocarbon compared with other dispersion. The results of HZSM-5 blend had the highest yield of gas products. The catalyst blended with HDPE had better results of catalyst activity. Moreover, these results were better than the mixing condition because waxy state before oil formation in pyrolysis of HDPE was semi-solid state. That was difficult to make the dispersion by mixing. So, the blended condition could be effective than the other condition.

5.2 Recommendations

The effect of pressure in semi-batch system may have an effect on oil products destitution. In this experiment, they were used constant pressure at 2.5 bar to operate which was low pressure and related to commercial operation in pyrolysis process. The reaction at ambient pressure in semi-batch system has result with large hydrocarbon in oil product, which was waxy oil at room temperature. That might be from the shorter cracking time in pyrolysis reactor.

HZSM-5 was a better catalyst for cracking reaction. The activity of catalyst can replace by using higher amount in Cat A because it has lower price than HZSM-5.

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APPENDIX

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APPENDIX A: GC standard calculation for gas samples

GC gas standard was used to analyze amount of gaseous hydrocarbons from C1 to C4 by the following method in chapter 3. The injection volume was 0.5 mL per samples. The density of GC standard gas was estimated around 0.0396 g/cm^3 . The table A shows the result of calibration of GC standard gas that used to calculate the amount of hydrocarbon in samples gas.

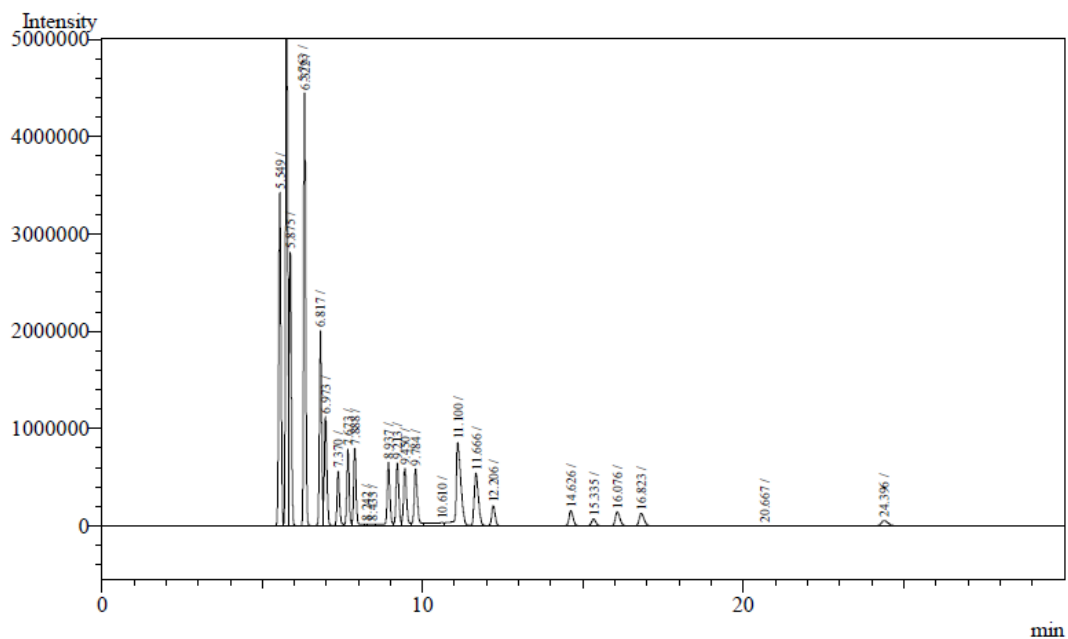


Figure A-1 GC gas standard curve.

Table A-1 GC standard for gaseous hydrocarbon calculation.

Peak#	Ret. Time	Area	Height	Weight (g)	Name	Factor (g/l area)
1	5.5515	17017356	3377335	0.000599	Methane	3.51963E-11
2	5.7655	26295087	5955973	0.000898	Ethane	3.41612E-11
3	5.87675	12706440	2749453	0.000419	Ethylene	3.29726E-11
4	6.32325	19507327	4362236	0.000659	Propane	3.37664E-11
5	6.81725	9499700	1946283	0.000314	Propylene	3.30811E-11
6	6.971	6365982	1080402	0.00013	iso-Butane	2.04548E-11
7	7.36875	3129936	397465	0.00013	n-Butane	4.16031E-11
8	7.67225	3999828	769546	0.000299	Propadiene	7.47434E-11
9	7.88675	4463826	773265	0.000194	Acetylene	4.3566E-11
					trans-2-	
10	8.8395	3021747	627751	0.000126	Butene	4.15994E-11
11	9.1385	3935685	623678	0.000126	1-Butene	3.19415E-11

12	9.38375	3888206	568644	0.000126	iso- Butylene	3.23293E-11
13	9.69275	4052334	565767	0.000126	cis-2- Butene	3.10199E-11
14	10.3805	1999372	736266	5.39E-05	iso- Pentane	2.69499E-11
15	11.08075	9148380	220365	5.39E-05	n-Pentane	5.88988E-12
16	11.65075	4870023	373949	0.000121	1,3- Butadiene	2.48848E-11
17	12.19375	1539804	199906	5.24E-05	trans-2- Pentene	3.4016E-11
18	14.603	1359330	147908	2.62E-05	2-Methyl- 2-Butene	1.92655E-11
19	15.3105	640368	67429	5.24E-05	1-Pentene	8.17878E-11
20	16.04175	1424115	137458	5.24E-05	cis-2- Pentene	3.67794E-11
21	16.787	1337905	122245	3.22E-05	n-Hexane Methyl	2.40528E-11
22	24.3375	791285.3	53230	0.000299	Acetylene	3.78124E-10
Total		1.41E+08	25856554	0.004889		

APPENDIX B: GC standard calculation for oil samples

The GC oil standard is mixed of normal chain hydrocarbon C6-C44 (17 components). It was used to calibration for estimate range of hydrocarbon in oil sample. The peaks of normal chain hydrocarbon were used to classify the hydrocarbon range.

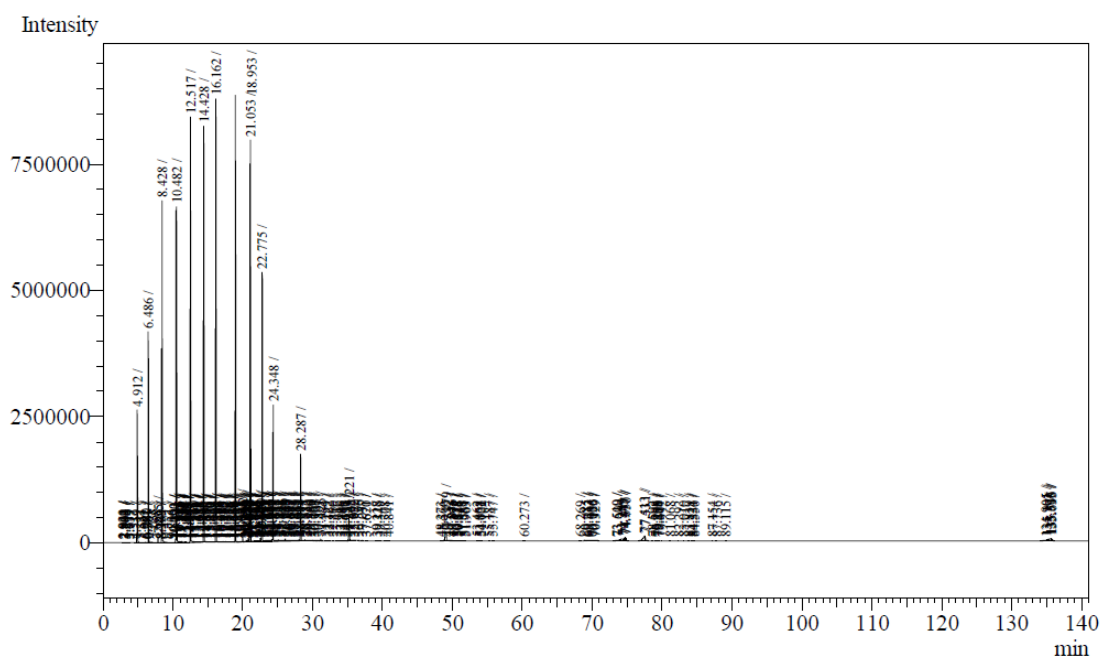


Figure B-1 GC oil standard curve.

Table B-1 GC standard for oil samples calculation

Component	Ret Time (min)
Tetratetracontane C44	135.6
Tetracontane C40	77.4
Hexatriacontane C36	74.8
Dotriacontane C32	49.2
Octacosane C28	35.3
Tetracosane C24	28.3
Eicosane C20	24.4
Octadecane C18	22.8
Hexadecane C16	21.1
Tetradecane C14	19.0
Dodecane C12	16.2
Undecane C11	14.5
Decane C10	12.5
Nonane C9	10.5
Octane C8	8.4
Heptane C7	6.5
Hexane C6	4.9

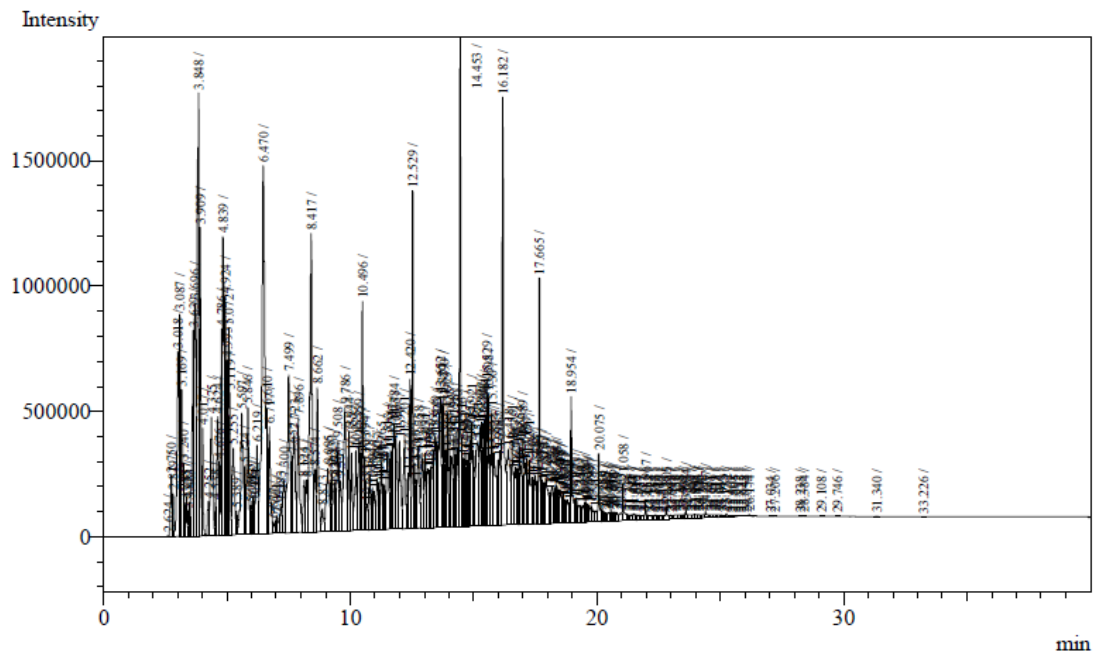


Figure B-2 Sample of GC oil curve.

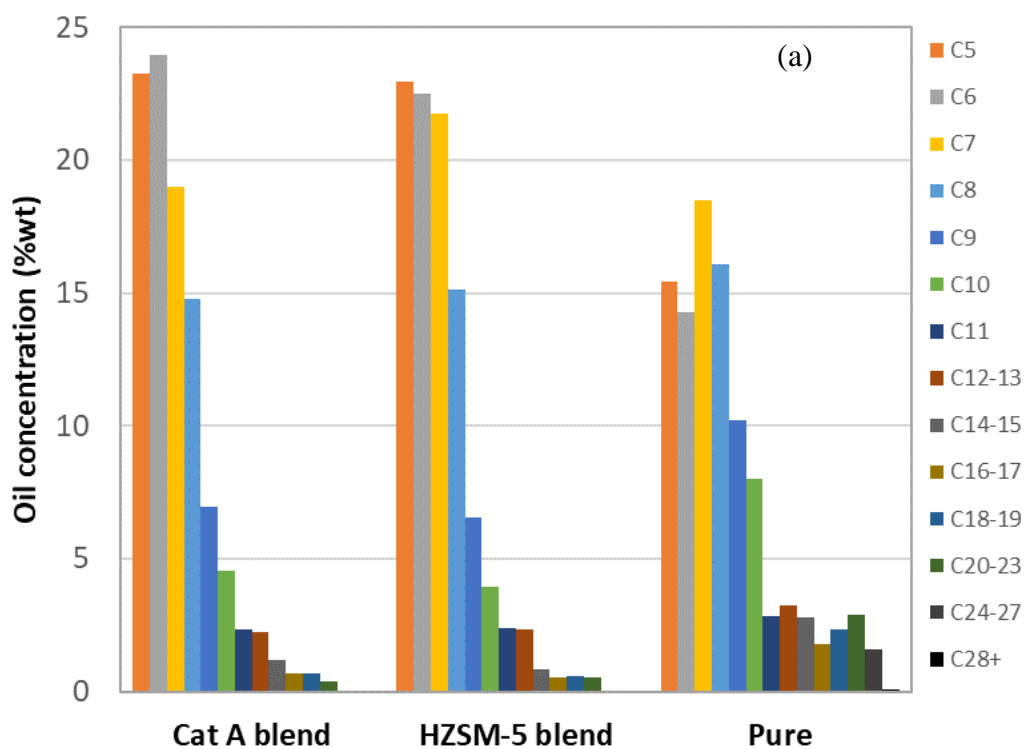
Example of GC oil calculation

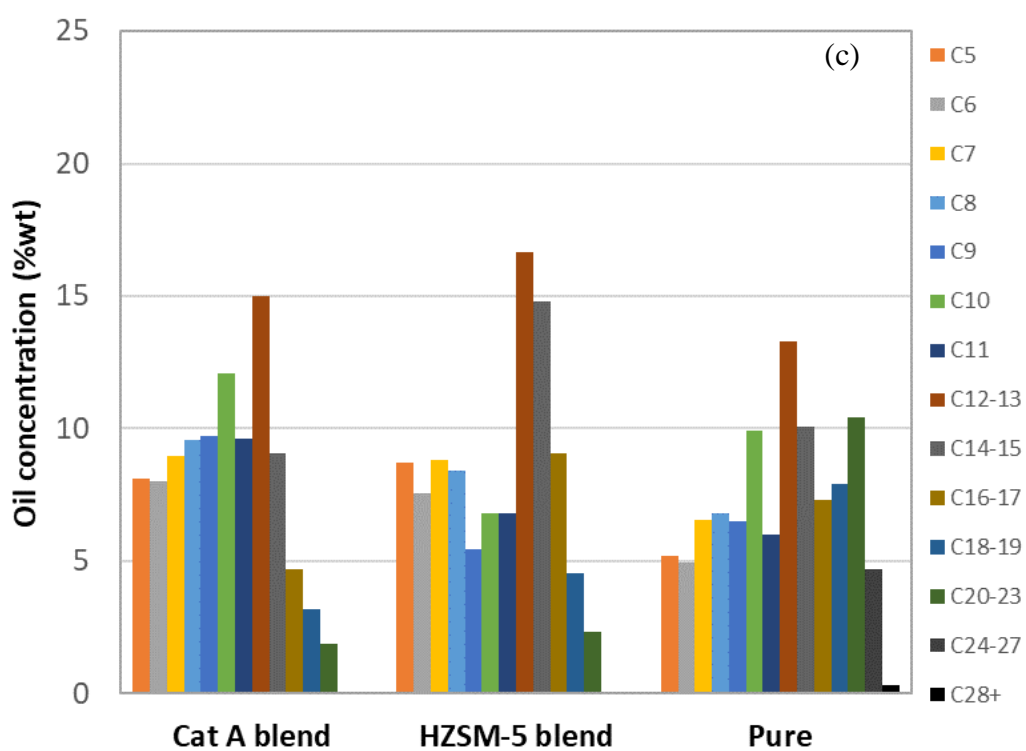
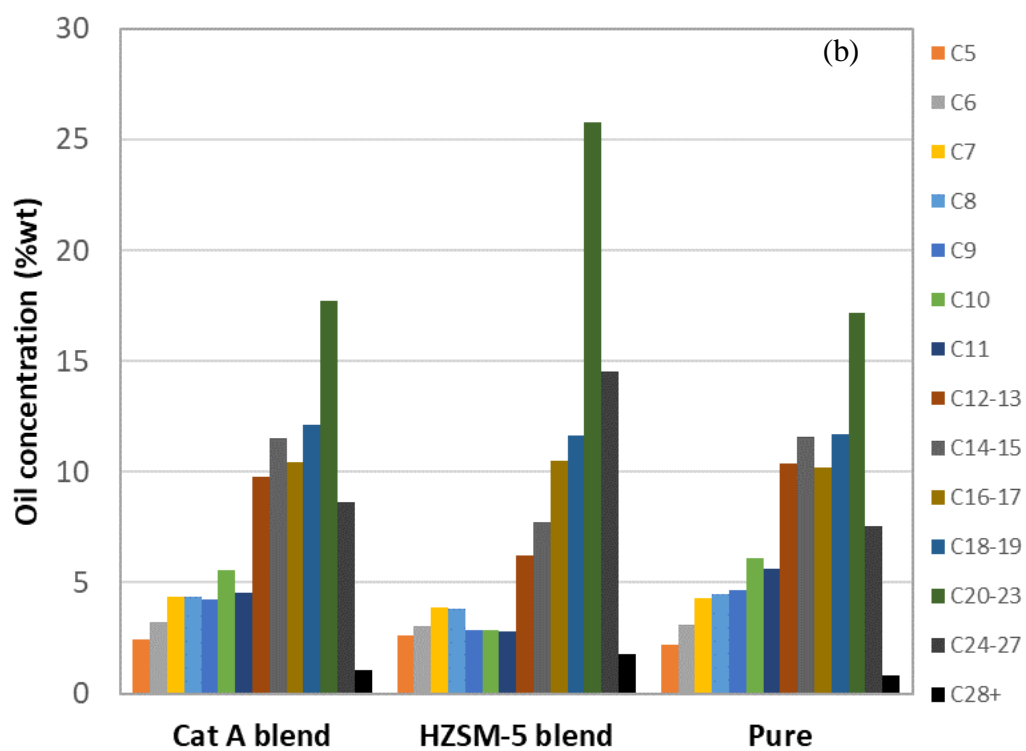
GC oil curve was used the carbon range in Table B-1 to classify carbon atom in hydrocarbon oil. The summation of area in specific time and above was used to determine concentration of carbon atom in % wt.

Component	Area 13_3	%wt 13_3
C5	48987003	17.87486
C6	34541030	12.60367
C7	19805766	7.226922
C8	33560400	12.24585
C9	23359901	8.52379
C10	38815937	14.16354
C11	34927925	12.74484
C12-13	29577929	10.79269
C14-15	6552067	2.390783
C16-17	1699107	0.619987
C18-19	1480603	0.540257
C20-23	722523	0.263641
C24-27	25139	0.009173
C28+	0	0
Total	2.74E+08	100

Appendix C: Oil products distribution

Oil product samples were measured for concentration of each oil components. The results show in figure C. Each graph shows concentration of oil product samples that were collected in each specific time and temperature.





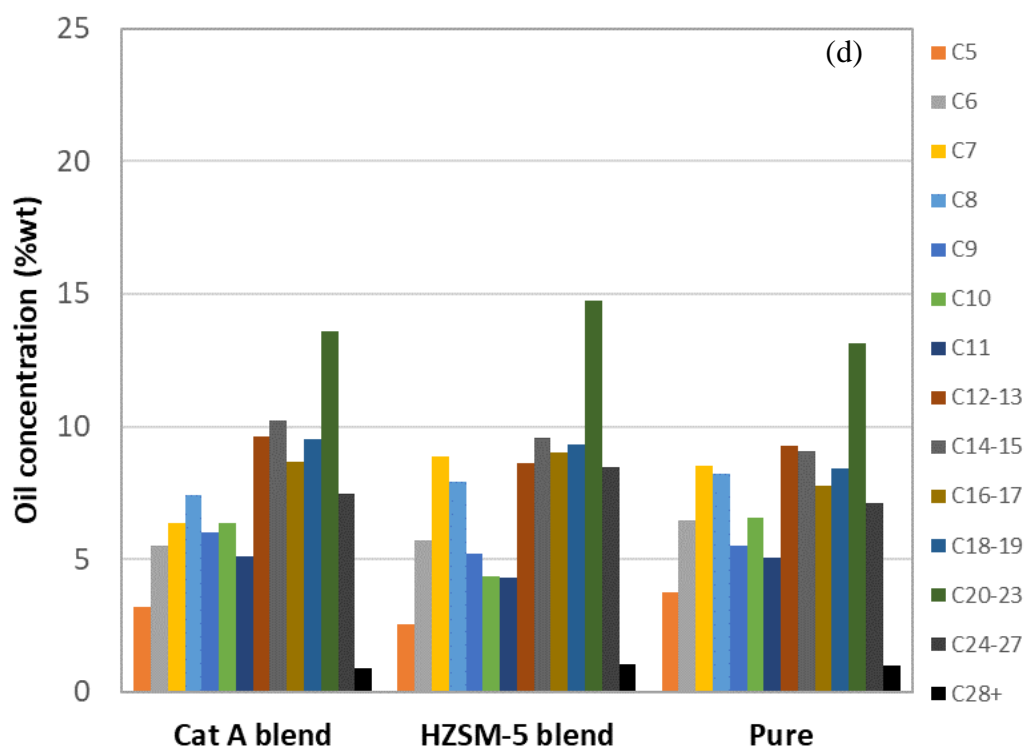
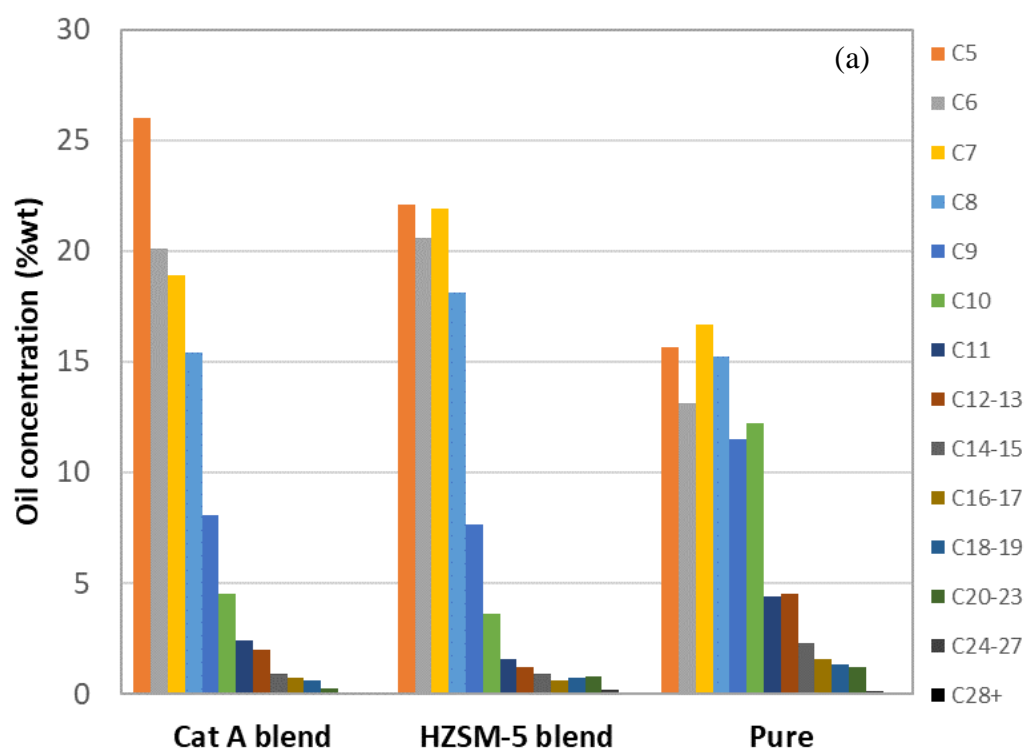
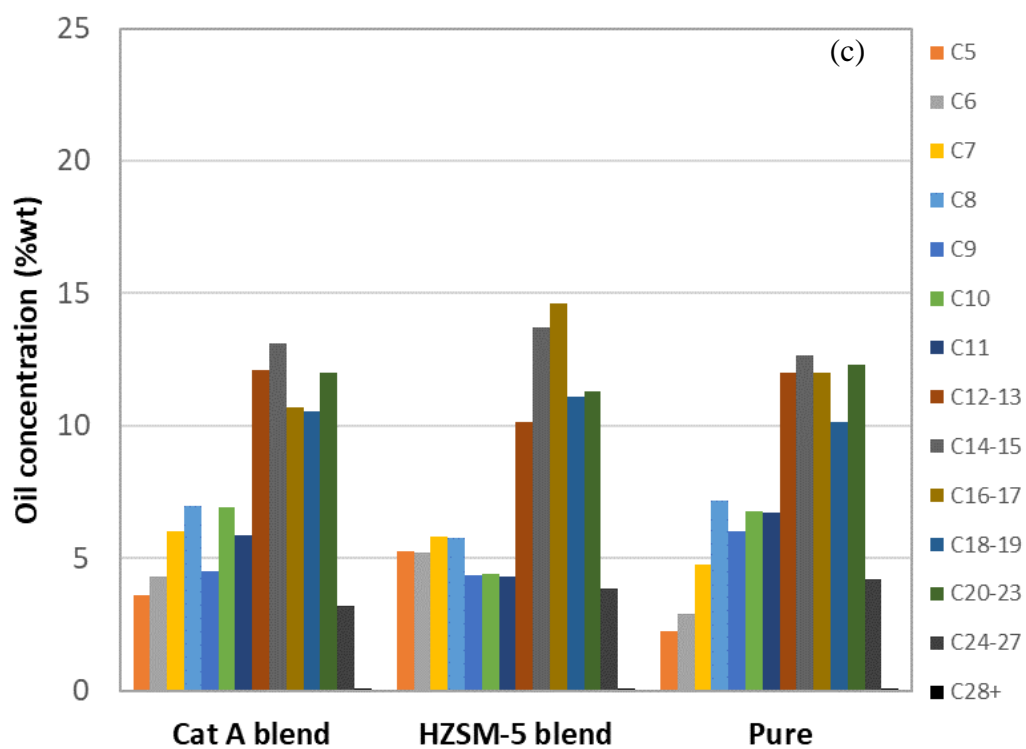
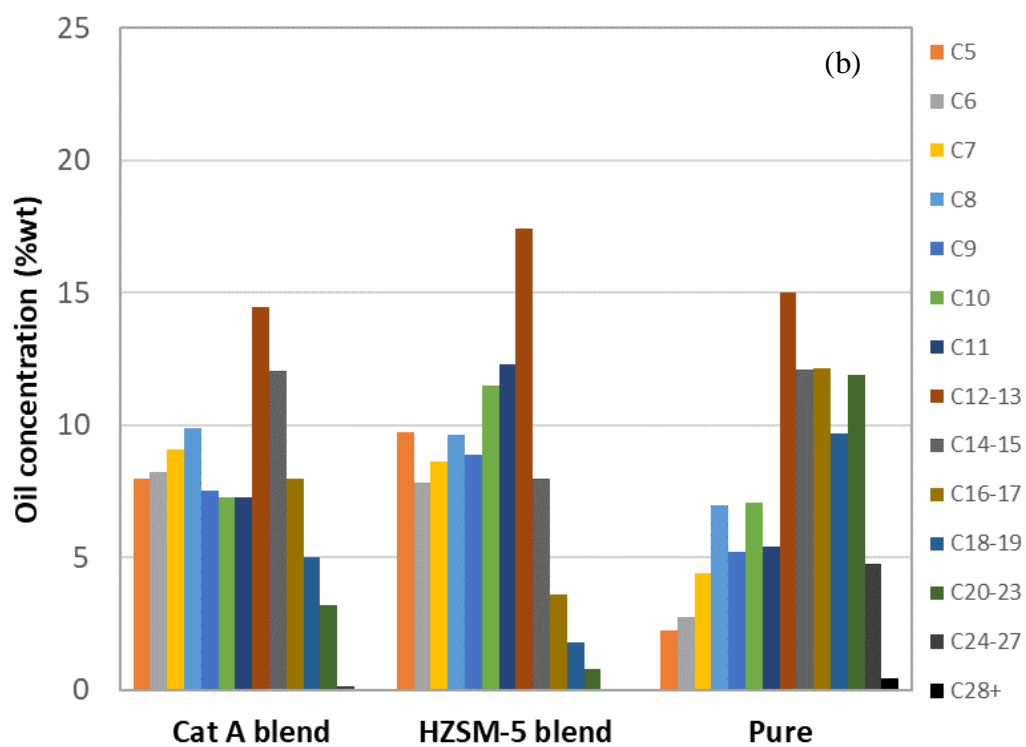


Figure C-1 Effect of catalysts on oil products distribution at 650 °C for 40 min (a), 60 min (b), 70 min (c), 100 min (d).





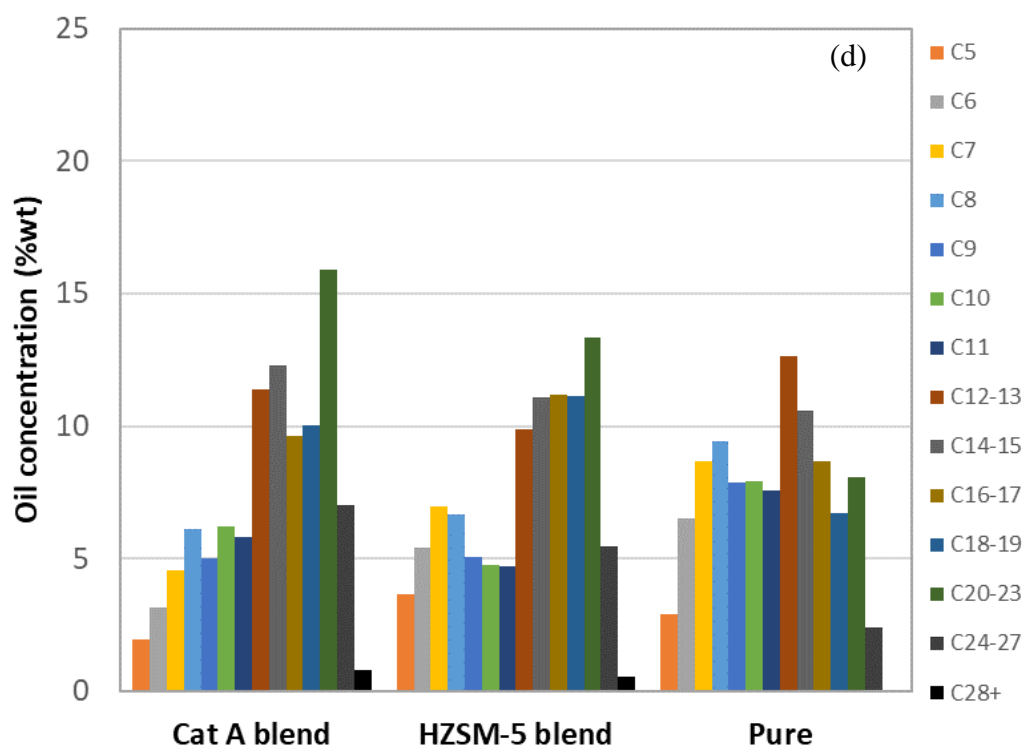
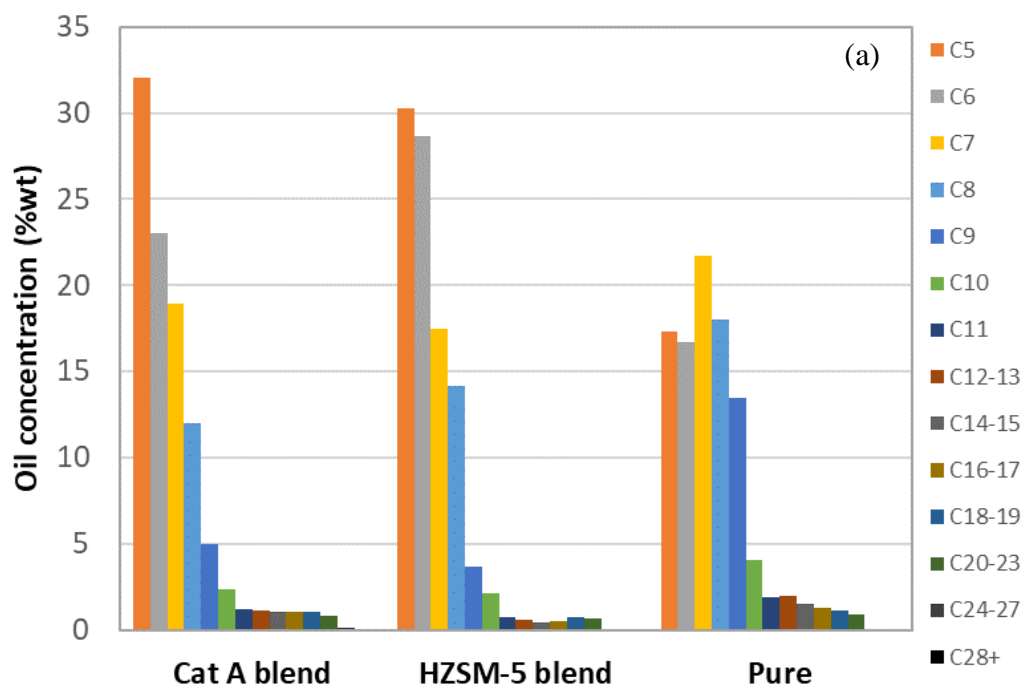
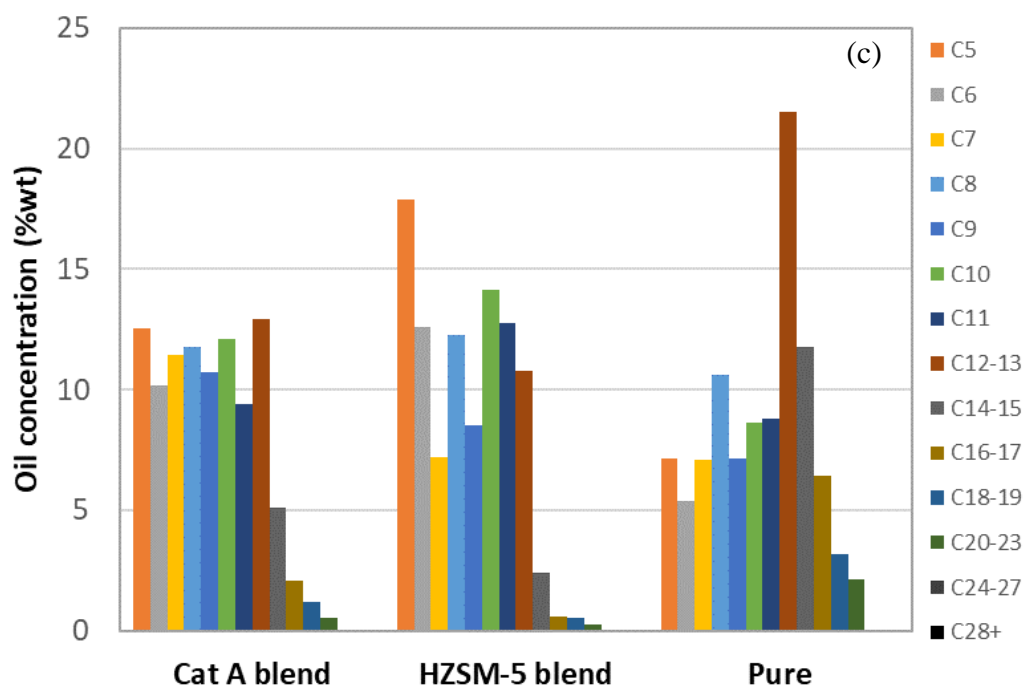
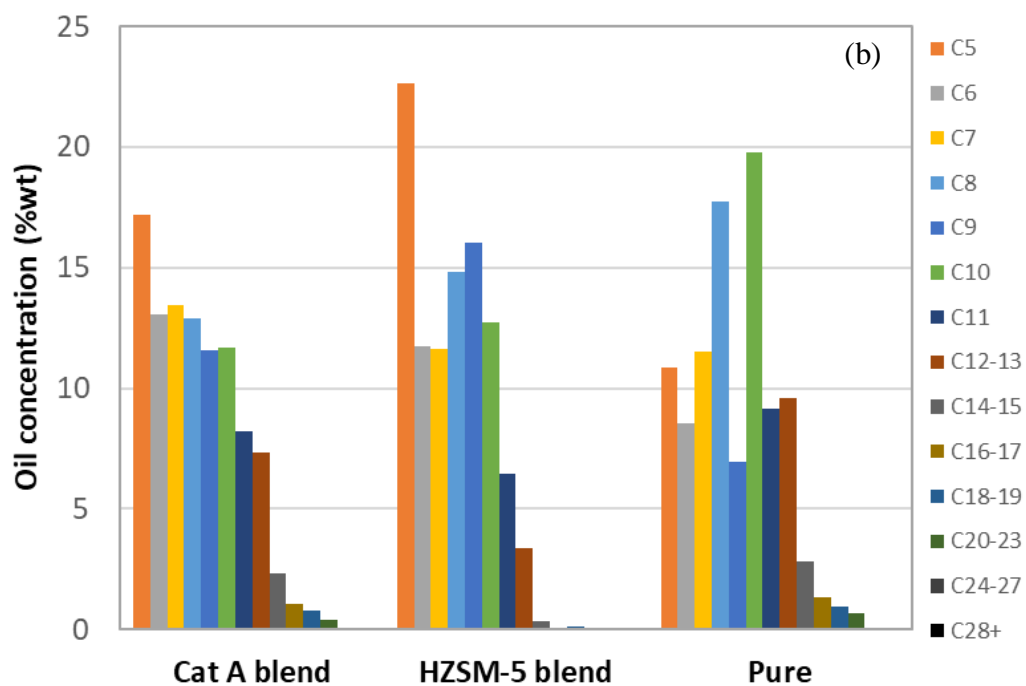


Figure C-2 Effect of catalysts on oil products distribution at 600 °C for 50 min (a), 75 min (b), 90 min (c), 125 min (d).





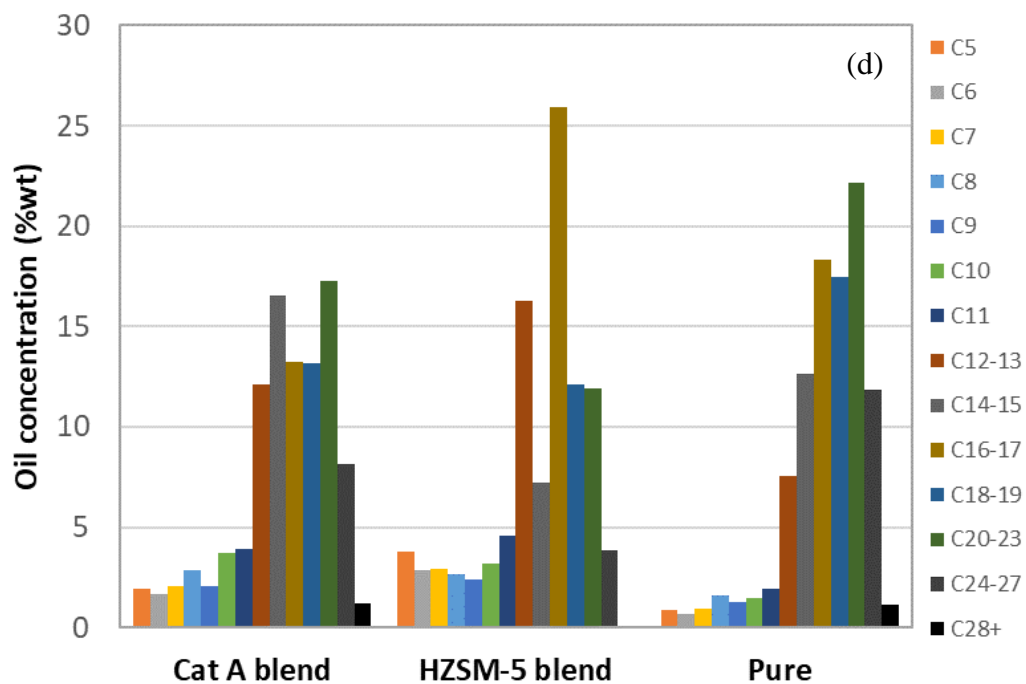
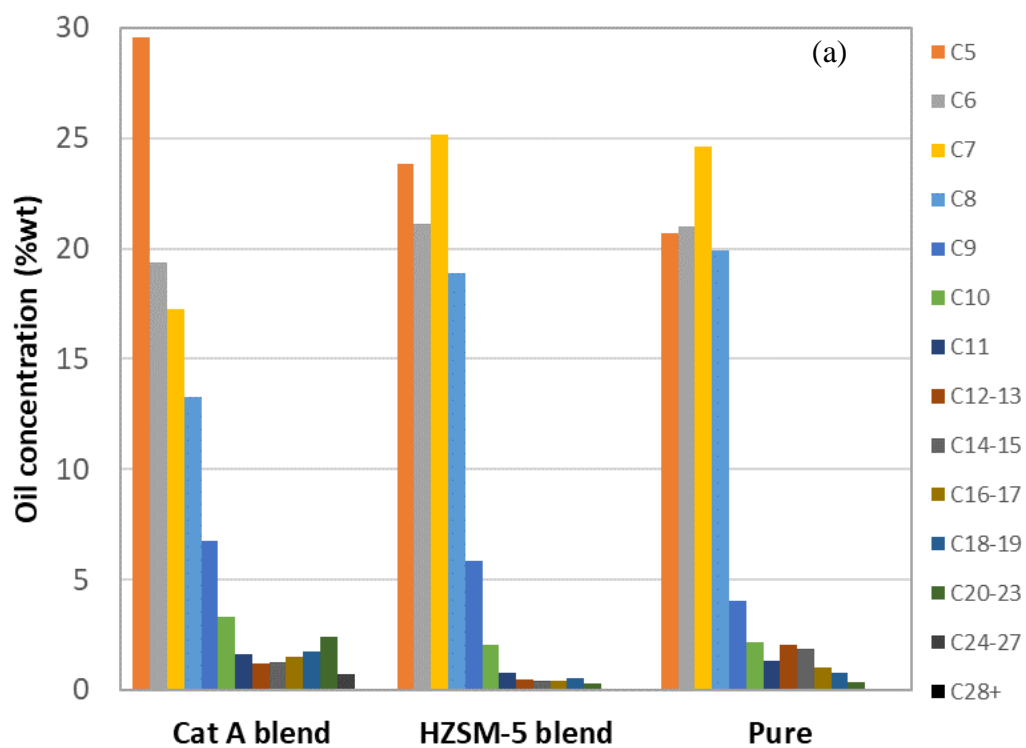


Figure C-3 Effect of catalysts on oil products distribution at 500 °C for 80 min (a), 120 min (b), 145 min (c), 180 min (d).



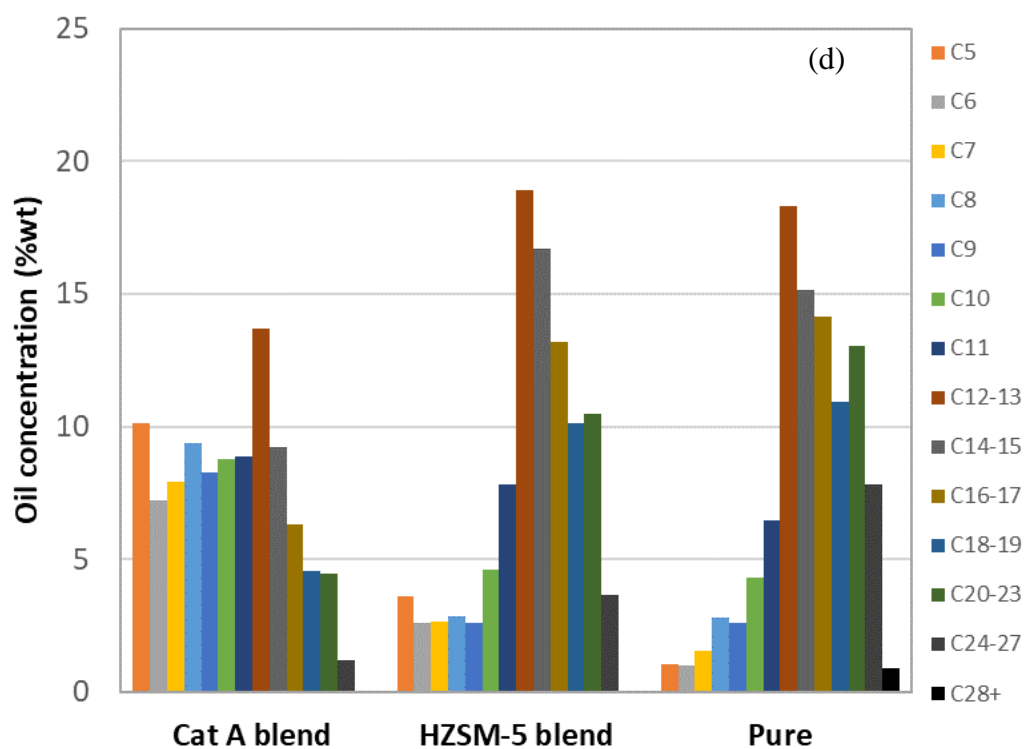
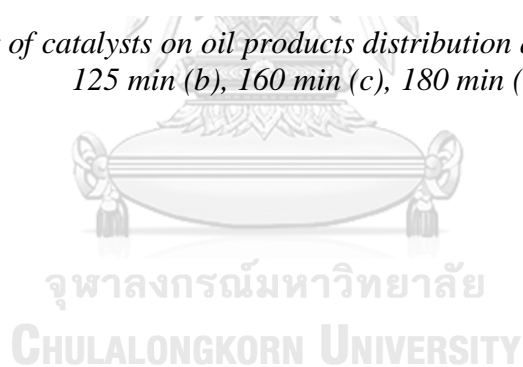
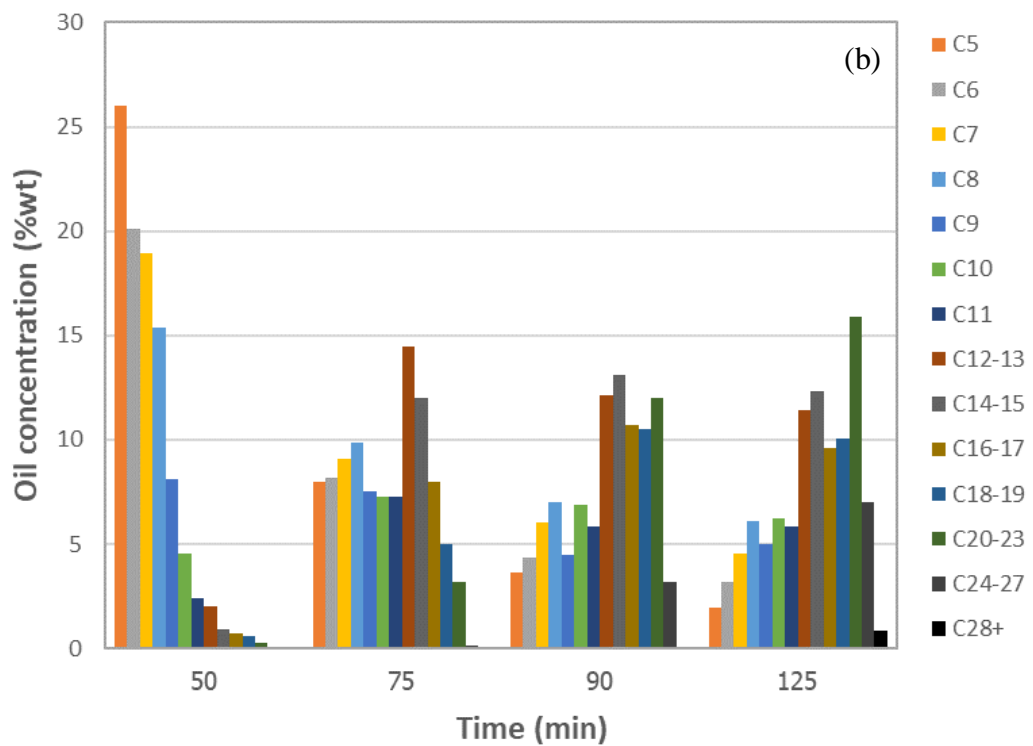
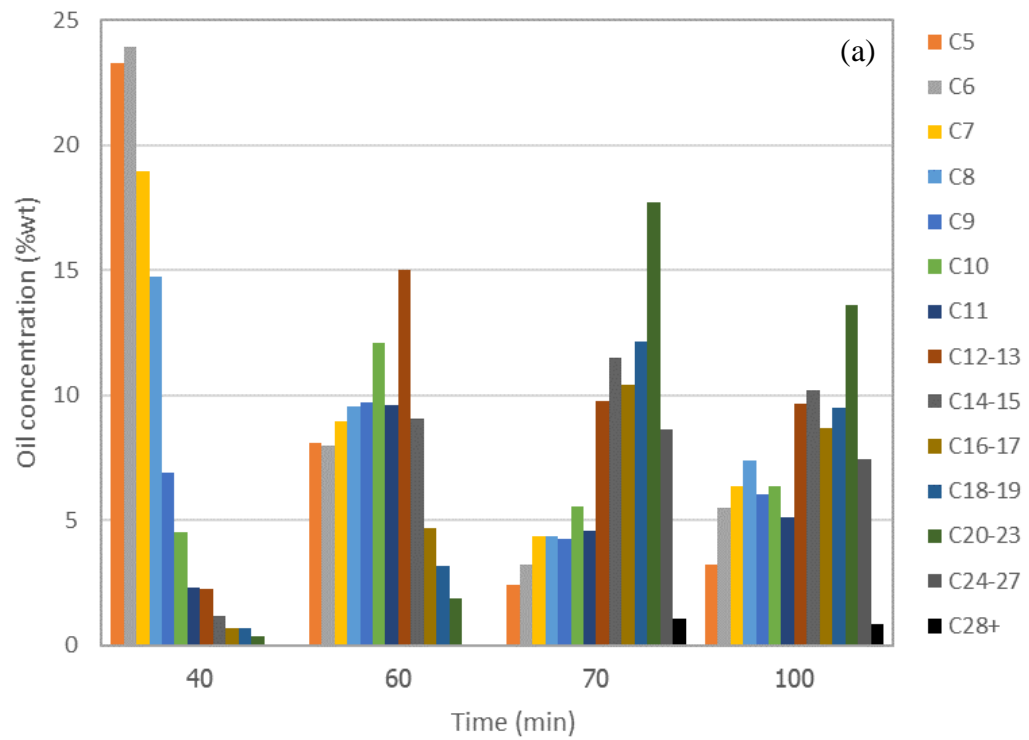


Figure C-4 Effect of catalysts on oil products distribution at 450 °C for 110 min (a), 125 min (b), 160 min (c), 180 min (d).





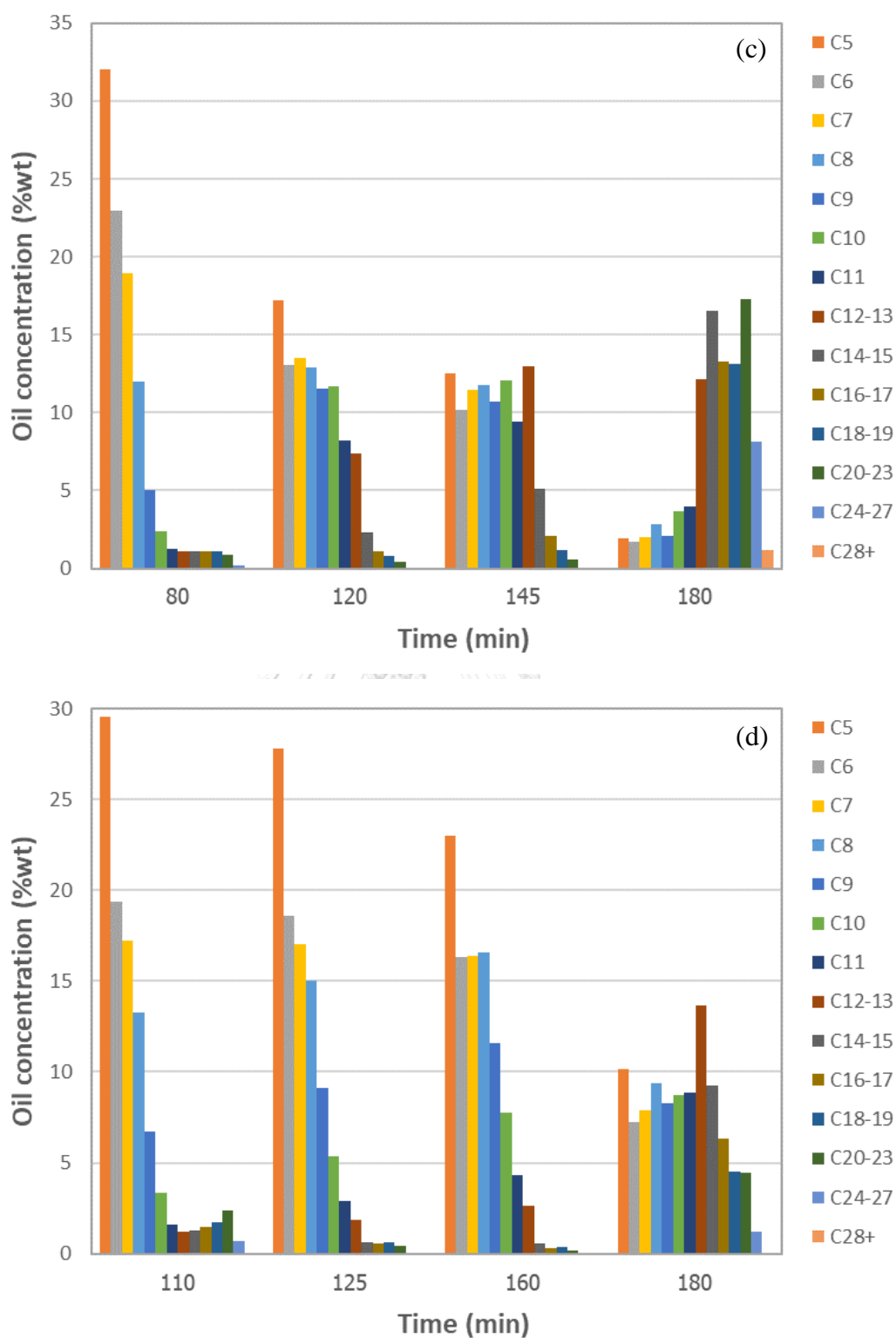
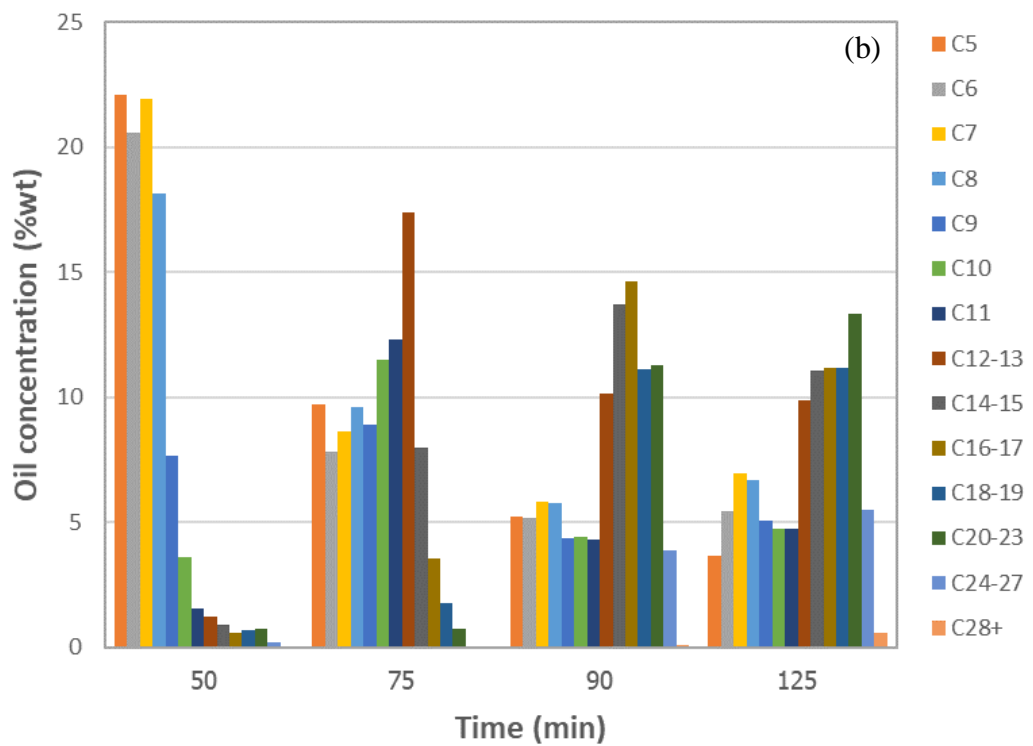
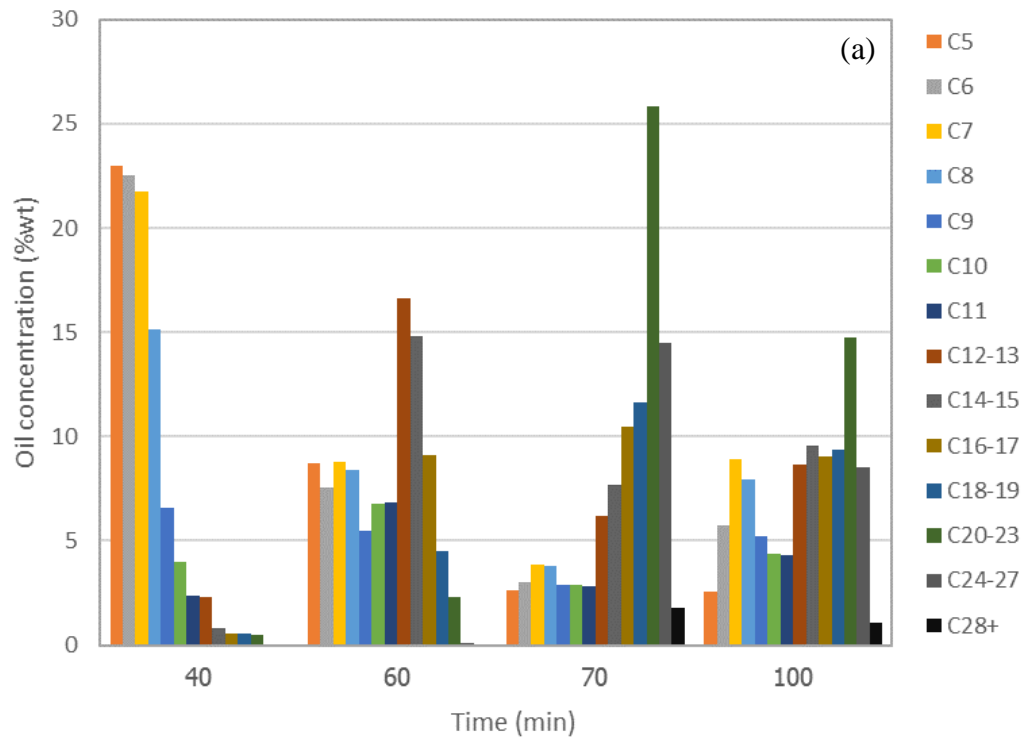


Figure C-5 Effect of reaction time of Cat A on oil products distribution at 650°C(a), 600°C(b), 500°C(c), 450°C(d).



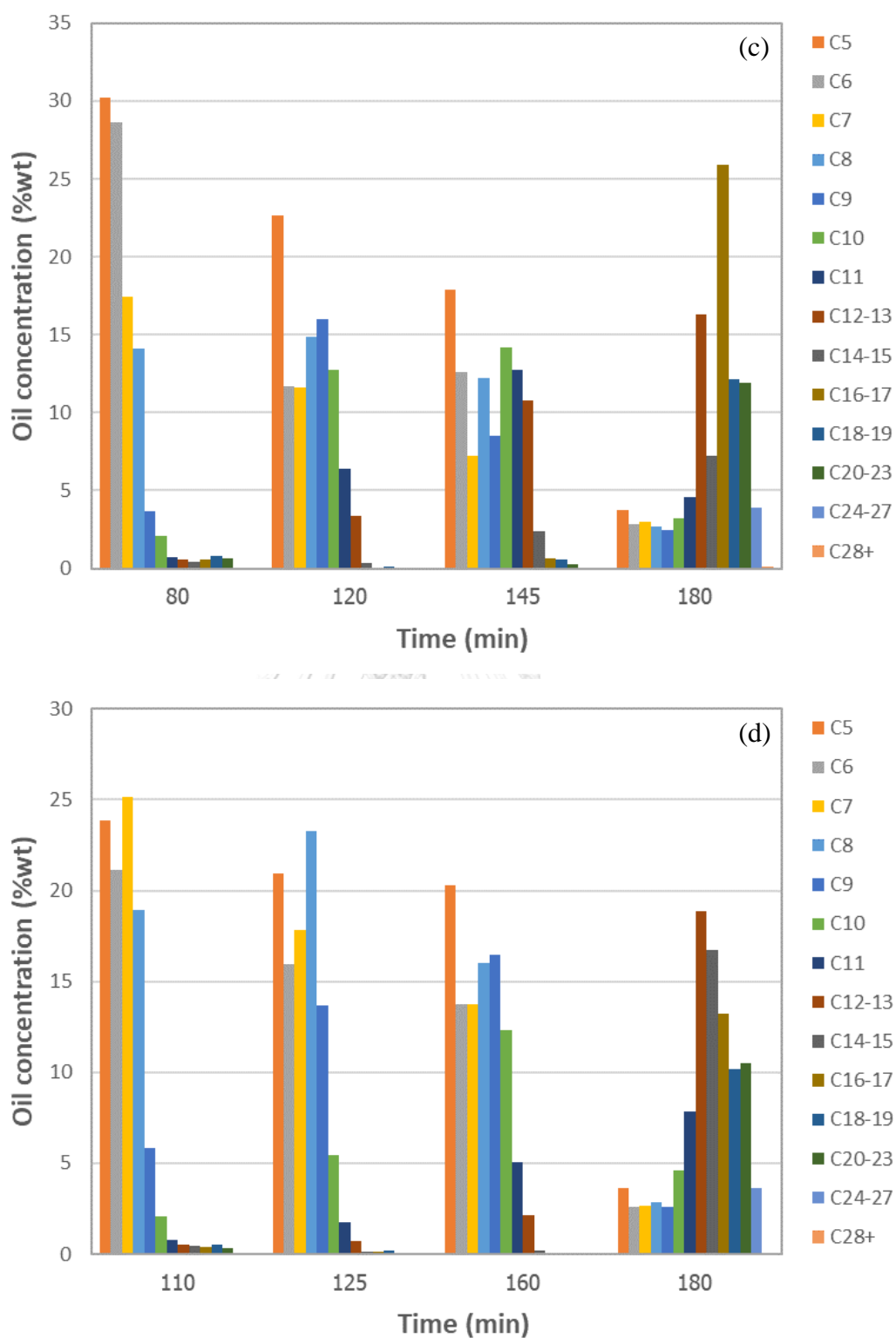
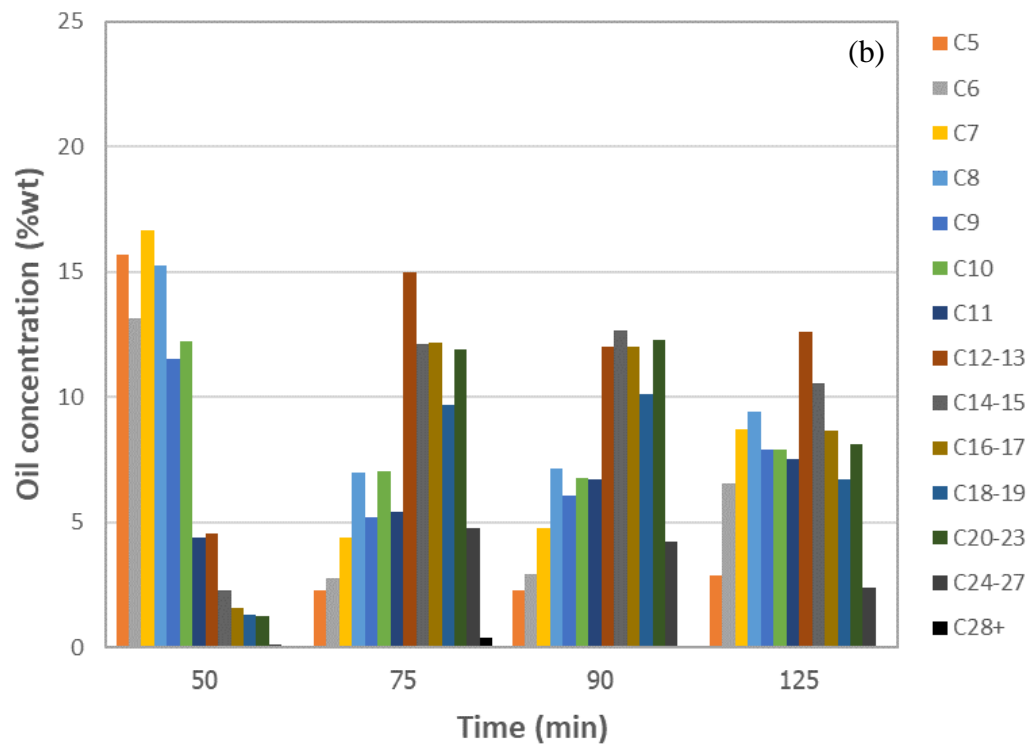
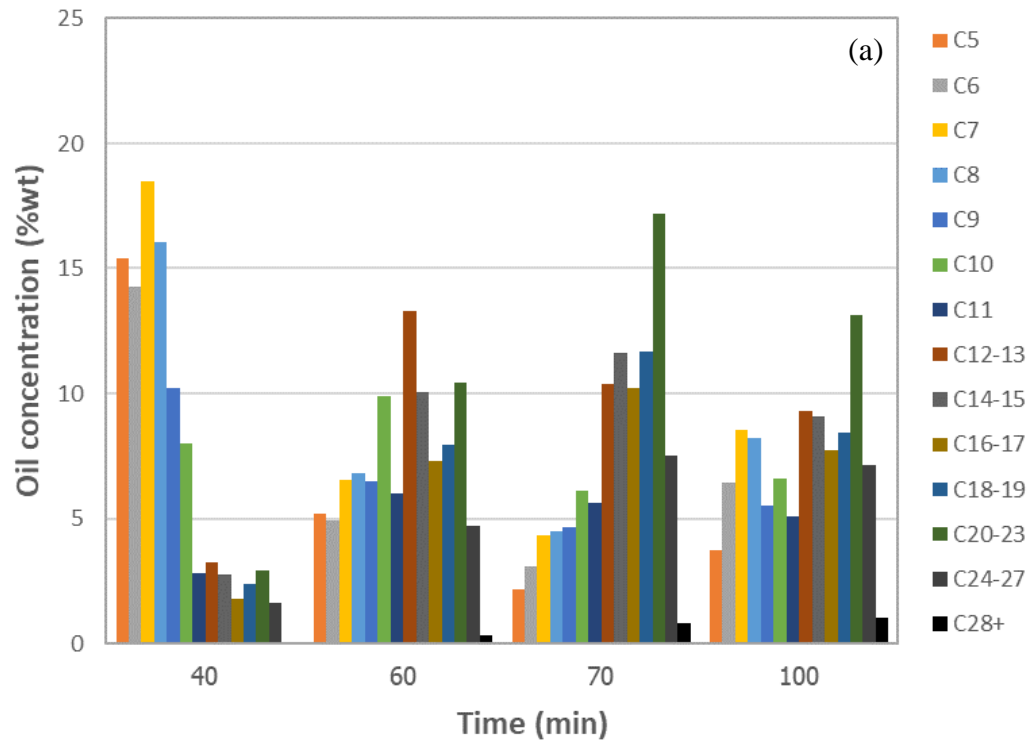


Figure C-6 Effect of reaction time of HZSM-5 on oil products distribution at 650°C(a), 600°C(b), 500°C(c), 450°C(d).



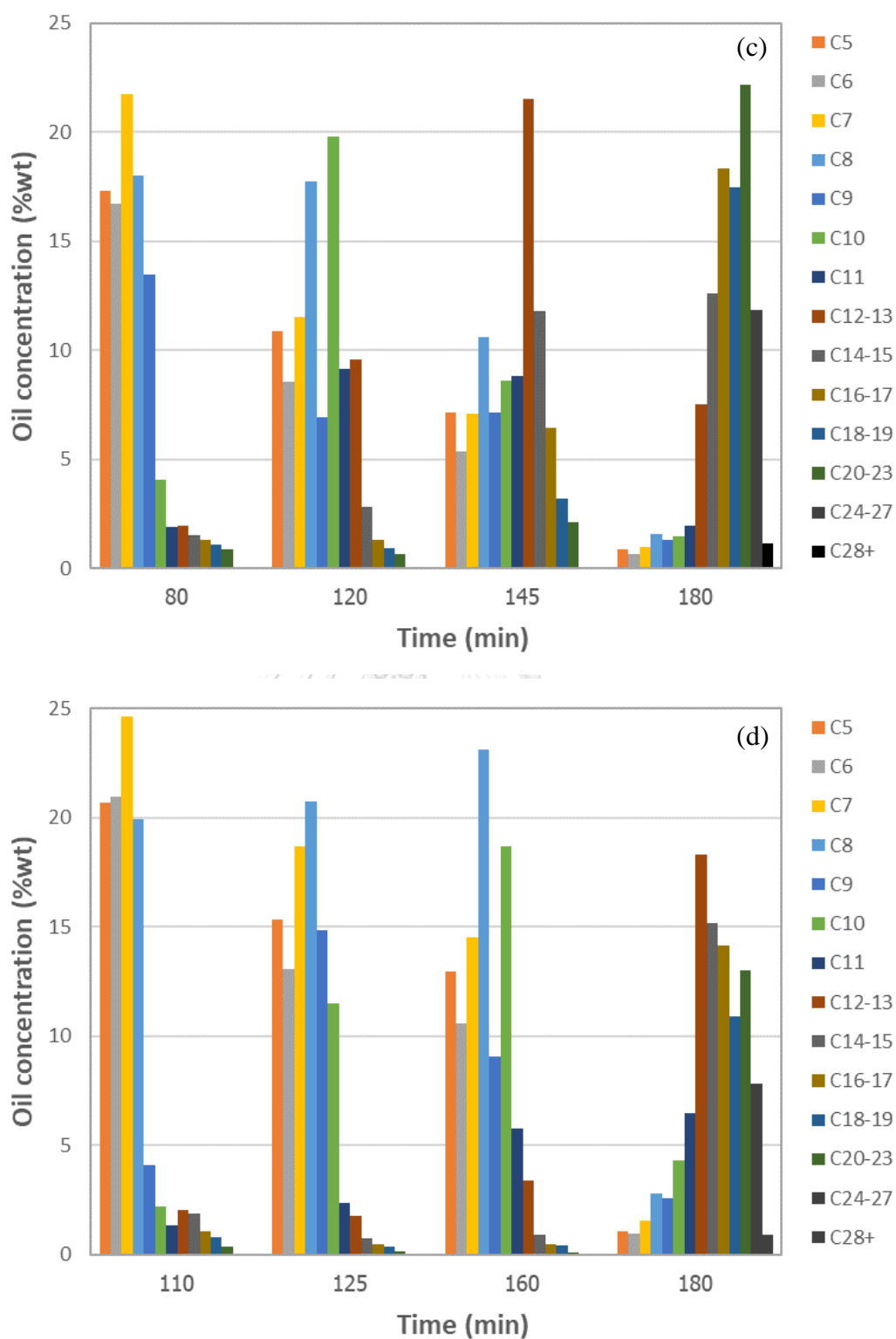


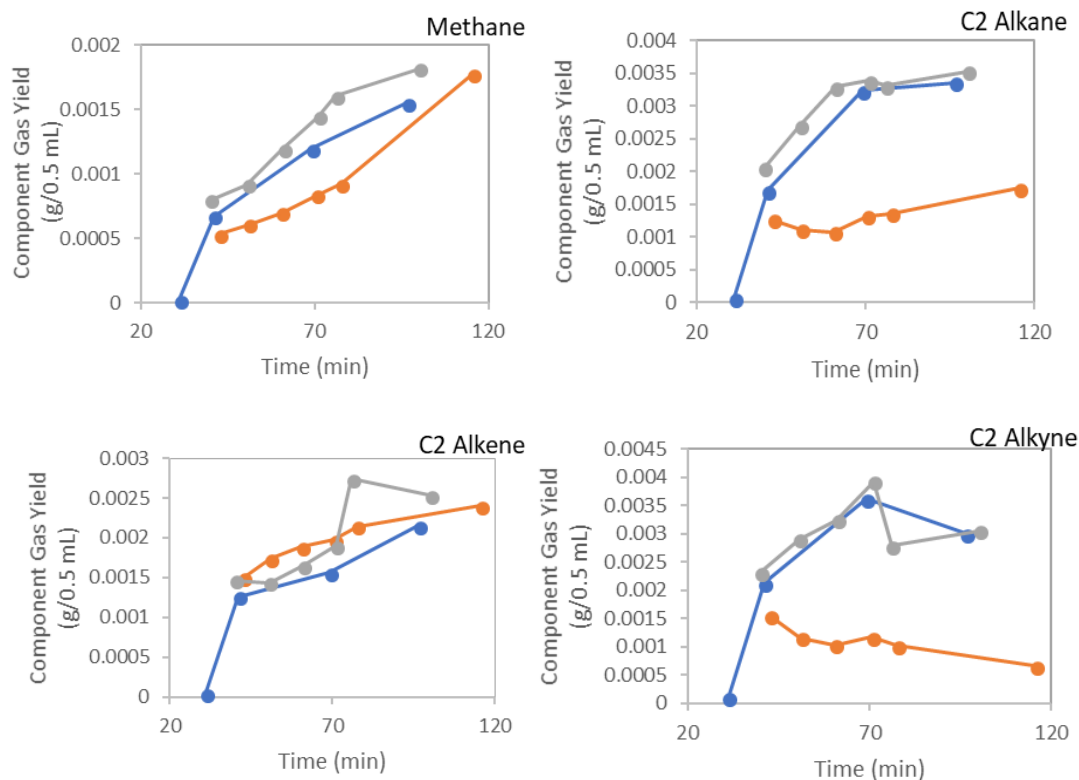
Figure C-7 Effect of reaction time of pure HDPE on oil products distribution at 650°C(a), 600°C(b), 500°C(c), 450°C(d).

Appendix D: Gas products distribution

Gas samples were measured for concentration of each component that followed the gas cerebration standard. The results in figure D show the amount of substance in gas samples that collected in each time and temperature. The gas components were grouped by using number of carbon atom per molecule and chemical bond. The category of each group shows in table C.

Table D-1 Gas products grouping

Group	Component
C1	Methane
C2 Alkane	Ethane
C2 Alkene	Ethylene
C2 Alkyne	Acetylene
C3 Alkane	Propane
C3 Alkene	Propylene
C3 Alkyne	Propadiene, Methyl Acetylene
C4 Alkene	trans-2-Butene, 1-Butene, iso-Butylene, cis-2-Butene
C4 Alkyne	1,3-Butadiene
C5 Alkane	iso-Pentane, n-Pentane
C5 Alkene	trans-2-Pentene, 2-Methyl-2-Butene, 1-Pentene, cis-2-Pentene
C6 Alkane	n-Hexane



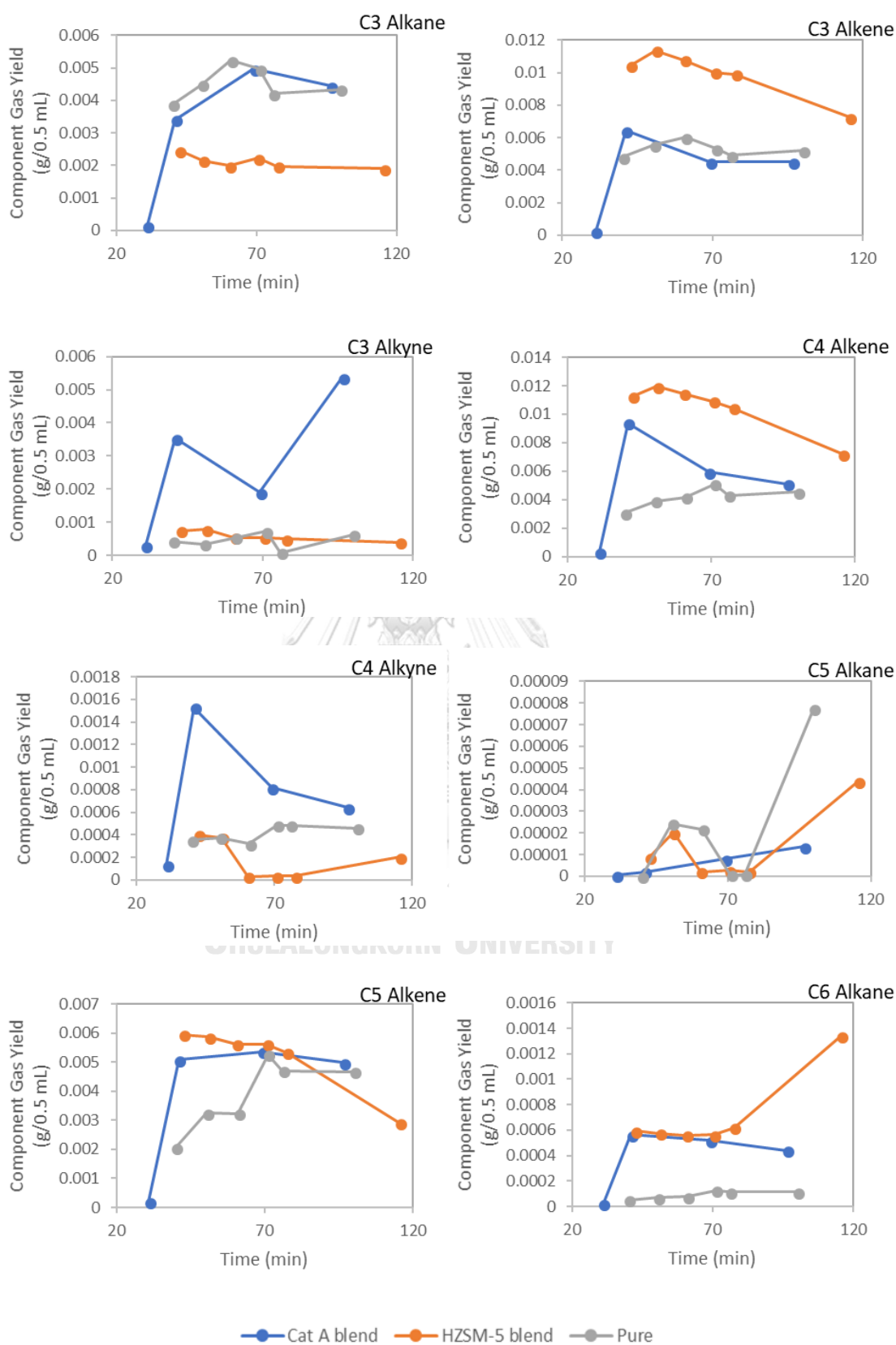
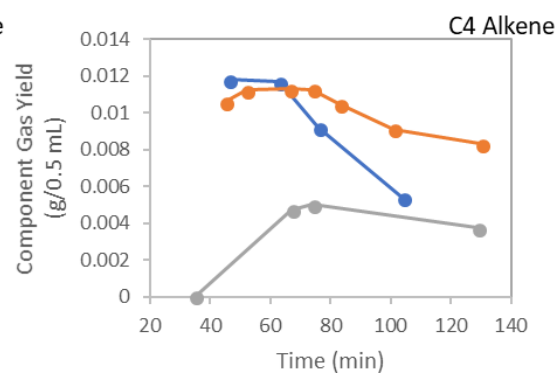
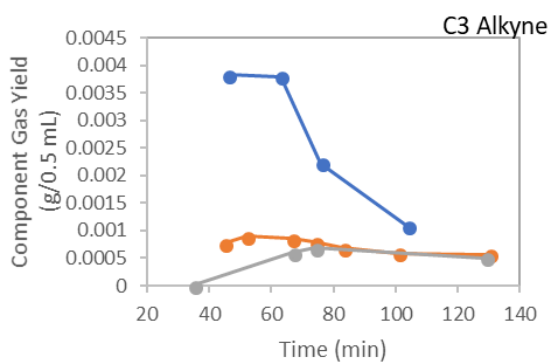
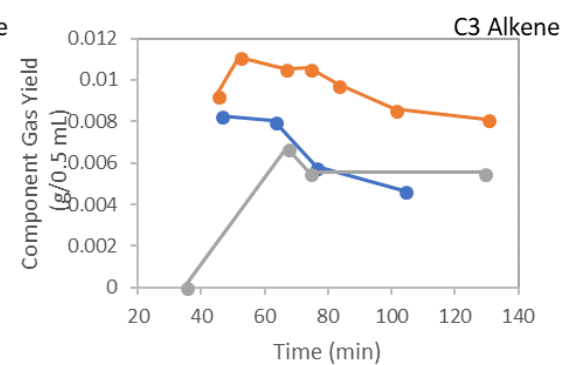
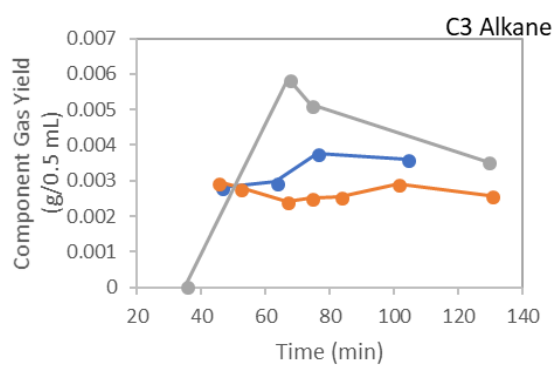
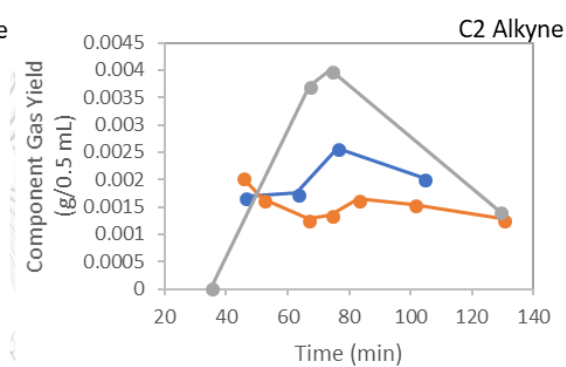
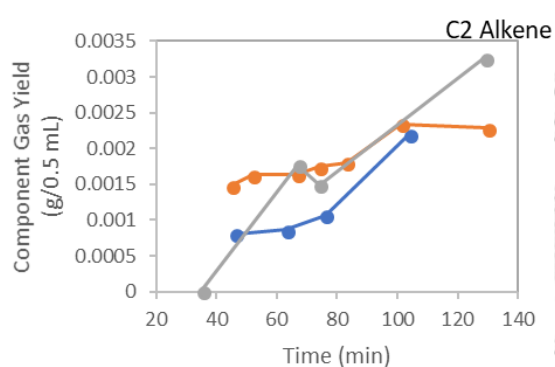
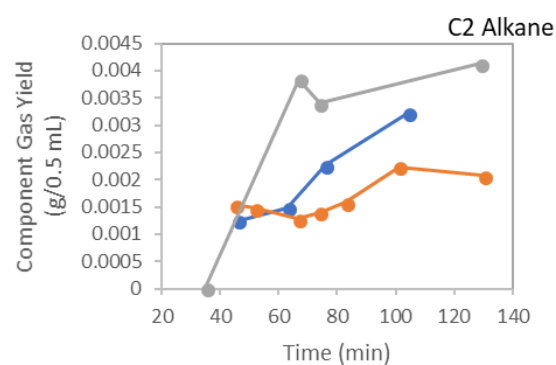
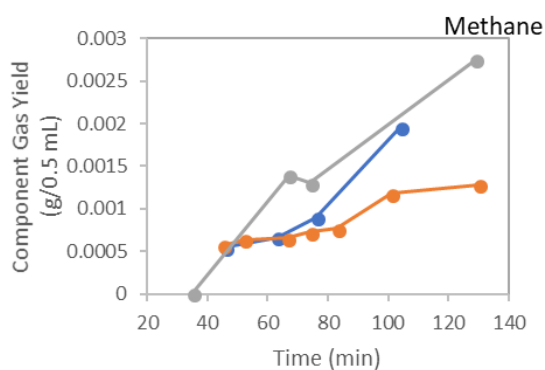


Figure D-1 Effect of catalysts on gas products distribution at 650 °C.



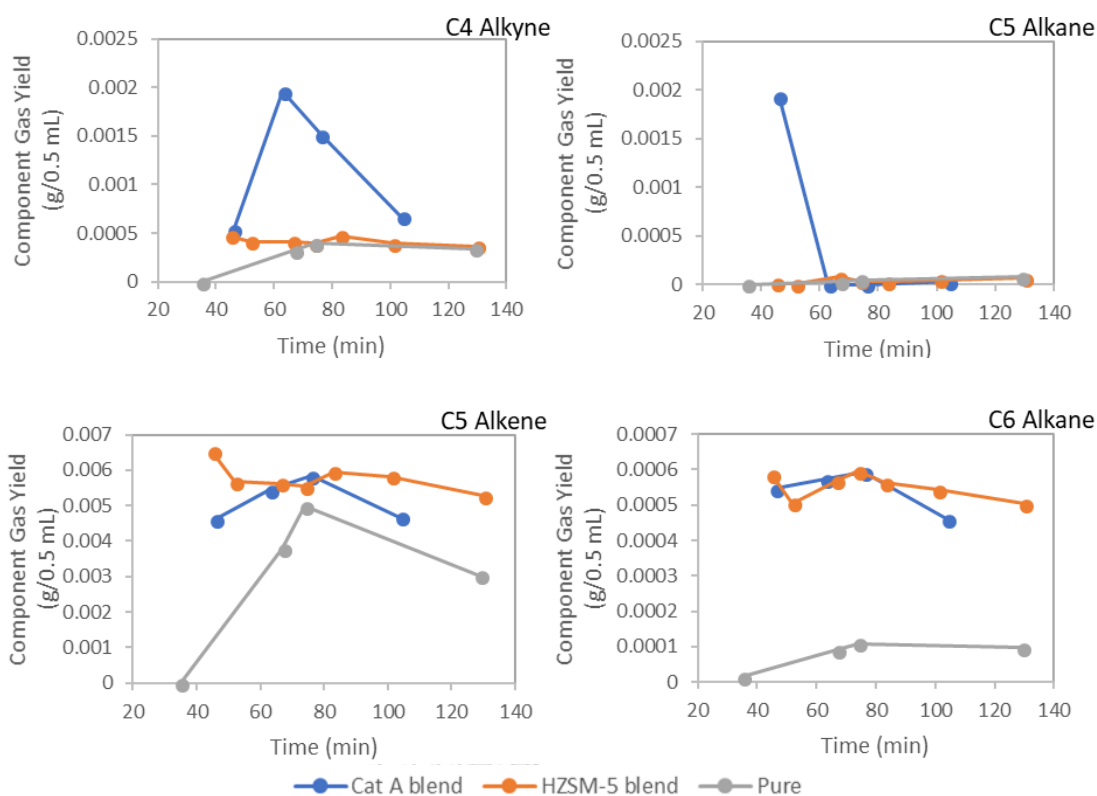
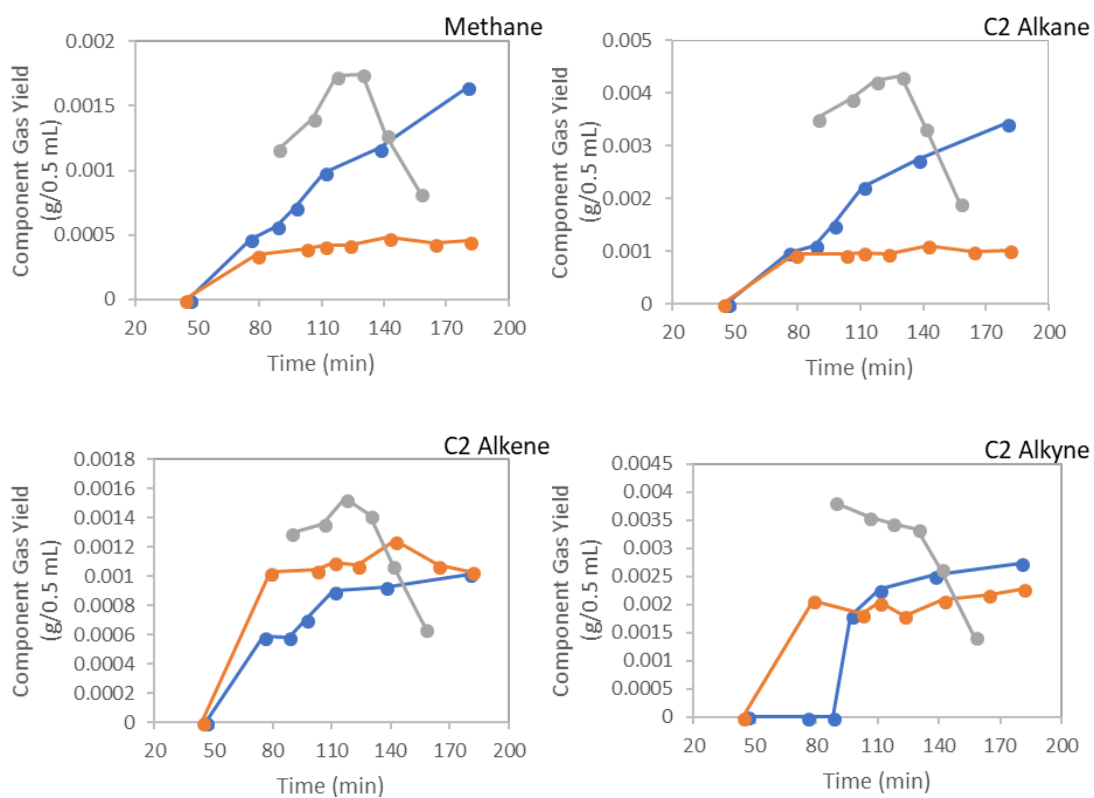


Figure D-2 Effect of catalysts on gas products distribution at 600 °C.



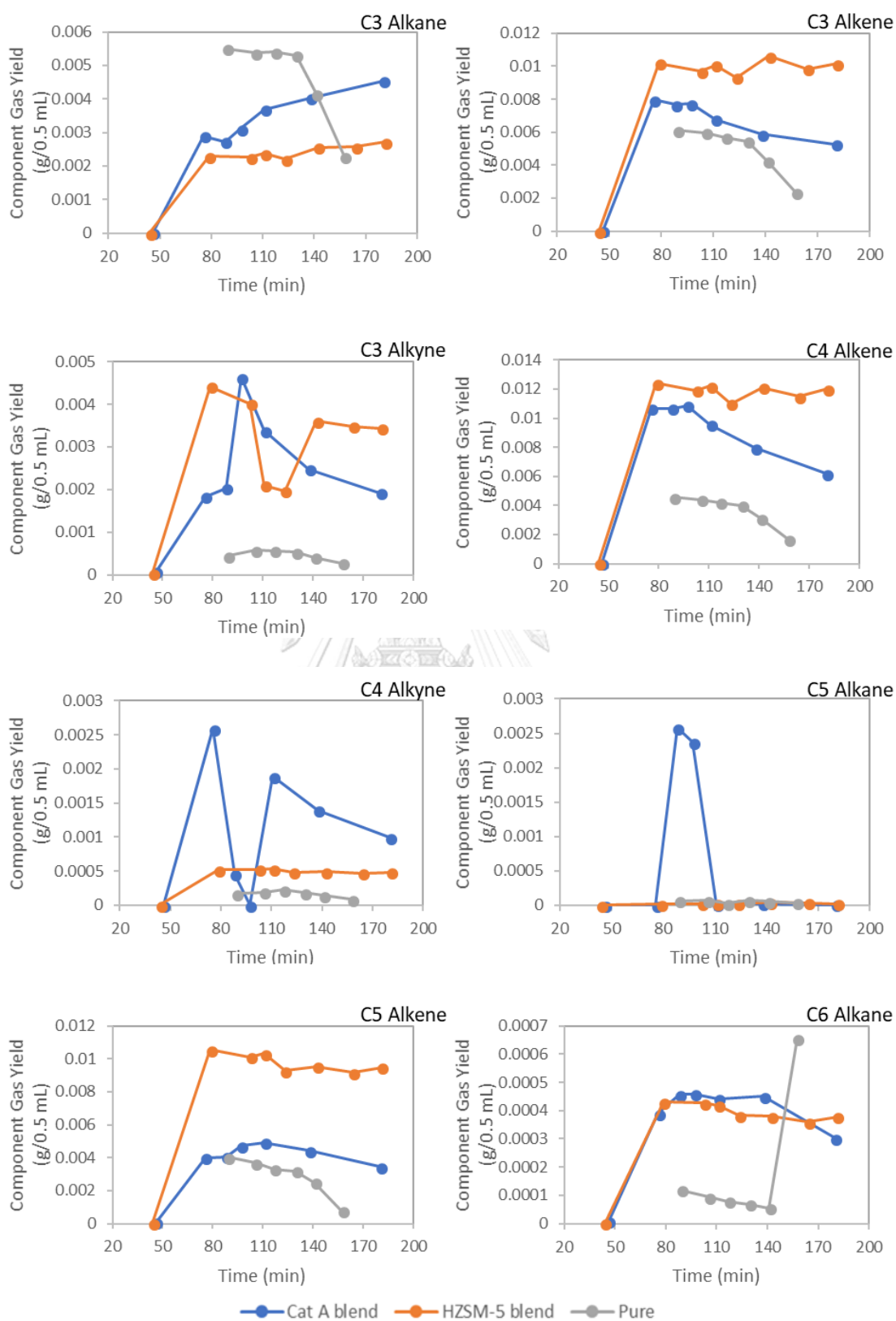
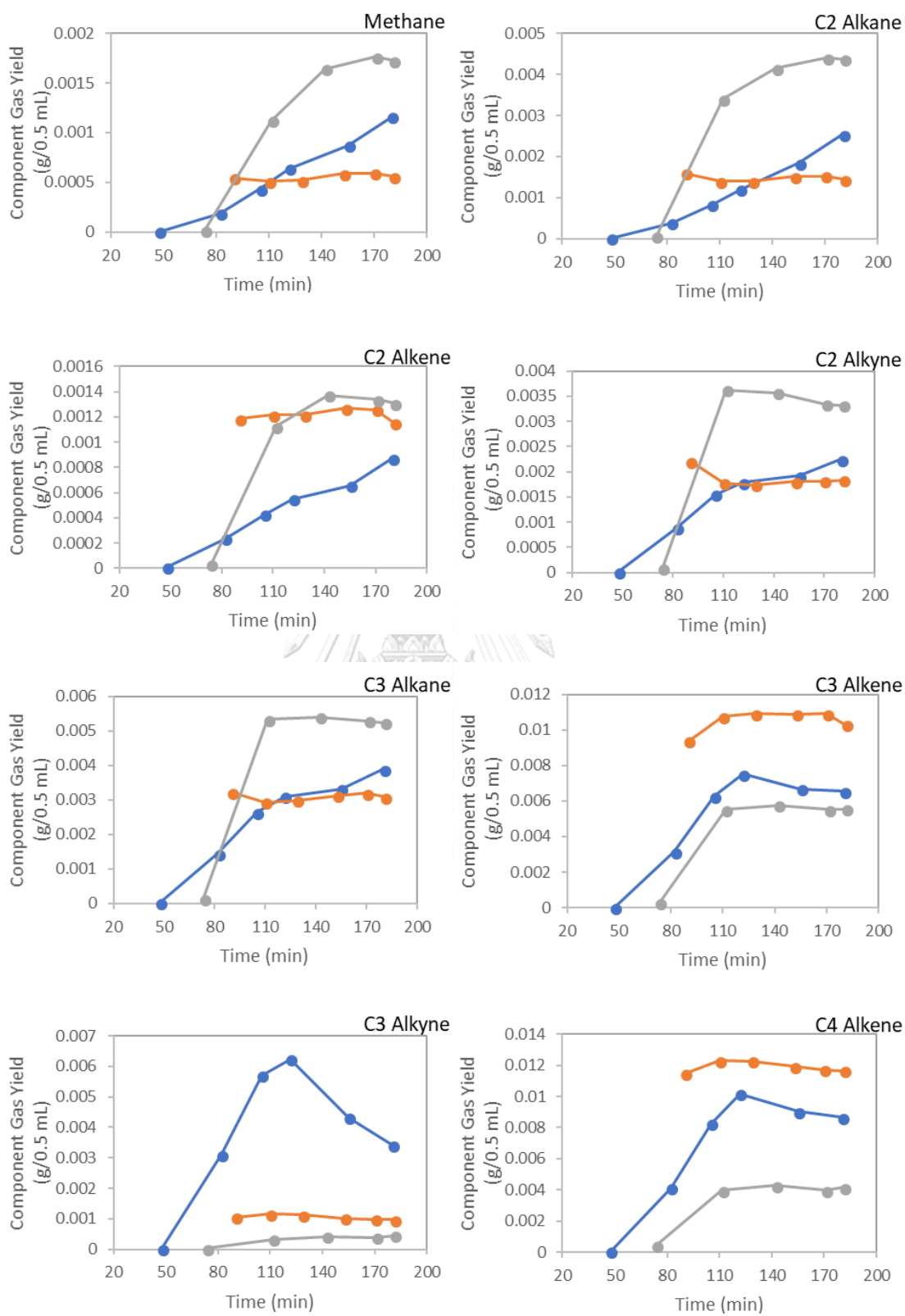


Figure D-3 Effect of catalysts on gas products distribution at 500 °C



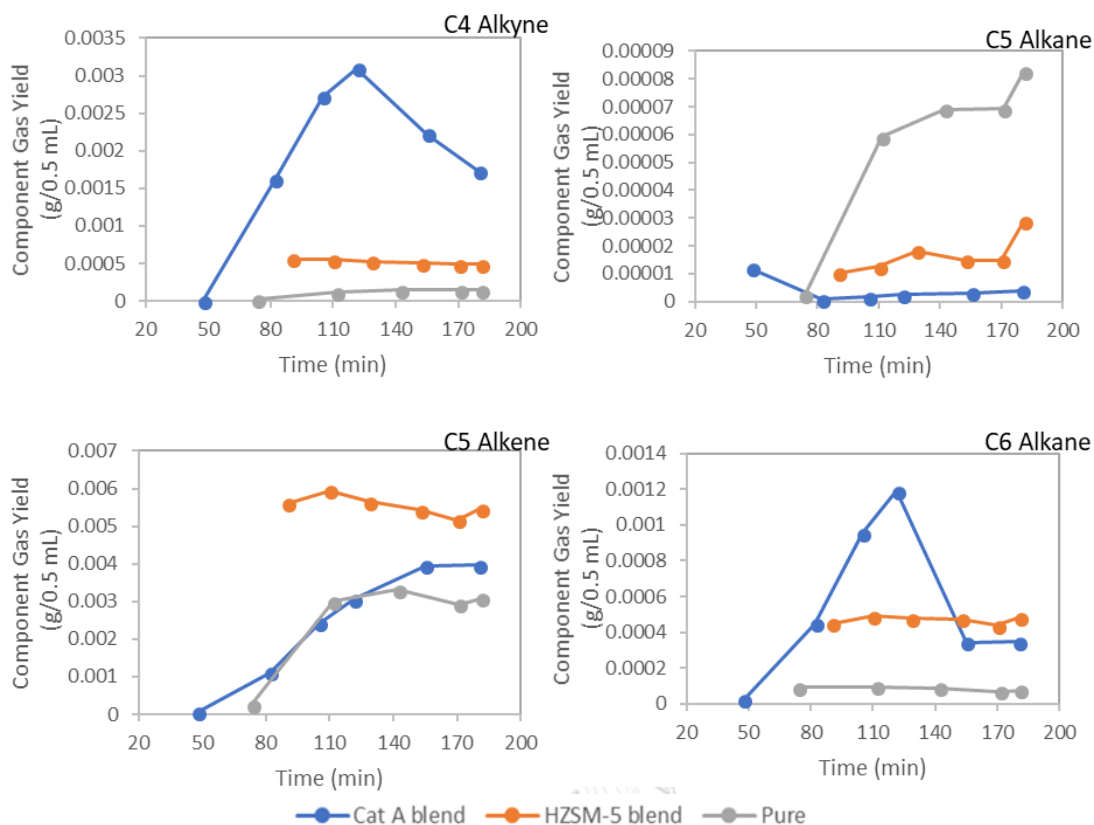
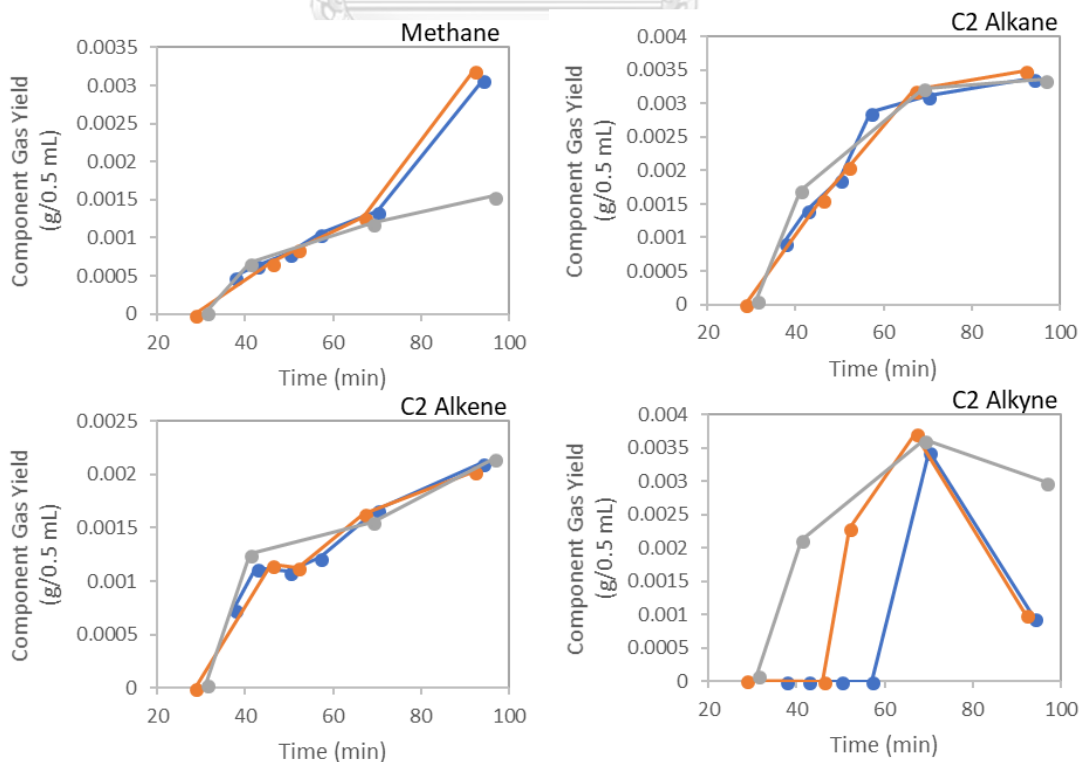


Figure D-4 Effect of catalysts on gas products distribution at 450 °C.



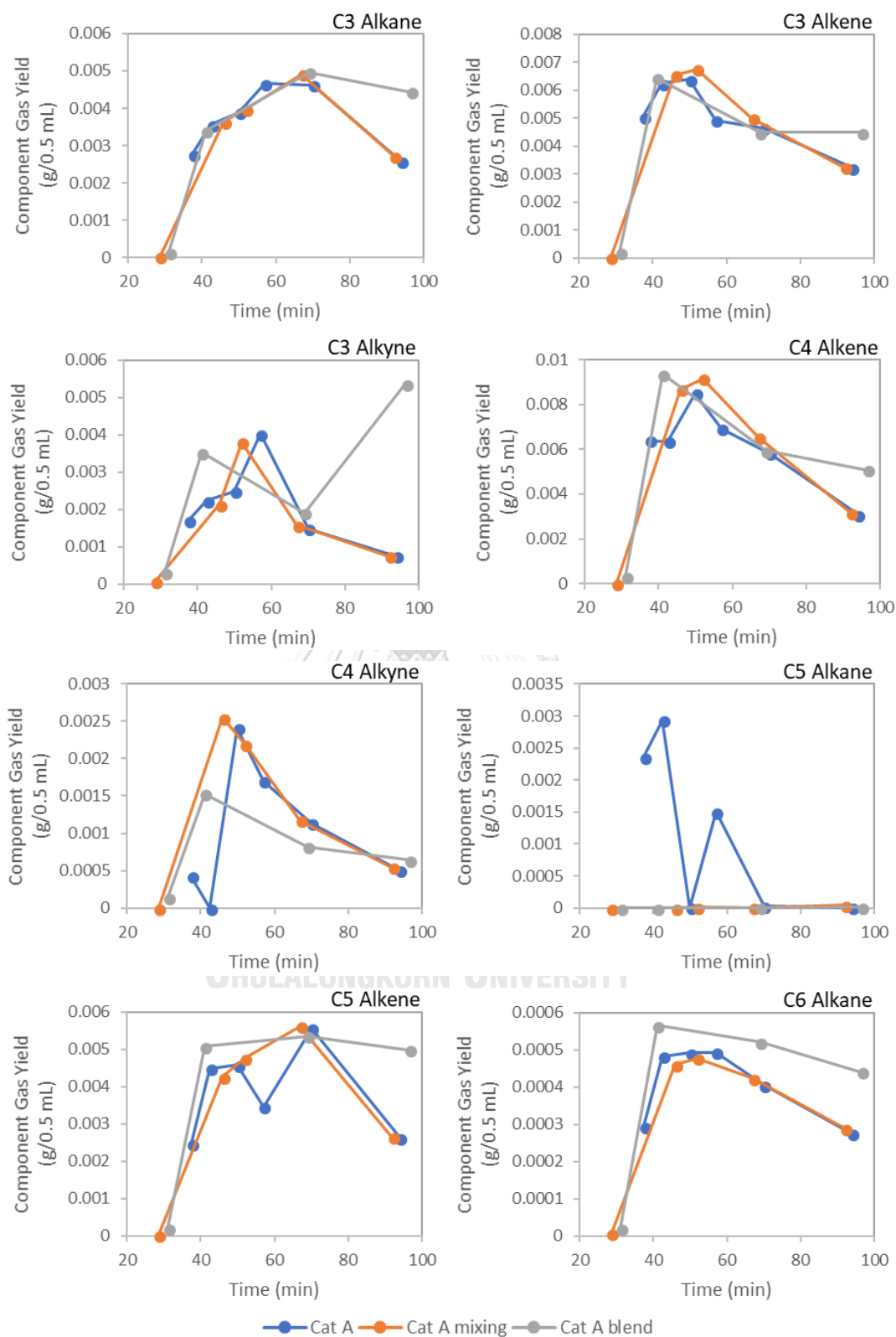
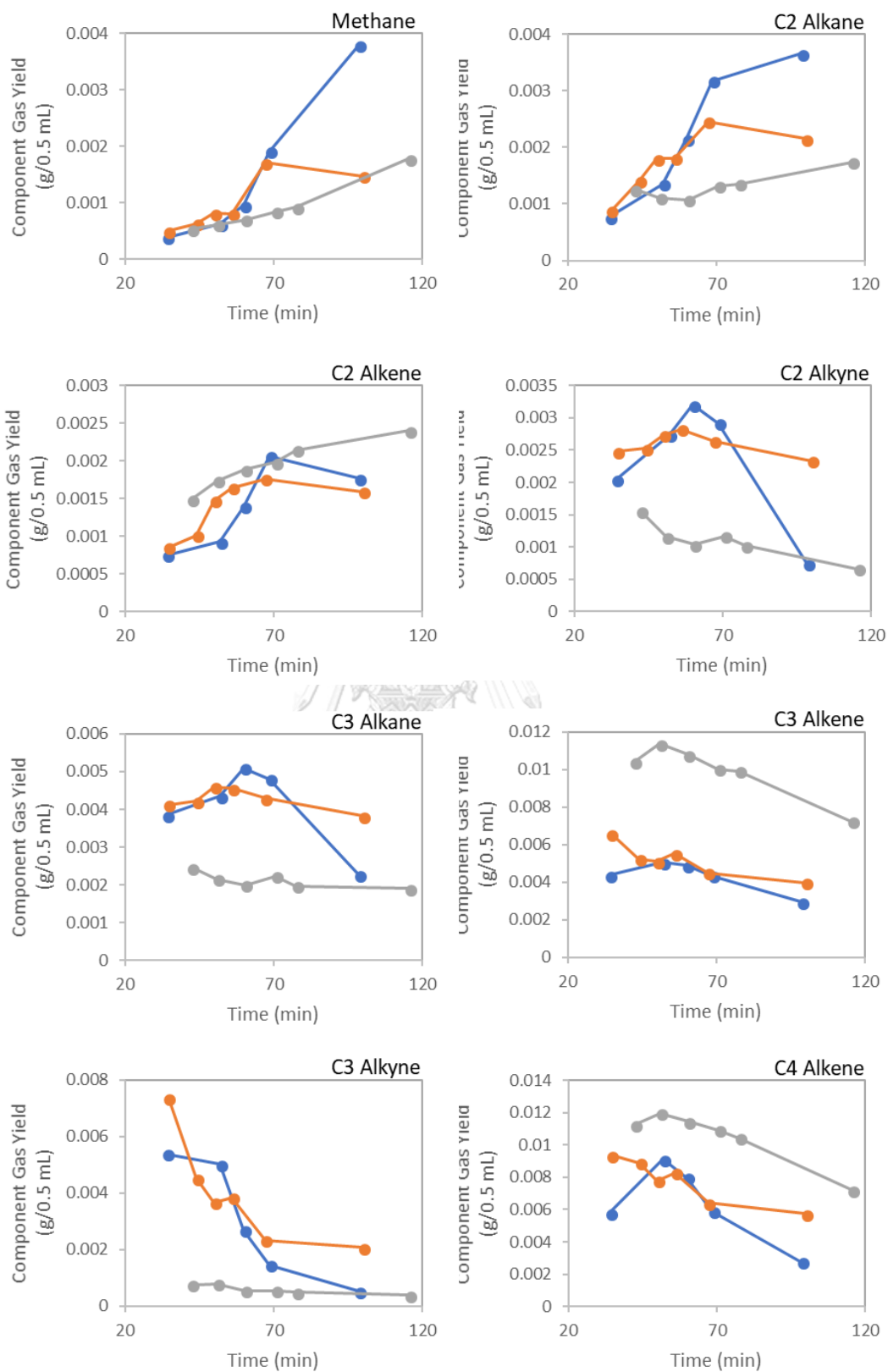


Figure D-5 Effect of catalyst dispersion on gas products distribution of Cat A, Cat A mixing, Cat A blend at 650 °C.



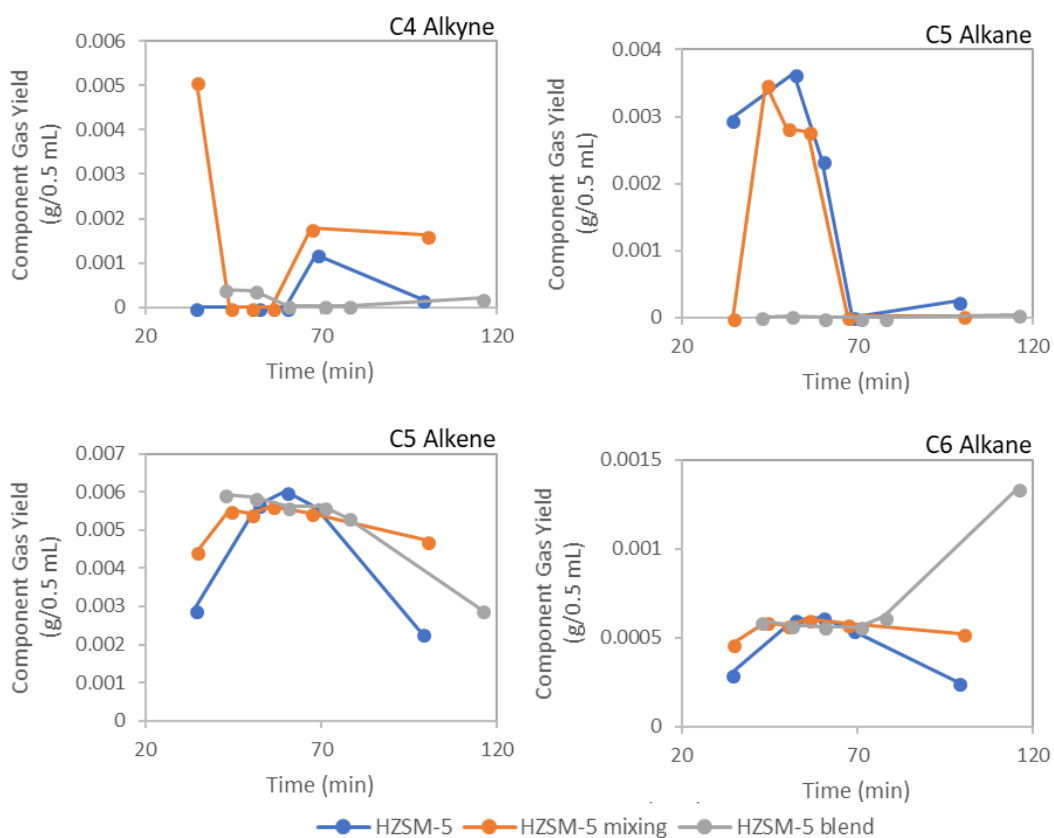
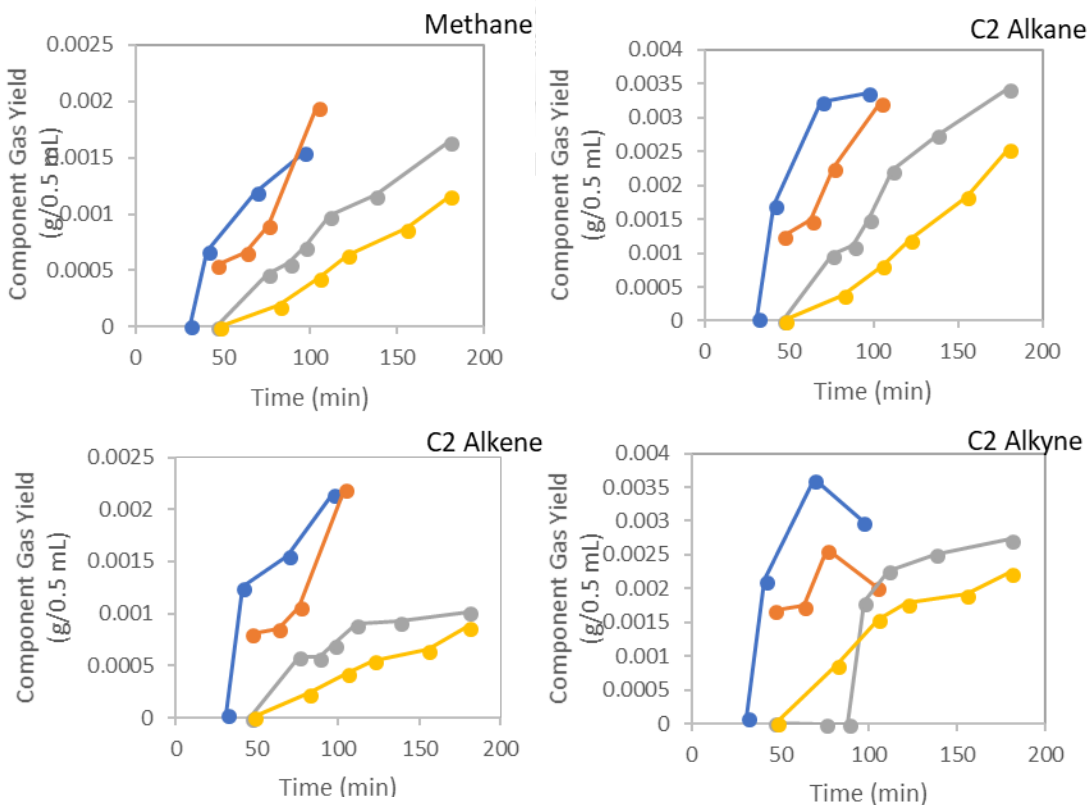


Figure D-6 Effect of catalyst dispersion on gas products distribution of HZSM-5, HZSM-5 mixing, HZSM-5 blend at 650 °C.



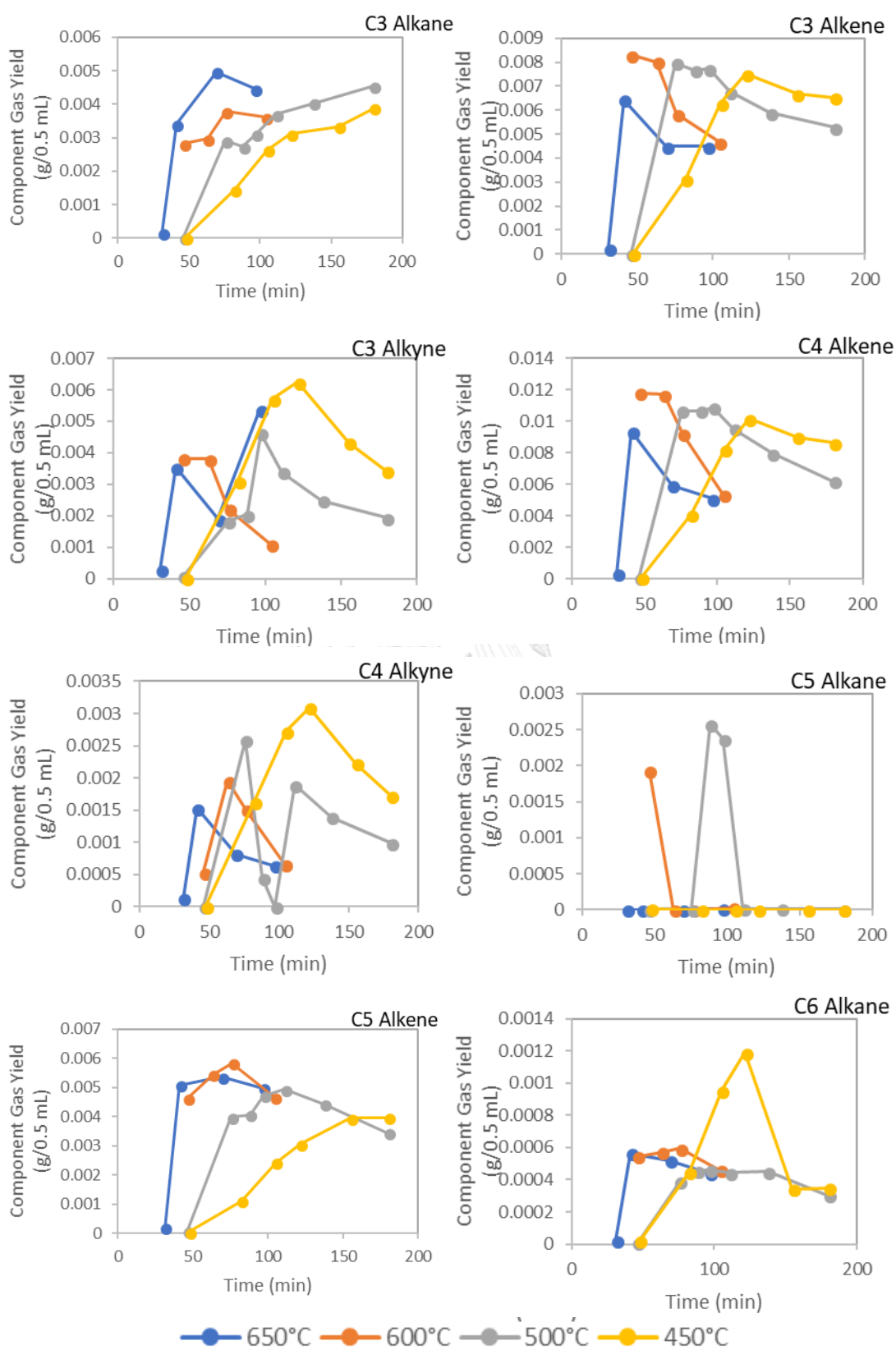
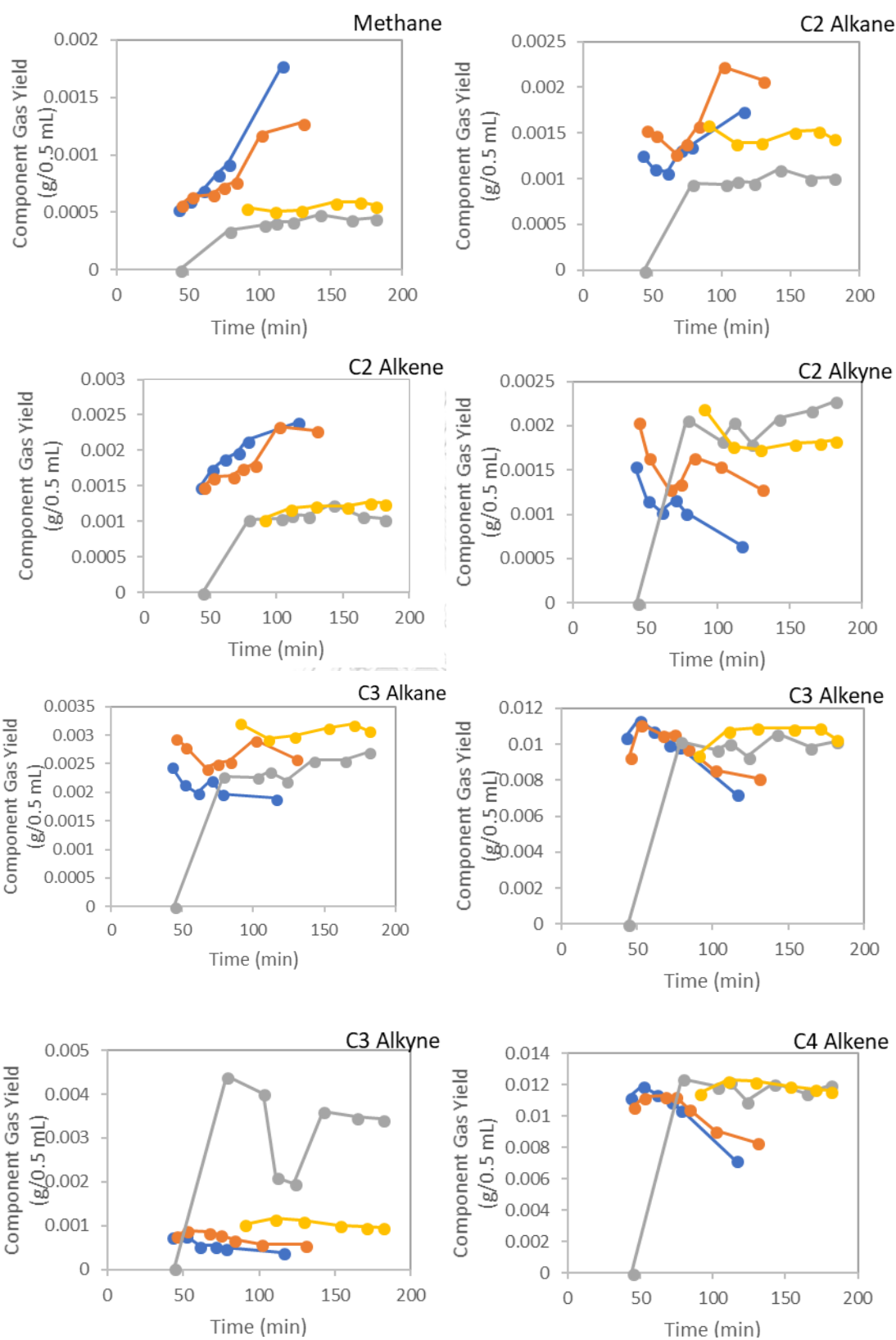


Figure D-7 Effect of reaction temperature of Cat A on gas products distribution



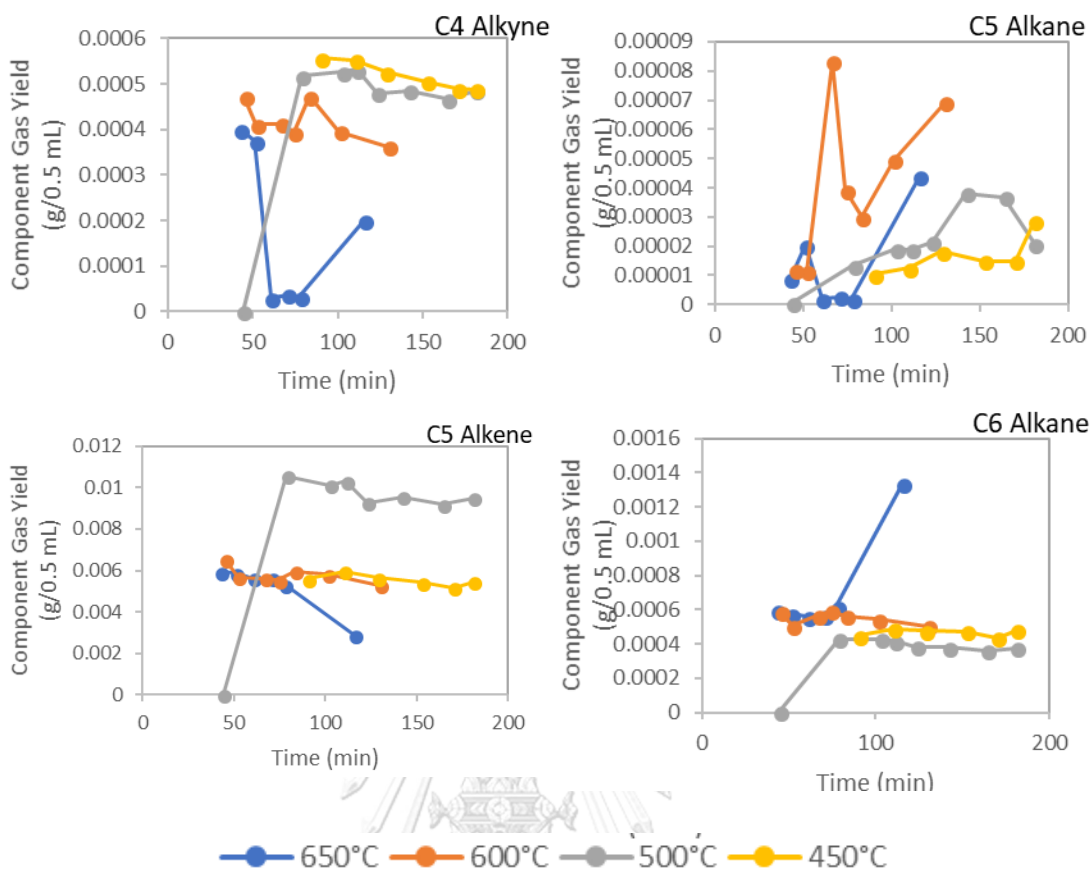
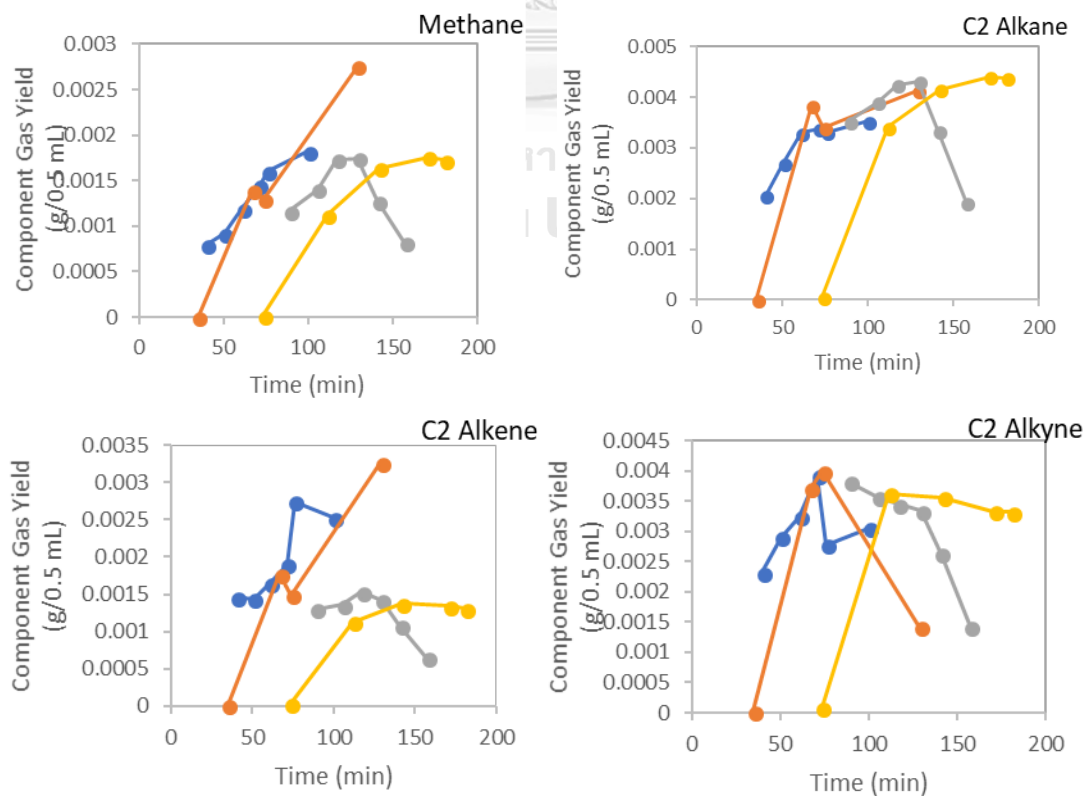


Figure D-8 Effect of reaction temperature of HZSM-5 on gas products distribution.



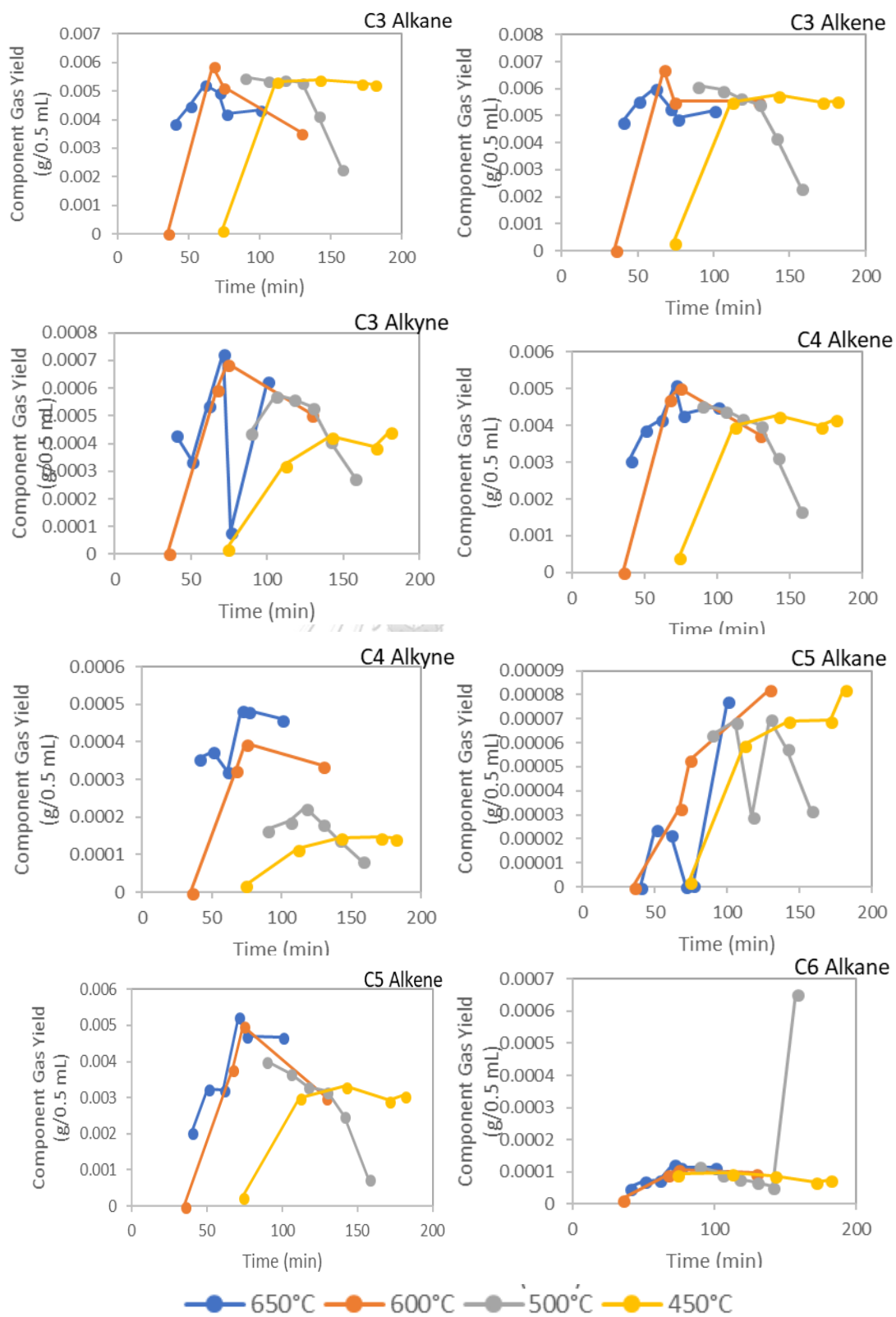


Figure D-9 Effect of reaction temperature of pure HDPE on gas products distribution.

Appendix E: Graph of reaction temperature, oil products rate, and gas products rate compared by types of catalyst

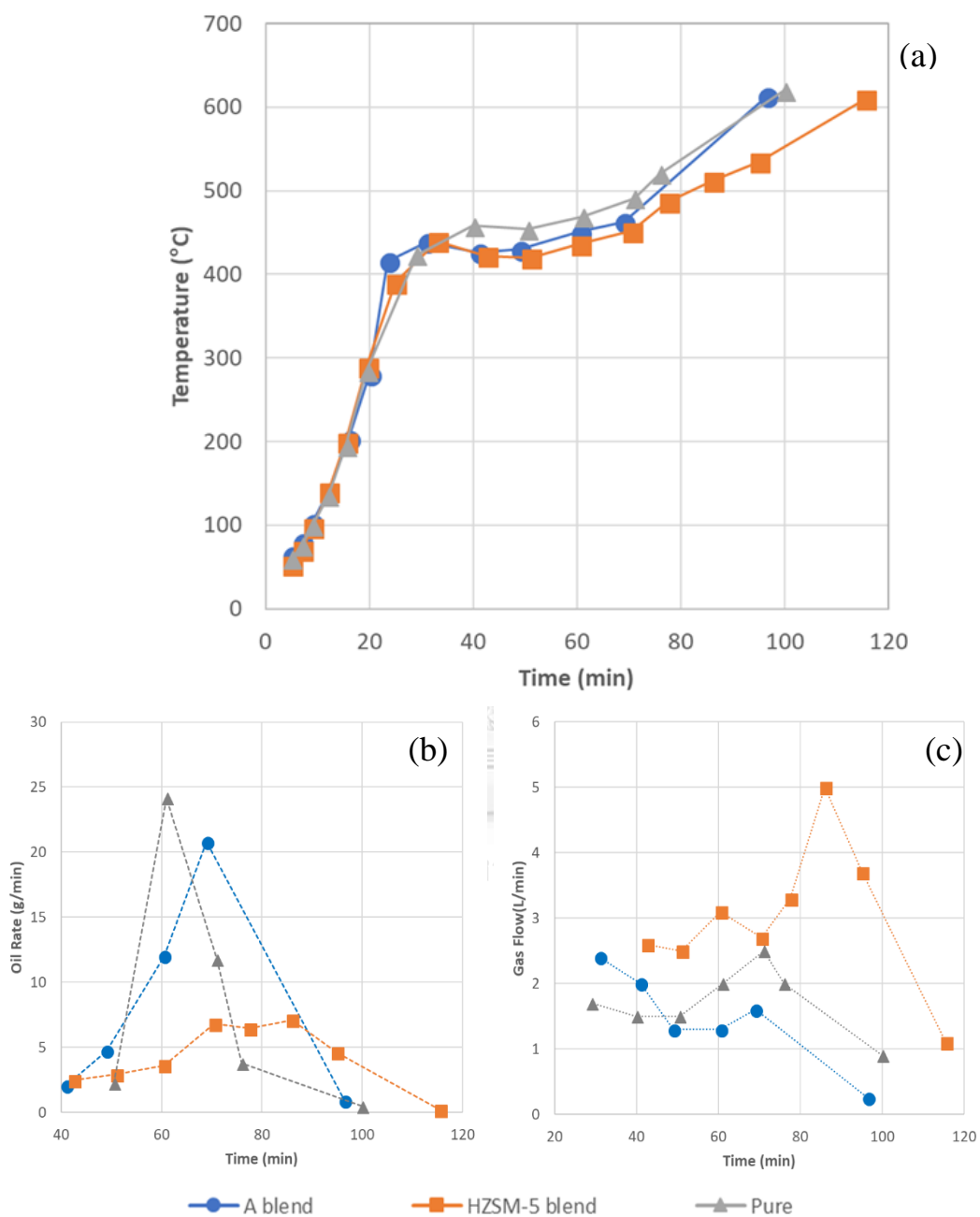


Figure E-1 Effect of catalysts on reaction temperature (a), oil products rate (b), and gas products rate (c) at 650 °C.

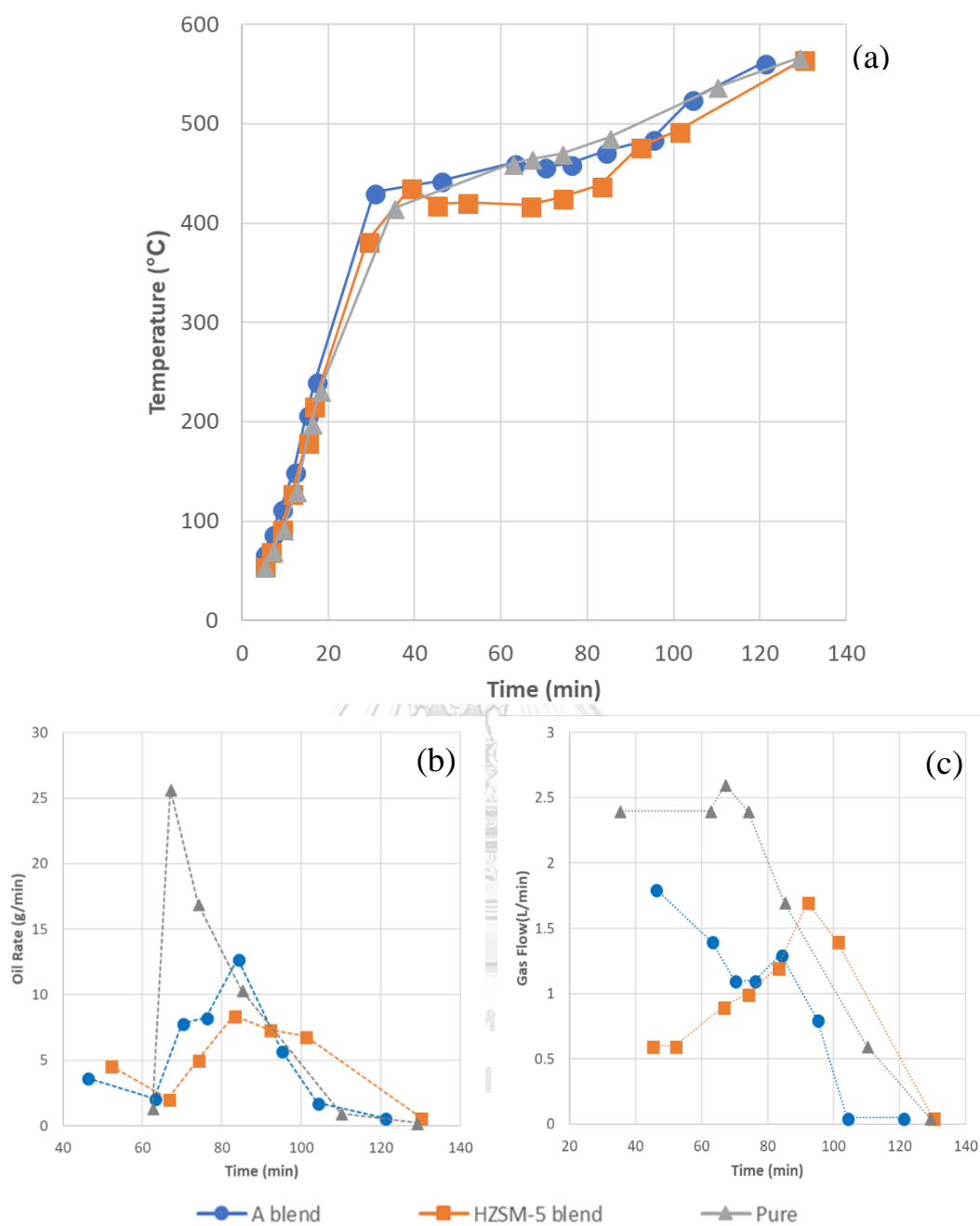


Figure E-2 Effect of catalysts on reaction temperature (a), oil products rate (b), and gas products rate (c) at 600 °C.

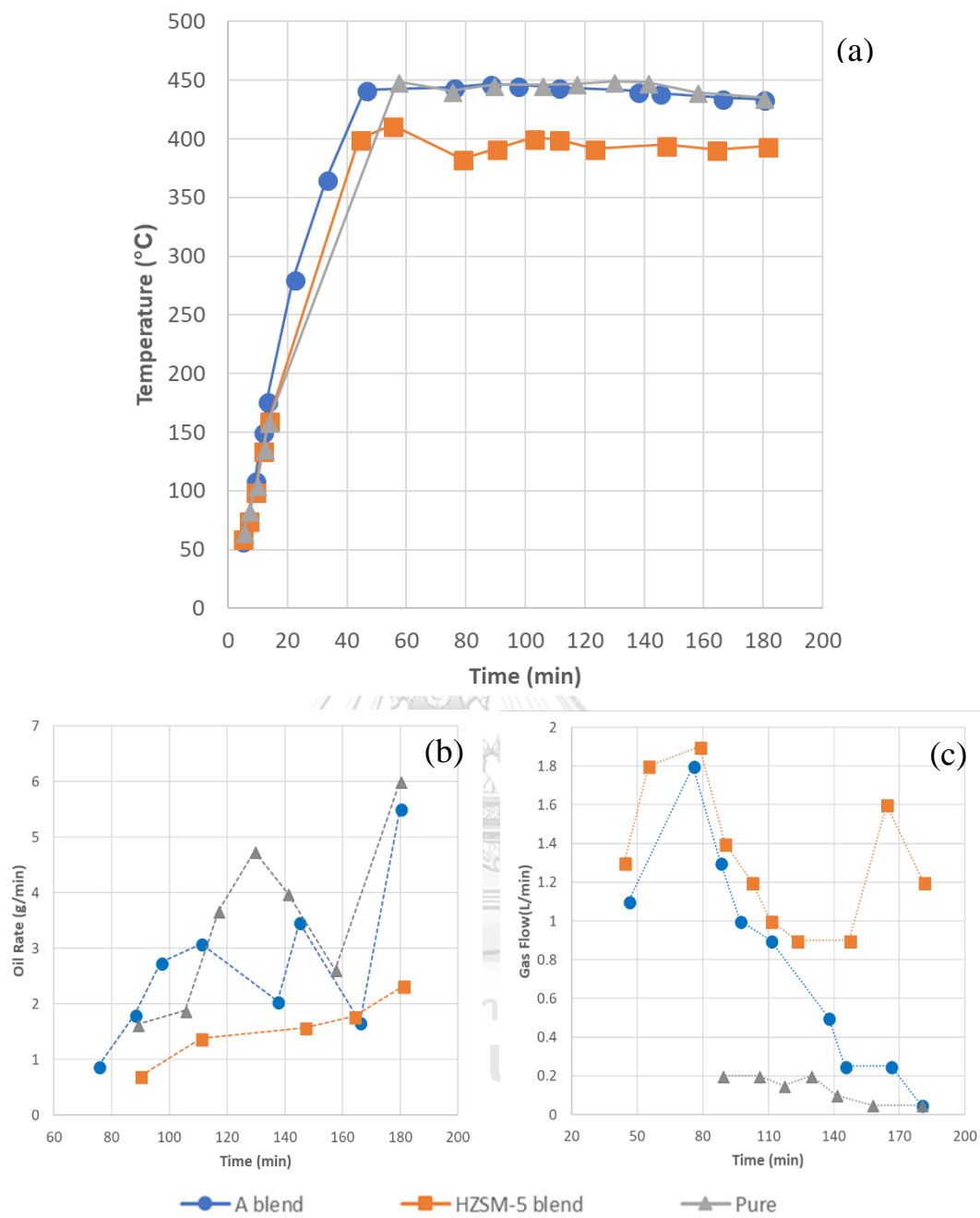


Figure E-3 Effect of catalysts on reaction temperature (a), oil products rate (b), and gas products rate (c) at 500 °C.

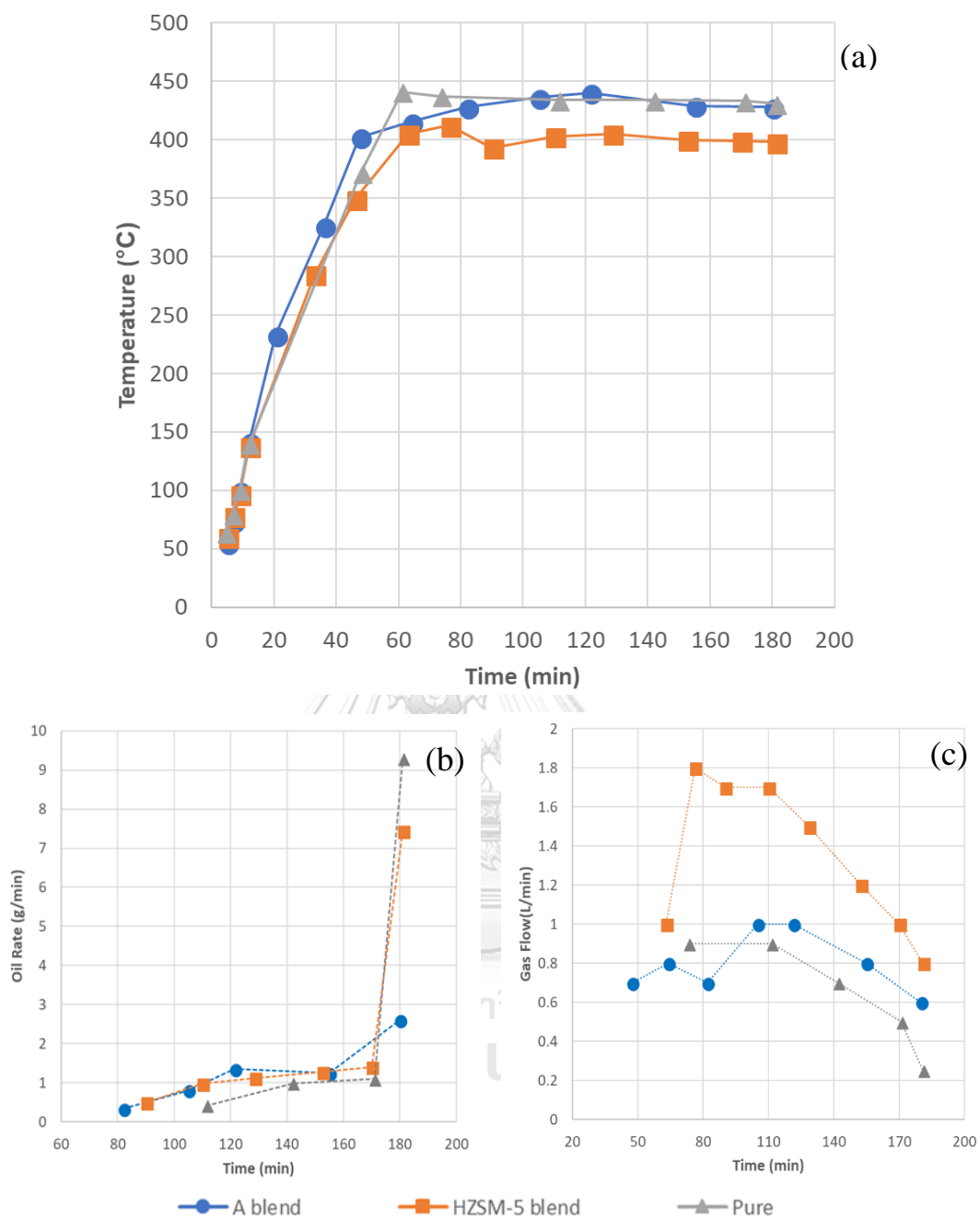
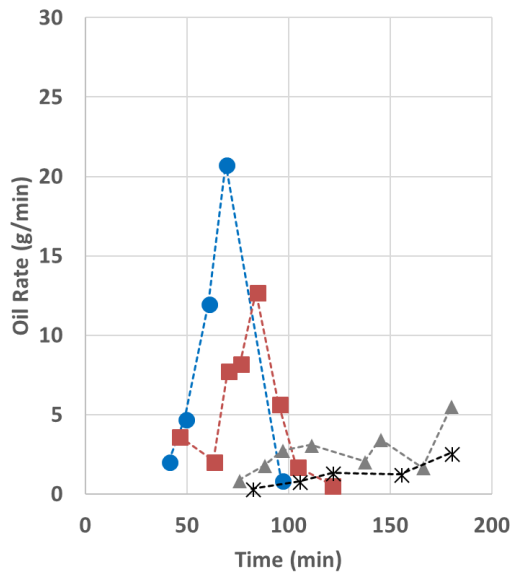
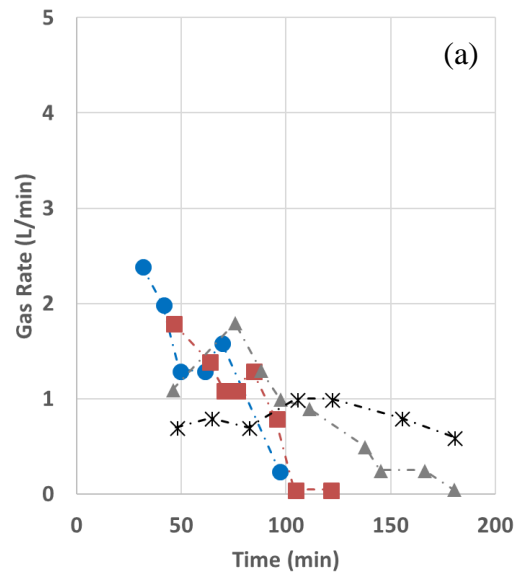


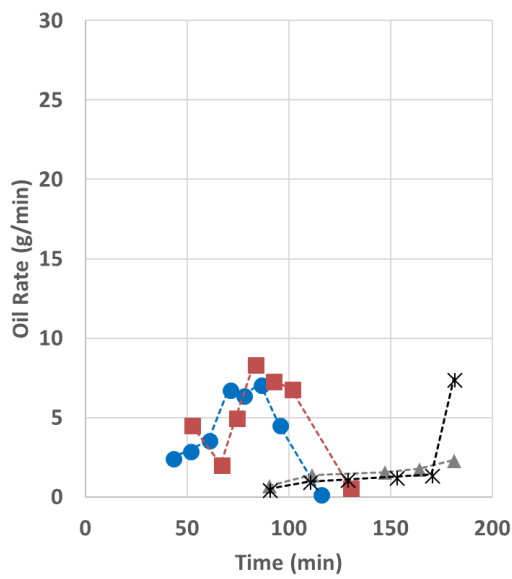
Figure E-4 Effect of catalysts on reaction temperature (a), oil products rate (b), and gas products rate (c) at 450 °C.



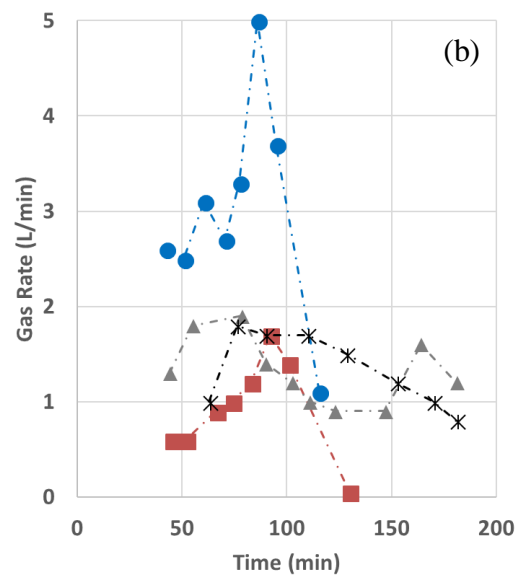
● 650°C ■ 600°C ▲ 500°C * 450°C



● 650°C ■ 600°C ▲ 500°C * 450°C



● 650°C ■ 600°C ▲ 500°C * 450°C



● 650°C ■ 600°C ▲ 500°C * 450°C

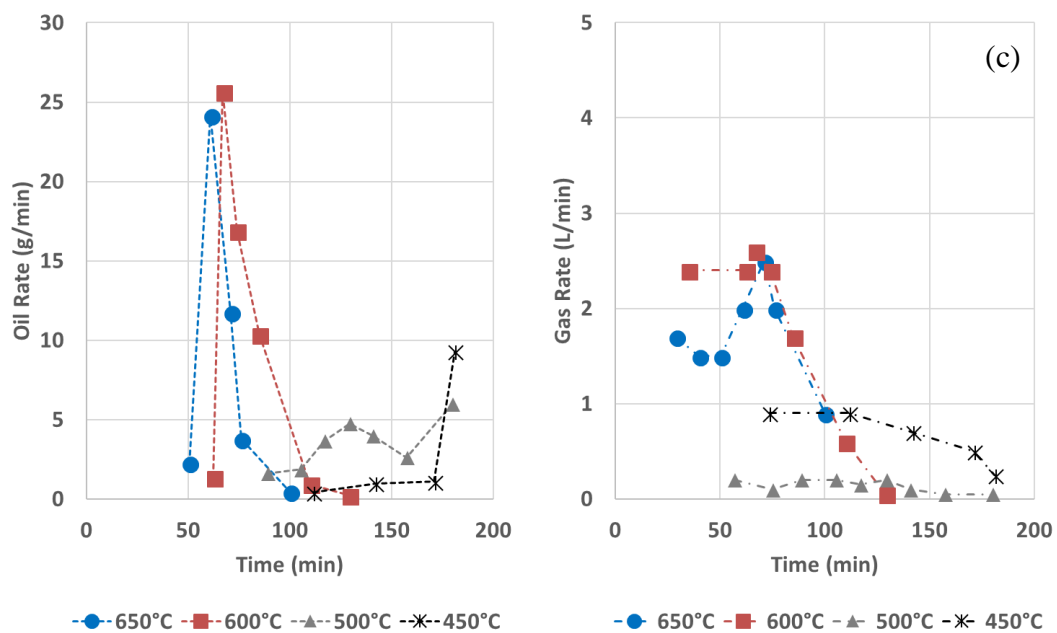


Figure E-5 Effect of temperature on oil products rate and gas products rate of Cat A(a), HZSM-5(b), and pure HDPE(c).

Appendix F: Conversion and gas products yield at different temperature

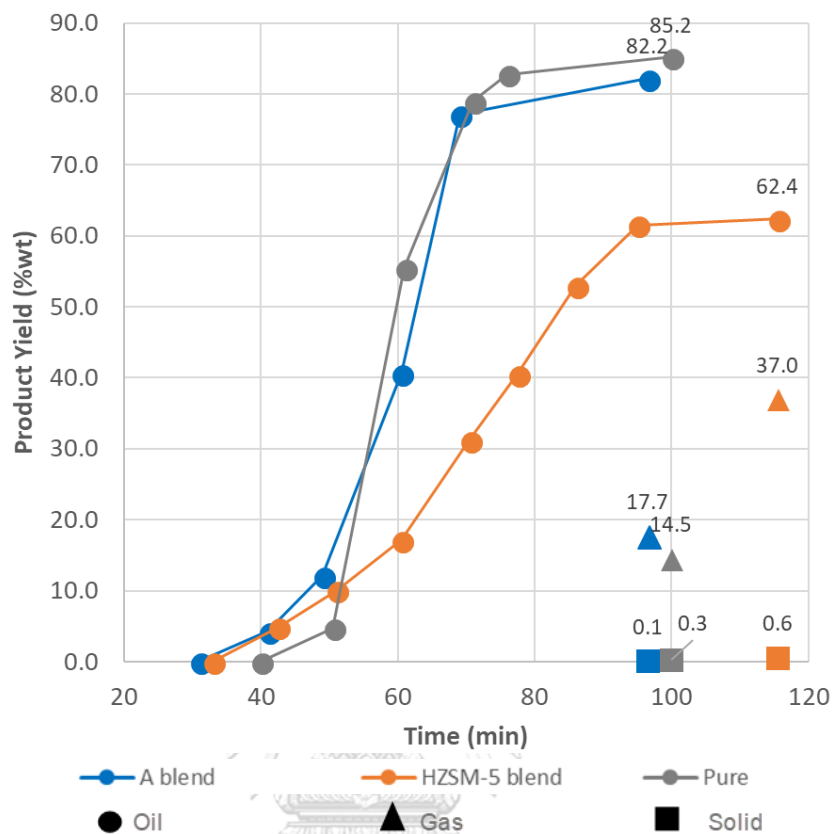


Figure F-1 Effect of catalysts on conversion and products yield at 650°C.

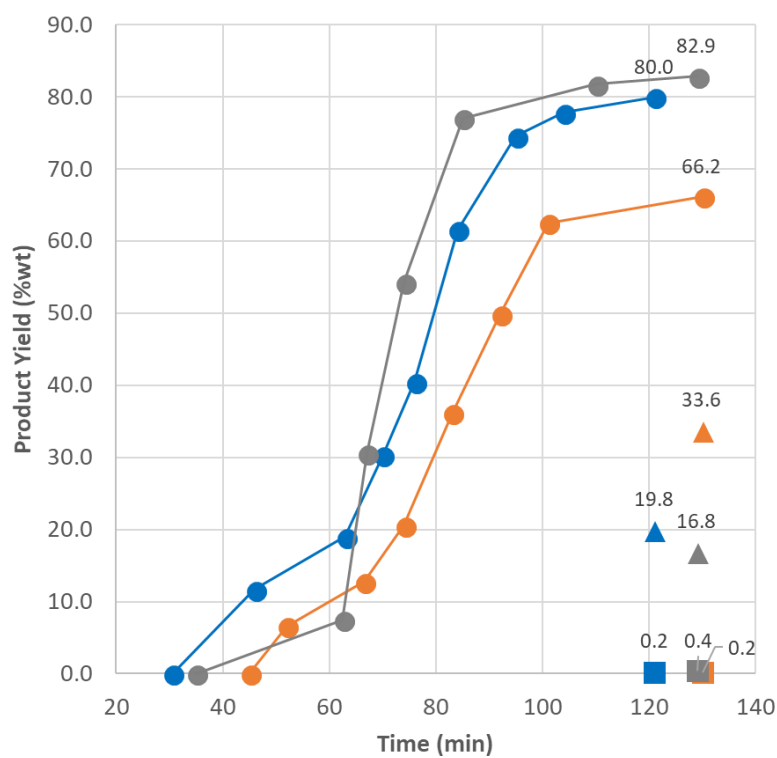




Figure F-2 Effect of catalysts on conversion and products yield at 600°C.

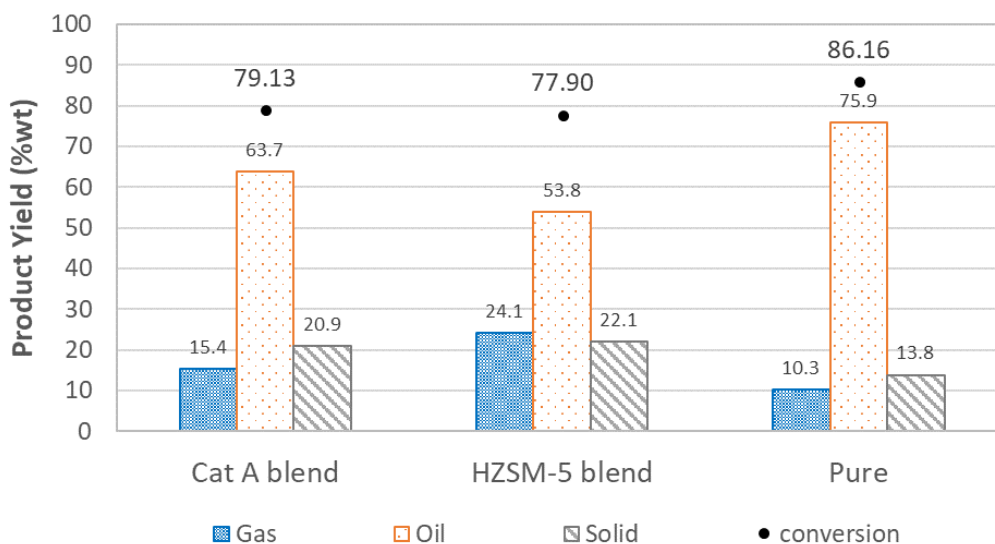


Figure F-3 Effect of catalysts on conversion and products yield at 500°C for reaction time 180 min.

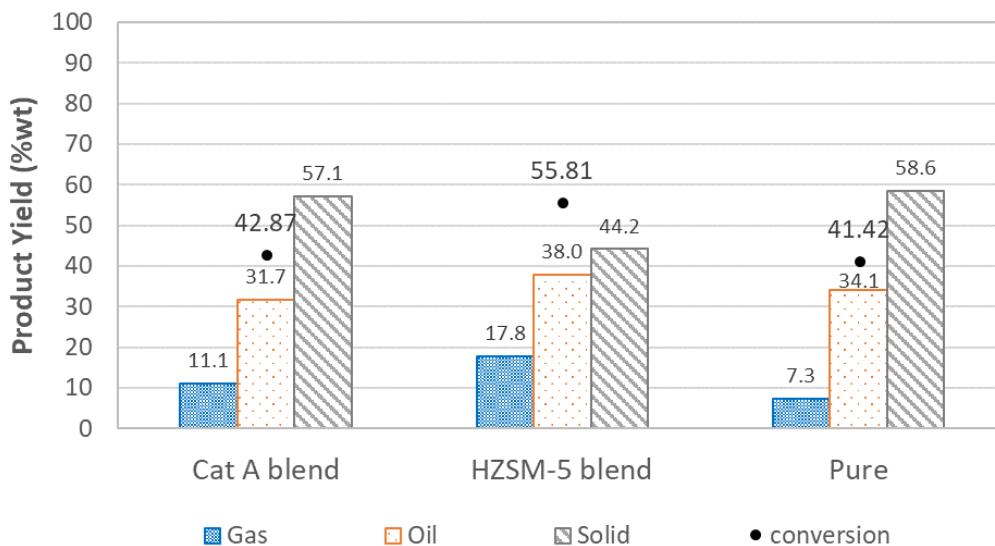


Figure F-4 Effect of catalysts on conversion and products yield at 450°C for reaction time 180 min.

Appendix G: Products distribution grouping by carbon number

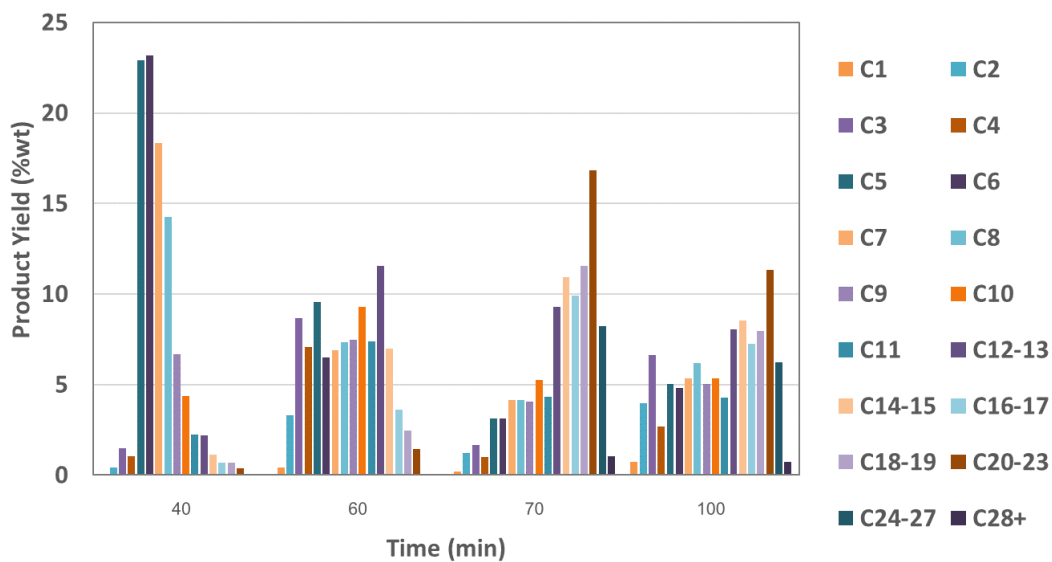


Figure G-1 Effect of reaction time of Cat A on products distribution at 650°C.

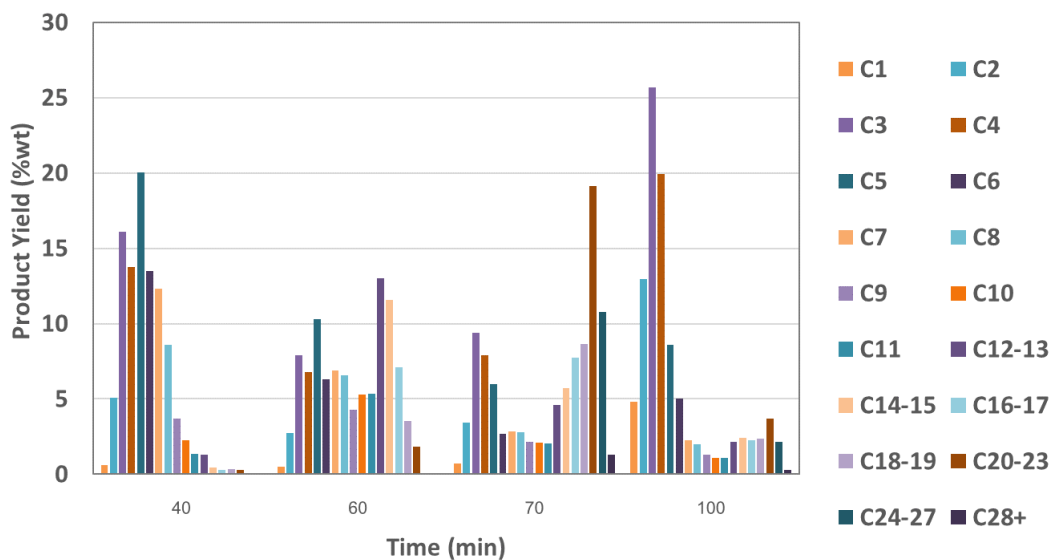
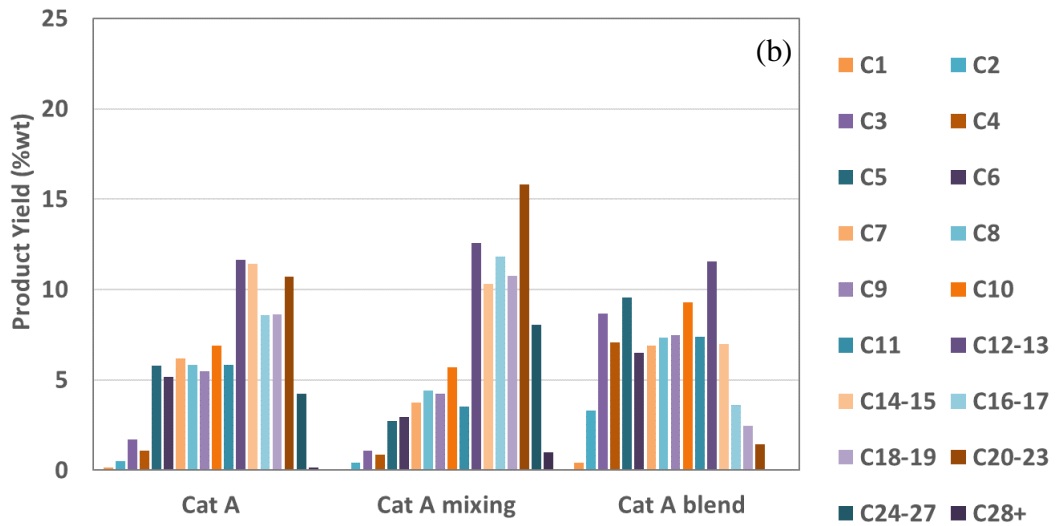
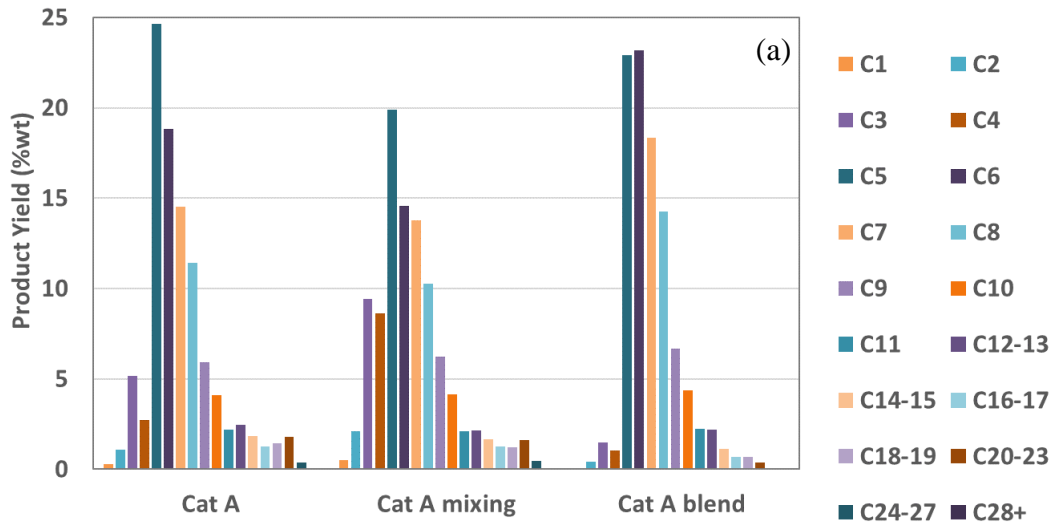


Figure G-2 Effect of reaction time of HZSM-5 on products distribution at 650°C.



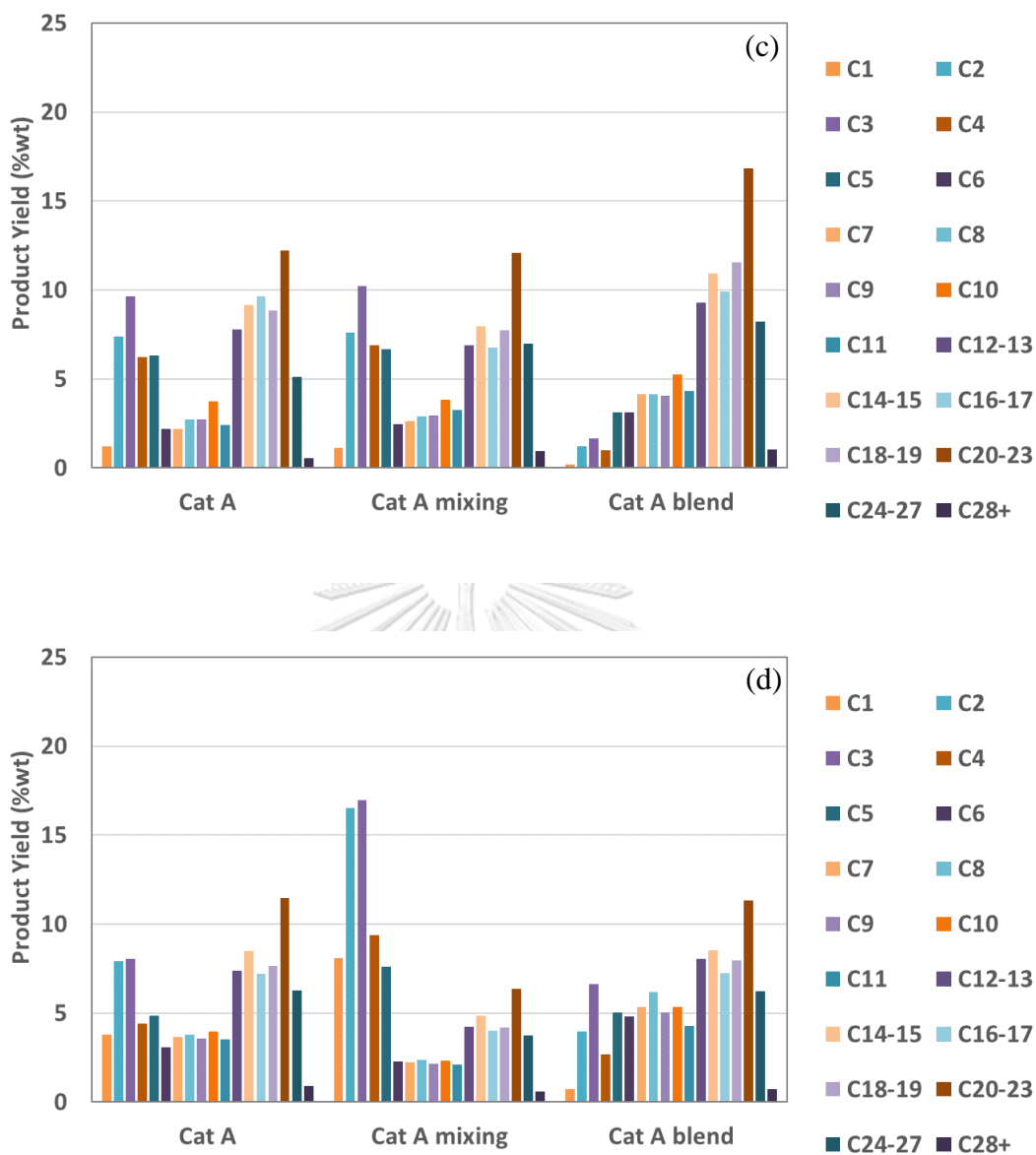
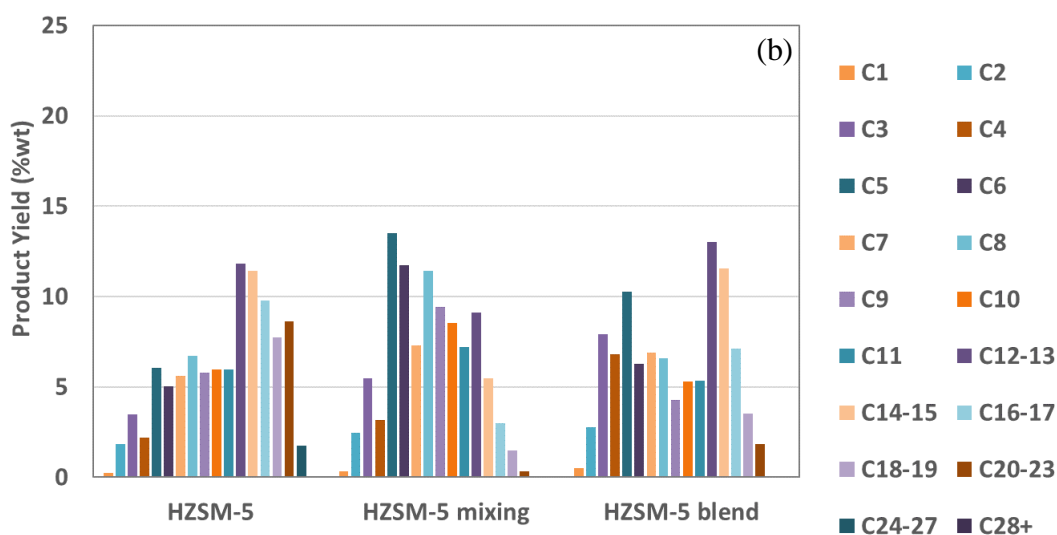
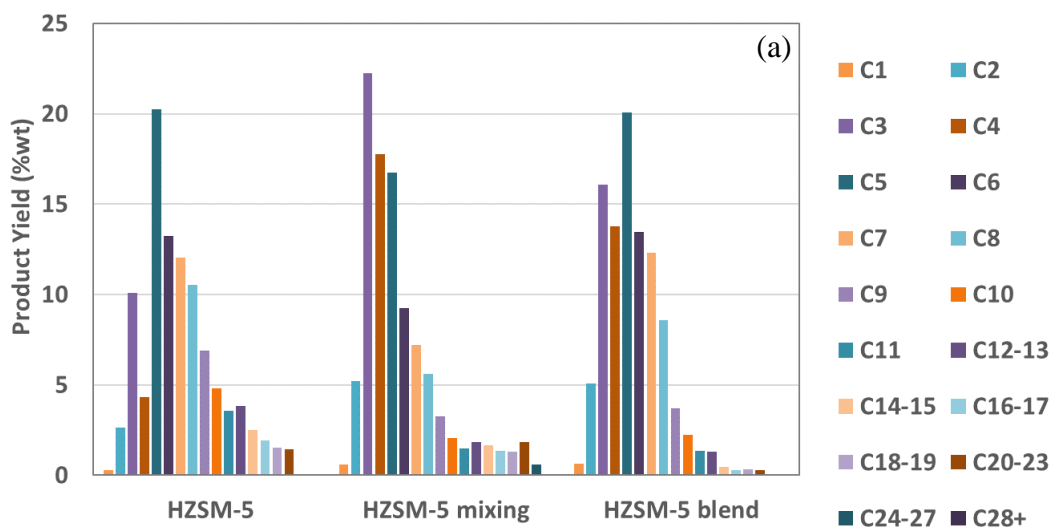


Figure G-3 Effect of catalyst dispersion on products distribution of Cat A at 650 °C for 40min(a), 60min(b), 70min(c), 100 min(d).



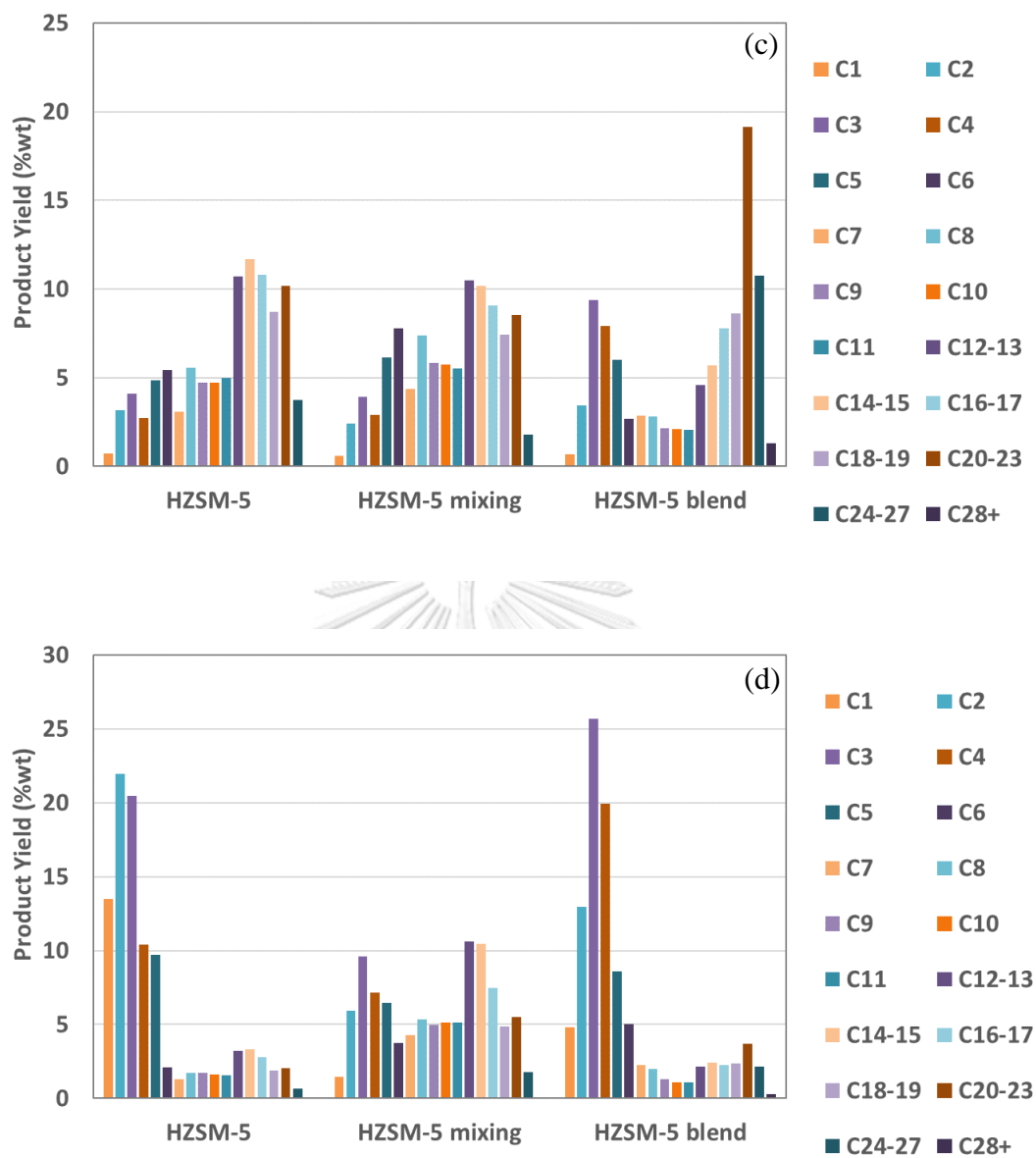
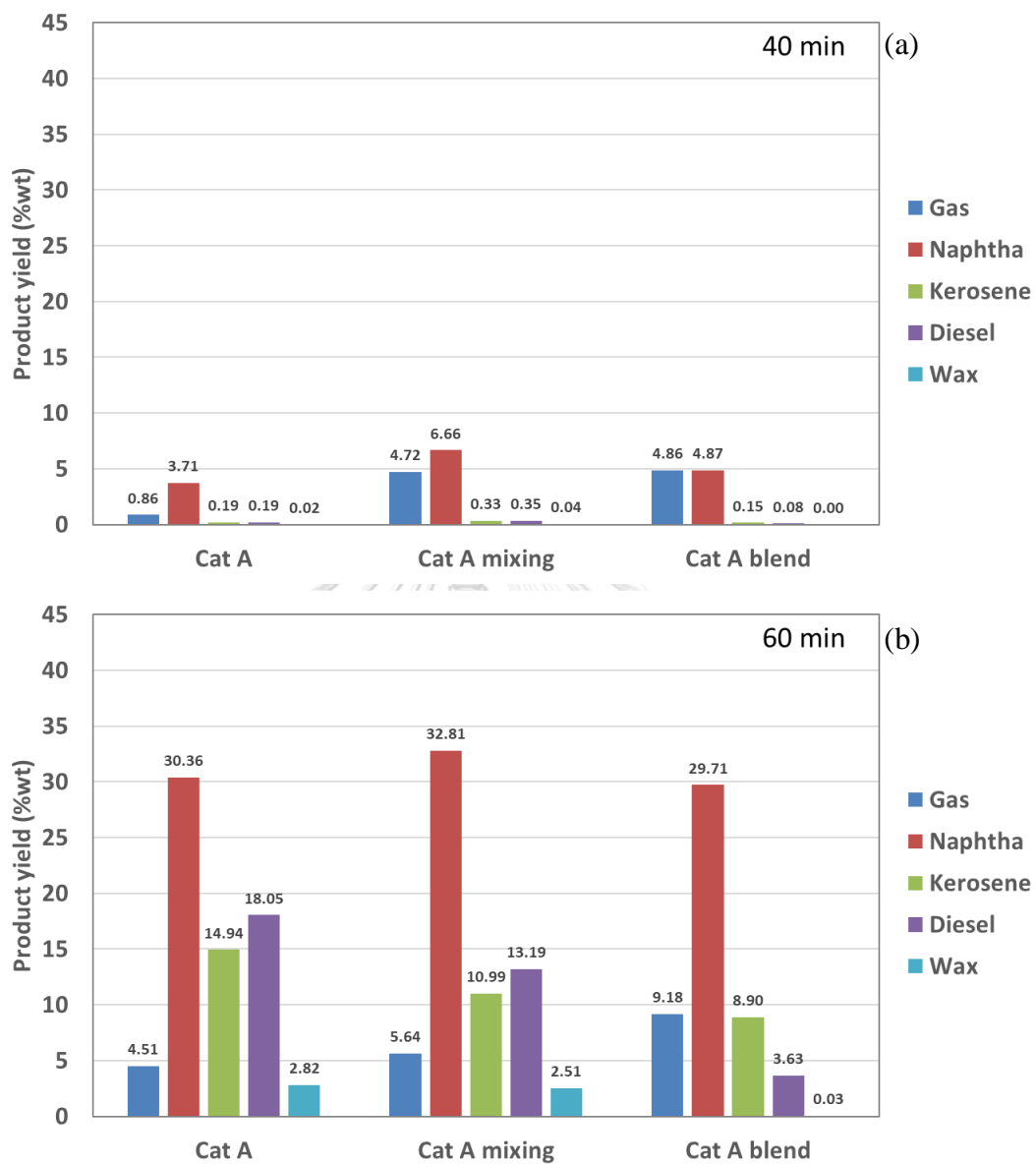


Figure G-4 Effect of catalyst dispersion on products distribution of HZSM-5 at 650 °C for 40min(a), 60min(b), 70min(c), 100 min(d).

Appendix H: Products distribution grouping by carbon number range



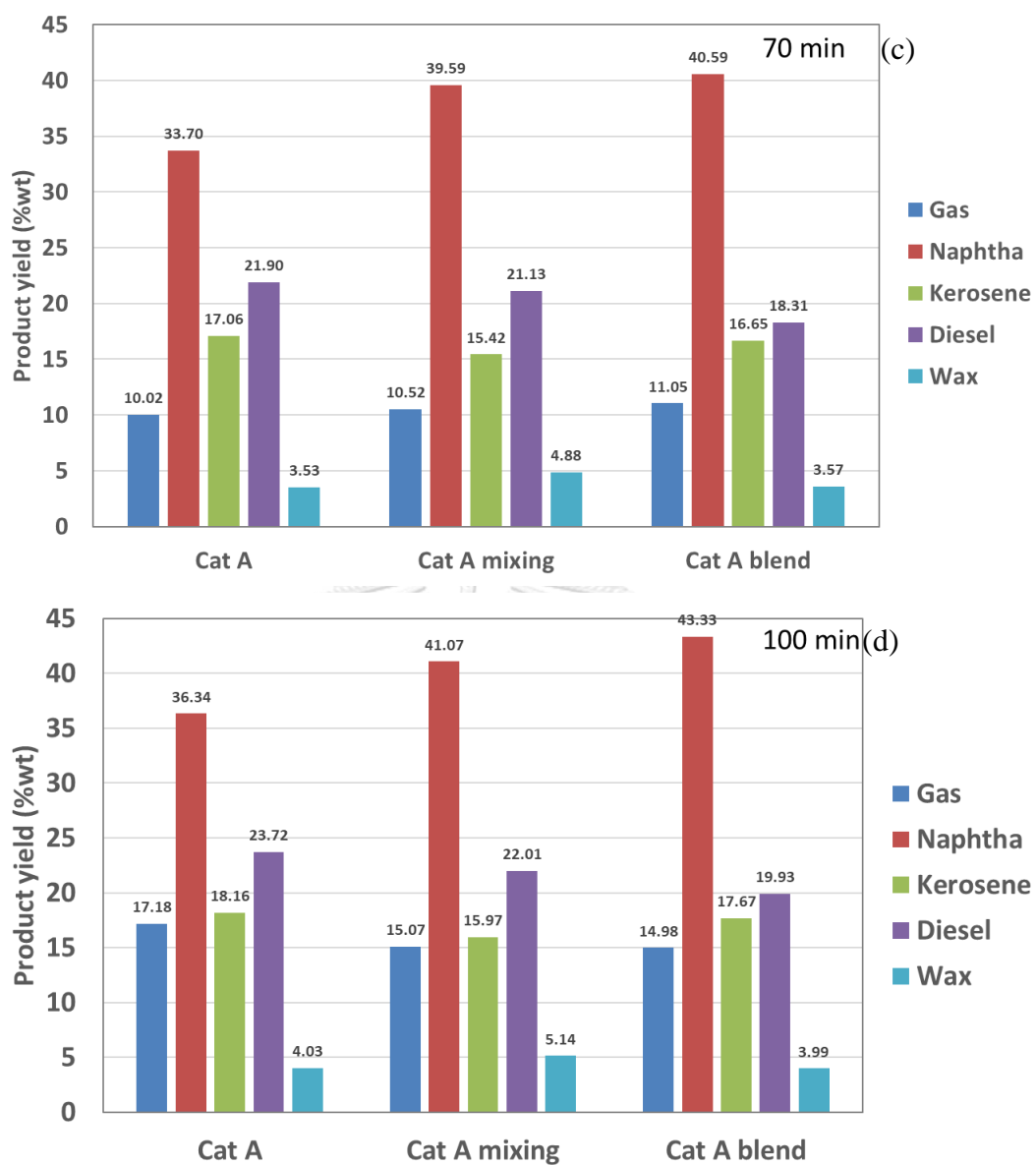
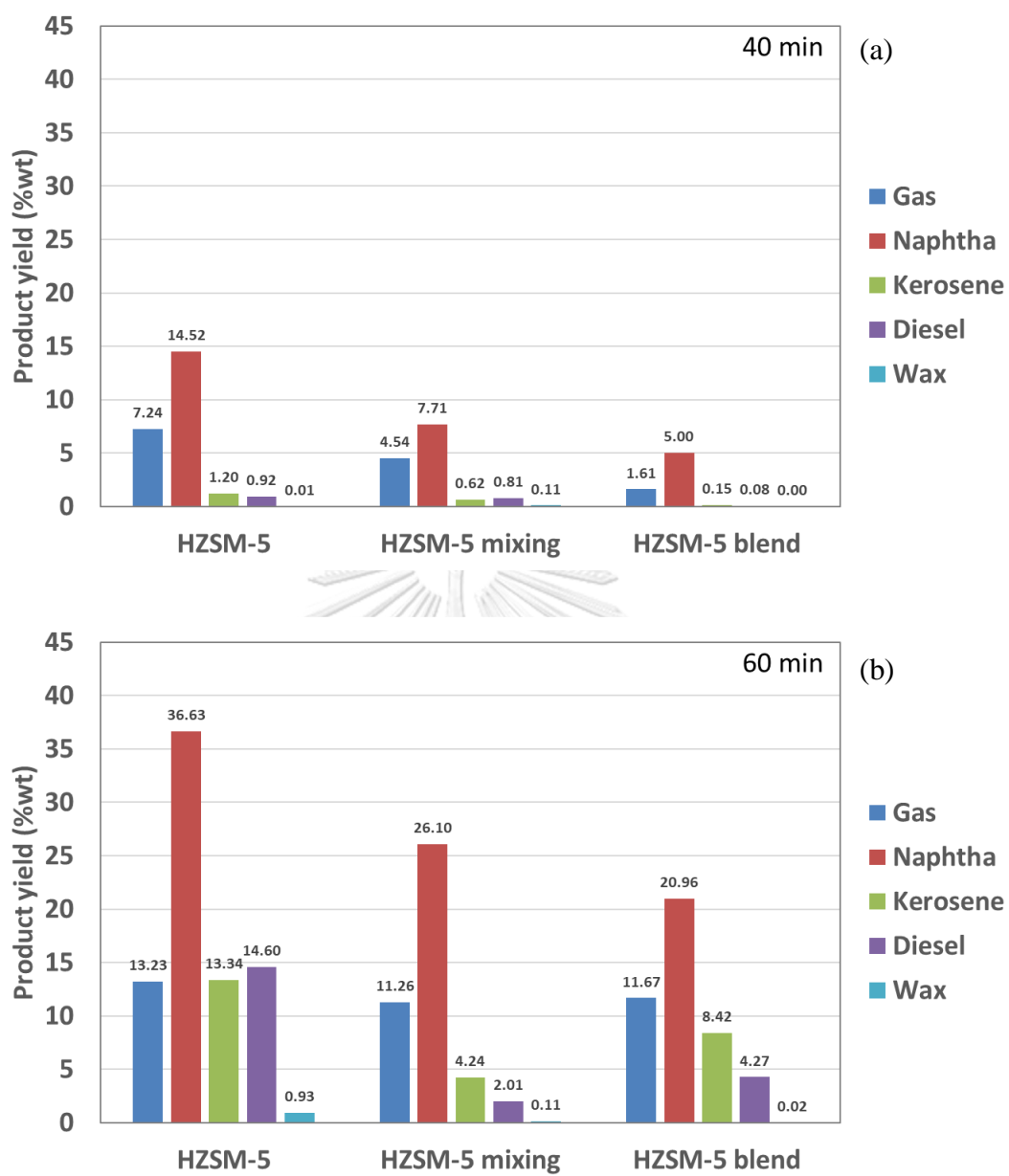


Figure H-1 Effect of catalyst dispersion on cumulative of products distribution of Cat A at 650 °C for 40min(a), 60min(b), 70min(c), 100 min(d).



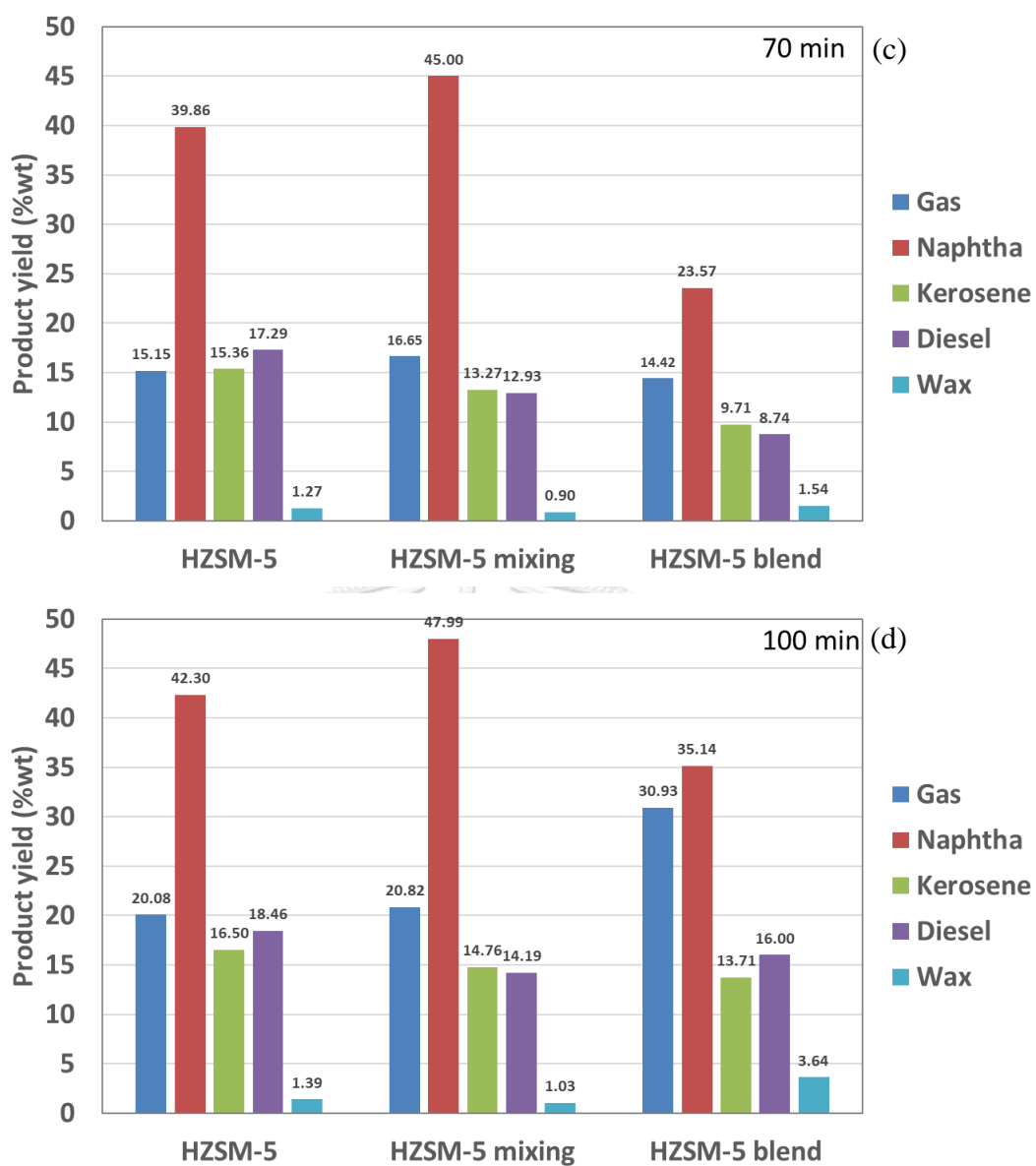


Figure H-2 Effect of catalyst dispersion on cumulative of products distribution of HZSM-5 at 650 °C for 40min(a), 60min(b), 70min(c), 100 min(d).

VITA

Mr. Ratchanon Chantanuson was born on May 14th, 1994. He obtained his bachelor's degree from Center of Excellence in Particle Technology (CEPT), Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in 2015 and continued studying his master's in the same department and adviser.





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