CRACKING OF LOW DENSITY POLYETHYLENE DISSOLVED IN BENZENE TO LIQUID FUELS USING ZEOLITE-BASED CATALYSTS

WONG SYIE LUING

UNIVERSITI TEKNOLOGI MALAYSIA

CRACKING OF LOW DENSITY POLYETHYLENE DISSOLVED IN BENZENE TO LIQUID FUELS USING ZEOLITE-BASED CATALYSTS

WONG SYIE LUING

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

AUGUST 2016

To my beloved parents and friends

ACKNOWLEDGEMENT

All thanks to God for giving me the wisdom, strength, protection, guidance, patience and courage to successfully complete the PhD program in Universiti Teknologi Malaysia. I would like to thank my supervisors, Dr. Norzita Ngadi and Dr. Tuan Amran Tuan Abdullah for their guidance and inspiration during the research. Your prompt attentions, motivations, assistance, encouragements and understanding are highly appreciated. A special thanks to Dr Ibrahim Inuwa too for assisting me throughout my research.

I wish to thank Mr Mohd Latfi bin Che Haron and Miss Zainab binti Salleh from the Analytical Laboratory in Faculty of Chemical Engineering, as well as Miss Ambiga from University Industry Research Lab (UIRL), the entire staff and students in Chemical Reaction Engineering Group (CREG) and Institute of Future Energy (IFE) for their technical assistance and all the helps given throughout my research in Universiti Teknologi Malaysia. I am also grateful to everyone in UTM whose names are too numerous to mention who were always there to ease my stress. Gratitude is also given to my research group members for many enlightening discussions and criticisms.

I am highly indebted to my parents whose blessings I believe have taking me this far in my academic life. I want to specially thank my family for their love, encouragement and support, together with their patience and endurance.

Finally, I wish to acknowledge the support from Ministry of Higher Education, Malaysia, as well as Universiti Teknologi Malaysia for the MyBrain15 scholarship and financial support given during my research.

ABSTRACT

Researchers proposed numerous solutions to plastic pollution, with the hope to tackle the intractable problems brought by plastic especially to mankind and environment. One of the proposed methods of solving the problem is the conversion of plastic waste to chemicals and fuels through pyrolysis and cracking. However, previous studies focused on polymer cracking in a batch process, which resulted in the wide distribution of the products. Thus, there is a need to develop polymer cracking process in continuous mode and improve the product quality by using a suitable catalyst. The aim of this research is to investigate on catalytic cracking of low density polyethylene (LDPE) in a fixed bed reactor into liquid fuel. LDPE was dissolved in different solvents with similar solubility parameter and the most suitable solvent was selected. The catalytic cracking was then carried out on the LDPE solution using a fixed bed reactor at atmospheric pressure. Parent zeolites and nickel-impregnated zeolites were screened as catalysts for the cracking of LDPE. The change in product composition at different reaction conditions was also studied, and a plausible reaction mechanism was proposed. This was followed by parametric study of the process involving five factors, namely temperature (A), catalyst mass (B), feed flow rate (C), N_2 flow rate (D), as well as concentration of LDPE solution (E), and the two responses were LDPE conversion (Y_1) and liquid yield (Y_2). Two level full factorial design was used to evaluate the factors. It was found that benzene is the most suitable solvent for LDPE dissolution. Catalytic cracking of the LDPE solution produced C1-C8 hydrocarbons in all runs. During the catalyst screening, zeolite Z2 (ZSM-5 zeolite, Si/Al: 1000) was found to be the most promising catalyst, as it was able to obtain high LDPE conversion (99.93%), high liquid yield (92.28%) and low coke formation (0.02%). The parametric analysis showed that four out of five factors (A, B, C and D) produced significant effects on Y_1 and Y_2. On the other hand, factor E was statistically insignificant on the responses. Analysis on products composition showed that cracking of LDPE over zeolite Z2 produced a high amount of aliphatic branched-chain compounds, together with the moderate amount of cyclic compounds (C7-C12). The reaction conditions also led to alkylation of benzene by the cracking products from LDPE. It is suggested that the catalytic cracking of LDPE is dominated by free radical mechanism, while the influence of carbenium ion mechanism is less pronounced due to low acidity of the catalyst. Hence, it is concluded that catalytic cracking of dissolved LDPE in fixed bed reactor with zeolite Z2 is able to convert LDPE into liquid fuel in gasoline range and has the potential to tackle the plastic pollution.

ABSTRAK

Para penyelidik mencadangkan pelbagai penyelesaian kepada pencemaran plastik, dengan harapan untuk menangani masalah yang dibawa oleh plastik terutamanya kepada manusia dan persekitaran. Salah satu penyelesaian yang dicadangkan adalah penukaran sisa plastik kepada bahan kimia dan bahan api melalui pirolisis dan perengkahan. Walau bagaimanapun, kajian-kajian sebelum ini lebih tertumpu kepada perengkahan polimer dalam proses berkelompok yang menghasilkan taburan produk yang luas. Maka, adalah perlu untuk mengkaji perengkahan polimer dalam mod berterusan, serta meningkatan kualiti produk dengan pemangkin yang sesuai. Tujuan kajian ini adalah untuk mengkaji perengkahan berpemangkin polietilena berketumpatan rendah (LDPE) dalam reaktor lapisan tetap kepada bahan api cecair. LDPE dilarutkan dalam pelarut yang berbeza dengan parameter kelarutan yang hampir sama, dan pelarut yang paling sesuai dipilih. Perengkahan berpemangkin kemudian dijalankan ke atas larutan LDPE menggunakan reaktor lapisan tetap mikro pada tekanan atmosfera. Zeolit asal dan zeolit yang mengandungi nikel telah digunakan sebagai pemangkin. Perubahan dalam komposisi produk pada keadaan tindak balas yang berbeza juga telah dikaji, dan mekanisma tindak balas yang munasabah telah dicadangkan. Ini diikuti dengan kajian parametrik proses melibatkan lima faktor, iaitu suhu (A), jisim pemangkin (B), kadar aliran suapan (C), kadar aliran N_2 (D), serta kepekatan larutan LDPE (E), dan dua respon yang dilihat adalah penukaran LDPE (Y_1) dan hasil cecair (Y_2). Reka bentuk penuh faktorial dua peringkat telah digunakan. Benzena merupakan pelarut yang paling sesuai untuk pelarutan LDPE. Perengkahan berpemangkin LDPE menghasilkan hidrokarbon C1-C8 dalam semua eksperimen. Dalam saringan pemangkin, zeolit Z2 (zeolit ZSM-5, Si/Al: 1000) didapati sebagai pemangkin yang sesuai, kerana ia menghasilkan penukaran LDPE yang tinggi (99.93%), hasil cecair yang tinggi (92.28%) dan pembentukan kok yang rendah (0.02%). Kajian parametrik menunjukkan bahawa empat daripada lima faktor (A, B, C dan D) menghasilkan kesan yang ketara ke atas Y_1 dan Y_2. Sebaliknya, faktor E adalah tidak penting secara statistik ke atas respon-respon yang dikaji. Analisis ke atas komposisi menunjukkan bahawa perengkahan LDPE dengan zeolite Z2 menghasilkan amaun sebatian rantai bercabang alifatik yang tinggi, bersama dengan amaun sebatian siklik (C7-C12) yang sederhana. Keadaan tindak balas juga membawa kepada alkilasi benzena oleh produk perengkahan dari LDPE. Adalah dicadangkan bahawa perengkahan berpemangkin LDPE dikuasai oleh mekanisma radikal bebas, manakala pengaruh mekanisma ion karbenium adalah kurang ketara akibat keasidan pemangkin yang rendah. Secara kesimpulannya, perengkahan berpemangkin LDPE dalam benzena dalam reaktor lapisan tetap dengan zeolite Z2 boleh menukar LDPE kepada bahan api cecair dalam lingkungan petrol dan mempunyai potensi untuk menangani pencemaran plastik.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ANOVA	-	Analysis of Variance
BET	-	Brunauer, Emmett and Teller method
BTX	-	benzene, toluene and xylene
CCD	-	central composite design
CSBR	-	conical spouted bed reactor
DOE	-	Design of experiment
EVA	-	Ethylene Vinyl Acetate
FCC	-	fluid catalytic cracking
FID	-	flame ionization detector
FTIR	-	Fourier-Transformed Infra-red
GC-MS	-	Gas chromatography coupled with mass selectivity detector
HDPE	-	High density polyethylene
HHV	-	higher heating value
HT-GPC	-	high temperature gel permeation chromatography
LCO	-	light cycle oil
LDPE	-	Low density polyethylene
LLDPE	-	linear low density polyethylene
LPG	-	liquefied petroleum gas
MAP	-	microwave assisted pyrolysis
MAT	-	automated microactivity unit
MPW	-	municipal plastic waste
MSW	-	municipal solid waste
N.A.	-	not available
OVAT	-	one-variable-at-a-time method
PE	-	Polyethylene
PET	-	Polyethylene terepththalate

PIONA	-	paraffins, olefins, napthenes and aromatics
PP	-	polypropylene
PS	-	Polystyrene
PS-PBD	-	polystyrene-polybutadiene
PVC	-	Poly(vinyl chloride)
RDF	-	refuse-derived fuel
RGA	-	Residual Gas Analyser
R^2	-	correlation coefficient
SEM	-	Scanning electron Microscope
TCD	-	thermal conductivity detector
TGA	-	Thermogravimetric analysis
TPO	-	temperature-programmed oxidation
TPR	-	Temperature-programmed reduction
VGO	-	vacuum gas oil
WPB	-	waste particle board
XRD	-	X-Ray diffraction
Zeolite Y	-	zeolite CBV 720
Zeolite Z1	-	zeolite CBV 2314
Zeolite Z2	-	Zeolite ZSM5
ZSM	-	Zeolite Socony Mobil–5

LIST OF SYMBOLS

°C	-	degree Celcius
g	-	Gram
wt%	-	weight percentage
mm	-	millimeter
L	-	Liter
mL	-	milliliter
µm	-	micrometer
nm	-	nanometer
Å	-	Armstrong (1 x 10^{-10} meter)
V	-	volt
VA	-	volt ampere
°	-	degree
min	-	minute

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Since their first synthesis in early 1900s, plastics have substituted many types of materials in production of consumer products, as they possessed superior qualities compared to traditional materials such wood, metal and ceramics. Among different types of plastics, polyethylene (PE) is widely used for numerous purposes, including the production of wrapping papers and plastic bags due to its light weight, strength, durability and low cost. As a result, the global demand of polyethylene is increasing. In 2012, annual LDPE production of 21 million tonnes was reported, following a steady growth of over 700,000 tonnes over a year [1].

Despite the advantages brought by plastic-made materials, their disposal causes a lot of problems to the environment, as they do not degrade in landfill, and remain buried in the soil for hundreds or even thousands of years thereby constituting an environmental pollution. It is estimated that plastic waste accounted for 8-12% of total municipal solid waste (MSW) around the globe, and is estimated to reach 9-13% by 2025 [2]. In order to solve the problem brought by the plastic waste, researchers have proposed many solutions, however, none of the proposed solutions can effectively solve the plastic pollution with positive reception from the public. Researchers are currently focusing on the potential of polymer cracking, which involves the depolymerization of plastic to small hydrocarbon molecules, which can be then utilized as fuels. Recently, a lot of effort was made by researchers in this area.

However, as most studies in polymer pyrolysis and cracking process were carried out in batch reactors, there are some difficulties to apply the process in polymer recycling industry. In order to achieve such development, polymer cracking has to be carried out in continuous process mode. Nonetheless, polymer waste in its solid waste is difficult to be fed into reactor continuously. Thus, there is a need to develop a method that enables smooth continuous feeding of polymer waste into the reactor for catalytic cracking, as there are many advantages associated with this process. Studies by several researchers [3-5] may serves as a possible solution to the mentioned problem. In their studies, the polymer is dissolved in compatible solvents to form solutions with reasonable viscosity. The polymer solution was then feed into the cracking reactor to produce liquids comparable to fuels. However, such studies are very scarce in literature, and only limited to small scale. Hence, it is necessary to investigate on catalytic cracking of polymer in larger scale.

1.2 Problem Statement

Due to the increasing demand on plastic-made consumer products, there is an urgent need to propose proper alternatives to plastic waste disposal. Among the proposed solutions, catalytic cracking seems to be an interesting option, since it converts plastic waste to liquid fuel. However, most studies on catalytic cracking of polymer were done in batch process, which is difficult to be applied in polymer recycling industry. There is a need to develop catalytic cracking of polymer in continuous mode, since such process is more scalable and suitable for industry requirements. Nevertheless, development of catalytic cracking of polymer in continuous mode is challenging due to the lack of comprehensive studies. In order to develop such process, the compatible solvent for the studied polymer has to be determined, since not all solvents can be used to satisfactorily dissolve the polymer. Another challenge faced by researchers in studying continuous catalytic cracking of polymer is the proper method to determine the polymer conversion during the process. For polymer cracking in batch reactor, the polymer conversion can be easily determined based on the weight of unreacted polymer in the reactor after the cracking process. Such method does not work on polymer cracking in continuous mode, since the unconverted polymer is mixed with the liquid product after the cracking process. Several strategies used in previous studies to overcome this problem, as explained in Section 2.5.2, are difficult to be replicated in most laboratories. Therefore, there is a need to propose an easy method for quantification of polymer conversion in continuous cracking.

In addition, the understanding on polymer cracking in continuous mode is still shallow, due to the limited works in literature. The findings on polymer cracking in batch mode can only be partially generalized on the continuous cracking of polymer, due to the differences of these processes. Thus, there is a need for a comprehensive study on continuous cracking of polymer, including the effects of different catalysts and reaction parameters towards the polymer conversion and liquid yield. It is also necessary to find out how these factors influence the composition of products, especially liquid, since such property is of utmost important to determine its suitability to be used as fuel.

1.3 Objectives of Research

The main objective of this research is to study on catalytic cracking of low density polyethylene (LDPE) dissolved in solvent in a fixed bed reactor. The specific objectives are listed in the following:

a. To screen solvent in dissolution of commercial LDPE.
b. To investigate the effects of different catalysts on the composition and yield of liquid and gaseous products in catalytic cracking of LPDE dissolved in best solvent in the fixed bed reactor.
c. To study the effects of different factors towards liquid product composition, and propose the reaction mechanism of the catalytic cracking of LDPE/benzene solution.
d. To determine the significant reaction parameters in catalytic cracking of LDPE using two-level full factorial design.

1.4 Scope of Research

In order to achieve the research objectives, the scope of this research is designed as follows:

(a) Screening was carried out on five solvents (benzene, chlorobenzene, toluene, xylene and trichloroethylene) to determine the best solvent for dissolution of commercial low density polyethylene (LDPE). Characterizations were also performed on LDPE in solid and solution state (using selected solvent), in term of elemental and proximate analysis, viscometry, Fourier-transformed Infra-red (FTIR) spectrometry, Thermogravimetric analysis (TGA), and bomb calorimetry.

(b) Zeolite Z1 (ZSM-5 type, CBV 2314, Si/Al: 23) was selected as the catalyst as it is the one of the widely used ZSM-5 zeolites in cracking of hydrocarbons, polymer and biomass [6-9]. Zeolite Y (USY type, CBV 720, Si/Al: 30) is another typical USY zeolite used for the same purpose [10-12]. They are reported to have large surface area with high amount of acidic sites that enables effective contact of the reactants on its surface for reactions. Thus, it is necessary to test their catalytic performance in the cracking of LDPE solution. Comparison between the performances of the two catalysts revealed the difference between ZSM5 zeolite and USY zeolite. Another aim of this research is to study the potential of a ZSM-5 zeolite (named as Z2, Si/Al: 1000) in catalytic cracking of LDPE solution. The use of such zeolite has not been reported in the literature, hence it is worthy to study its potential in LDPE cracking process. Another aim of this study is to study the effect of Ni impregnation of the catalytic properties of zeolites, which is not yet reported in catalytic cracking of dissolved polymer. Nickel is chosen due to its ability to improve products quality as explained in Section 2.7.3. According to literature, metal loadings of 0.5% -15% is often used by researchers in this field [13-16]. Therefore, a metal loading of 10wt% was chosen for this research. Characterizations of the zeolites were carried out using Brunauer, Emmett and Teller (BET) analysis method for surface area, Scanning electron Microscope (SEM), X-Ray diffraction (XRD), Temperature-programmed reduction (TPR), and Temperature–programmed desorption of ammonia (TPD-NH_3). Catalytic cracking of LDPE solution was then carried out in the fixed bed reactor using a total of six catalysts (Y, Ni-Y, Z1, Ni-Z1, Z2, Ni-Z2), and the liquid products from the cracking process were characterized using Gas chromatography coupled with mass selectivity detector (GC-MS), Fourier-Transformed Infra-red (FTIR) spectroscopy, as well as bomb calorimetry. The coke formation on catalyst was also studied using temperature-programmed oxidation in thermobalance (TGA-TPO). The most promising catalyst was selected based on polymer conversion, liquid yield and coke yield.

(c) By using the selected catalyst, a parametric study was carried out on catalytic cracking of LDPE solution in fixed bed reactor. Two-level full factorial design was generated using Minitab for the purpose. The factors studied were temperature (400-600 ºC), mass of catalyst (0.1-0.2 g), flow rate of LDPE solution (1-3 ml/min), flow rate of carrier gas (20-80 ml/min), as well as concentration of LDPE solution (0.005-0.2 g LDPE/ml benzene), while the responses studied were LDPE conversion and liquid yield.

(d) Compositions of liquid products were determined after performing catalytic cracking at varying reaction conditions. The effects of significant factors determined from scope (c) towards the liquid products were then determined. The plausible mechanism was proposed for catalytic cracking of LDPE, based on the composition of products at varying reaction parameters.

1.5 Significance of Research

Following a great number of detailed studies in thermal and catalytic cracking of various polymers in batch reactors, there is a need to develop polymer cracking process in continuous mode. Such conversion is important in commercialization of polymer cracking process, as it offers higher versatility compared to polymer cracking in batch mode. Compared to the latter, the former process is easier to be controlled, and thus leads to more stable products quality. In addition, polymer cracking in continuous mode reduces the time solely for reactor heating (during start-up) and cooling (before products discharge) when compared to batch units, which requires heating and cooling every batch. These improvements ultimately results in higher efficiency of the process.

In addition, development of polymer cracking in continuous mode also opens more possibilities for the process. For instance, it is possible to selectively separate the plastic waste to different types of polymers by using different solvents and dissolution temperatures [17]. Such separation, termed as selective dissolution, may increase the efficiency for polymer cracking process [18], and more studies on this possibility are under way. It is also interesting to investigate the possibility to carrying out the continuous polymer cracking in fluid catalytic cracking (FCC) unit in petroleum refinery. Such process is feasible due to the similar structure of dissolved polymer and crude oil [19, 20].

In order to realize the mentioned potentials, comprehensive studies on continuous polymer cracking are necessary to enable in-depth understanding by the researchers. To the best of our knowledge, no study is reported in the open literature using a continuous catalytic cracking of LDPE to generate liquid fuel. Thus, the result from this research is expected to expand the frontier of knowledge in the field of plastic waste recycling.

1.6 Thesis Outline

This thesis consists of five chapters. Each chapter provides information on specific research area:

Chapter 1 contains the research background, research objectives and scopes, as well as significance of research. Chapter 2 discusses the literature review including background knowledge on catalytic cracking of polymers, design of experiment (DOE), analysis techniques that are commonly used for characterization purpose in catalytic cracking etc. Chapter 3 describes the experimental setup and the procedures followed during the research work. These include characterization methods on polymer feed, catalysts and products design and fabrication of the fixed bed reactor, as well as study on effects of reaction parameters towards process performances and products compositions. Chapter 4 deals with data processing and discussions on the results, followed by proposed mechanism on catalytic cracking of dissolved LDPE. Chapter 5 presents the conclusions derived from this research and the recommendations for future studies.

REFERENCES

1. Merchant Research and Consulting, L., *Global LDPE Production Grew by Over 700,000 Tonnes in 2012,* Available from:<http://mcgroup.co.uk/news/20130705/global-ldpe-production-grew-700000-tonnes.html>. [4 October 2013].
2. Hoornweg, D. and Bhada-Tata, P., *What a Waste- A Global Review of Solid Waste Management,* Available from:<http://web.worldbank.org/WBSITE/EXTERNAL/TOPICS/EXTURBANDEVELOPMENT/0,,contentMDK:23172887~pagePK:210058~piPK:210062~theSitePK:337178,00.html>. [9 January 2016].
3. Ng, S.H. Conversion of Polyethylene Blended with VGO to Transportation Fuels by Catalytic Cracking. *Energy & Fuels*. 1995. 9(2): 216-224.
4. Ng, S.H., Seoud, H., Stanciulescu, M., and Sugimoto, Y. Conversion of Polyethylene to Transportation Fuels through Pyrolysis and Catalytic Cracking. *Energy & Fuels*. 1995. 9(5): 735-742.
5. Arandes, J.M., Abajo, I., LopezValerio, D., Fernandez, I., Azkoiti, M.J., Olazar, M., and Bilbao, J. Transformation of several plastic wastes into fuels by catalytic cracking. *Industrial & Engineering Chemistry Research*. 1997. 36(11): 4523-4529.
6. Lauritzen, A.M. and Madgavkar, A.M. *Process for the conversion of lower alkanes to aromatic hydrocarbons and ethylene* Google Patents. 2009
7. Mullen, C.A. and Boateng, A.A. Production of Aromatic Hydrocarbons via Catalytic Pyrolysis of Biomass over Fe-Modified HZSM-5 Zeolites. *ACS Sustainable Chemistry & Engineering*. 2015. 3(7): 1623-1631.
8. Dorado, C., Mullen, C.A., and Boateng, A.A. Origin of carbon in aromatic and olefin products derived from HZSM-5 catalyzed co-pyrolysis of cellulose and plastics via isotopic labeling. *Applied Catalysis B: Environmental*. 2015. 162: 338-345.

9. Dorado, C., Mullen, C.A., and Boateng, A.A. H-ZSM5 Catalyzed Co-Pyrolysis of Biomass and Plastics. *ACS Sustainable Chemistry & Engineering*. 2013. 2(2): 301-311.
10. Neves, I.C., Botelho, G., Machado, A.V., and Rebelo, P. Catalytic degradation of polyethylene: An evaluation of the effect of dealuminated Y zeolites using thermal analysis. *Materials Chemistry and Physics*. 2007. 104(1): 5-9.
11. French, R. and Czernik, S. Catalytic pyrolysis of biomass for biofuels production. *Fuel Processing Technology*. 2010. 91(1): 25-32.
12. Sirous Rezaei, P., Shafaghat, H., and Daud, W.M.A.W. Suppression of coke formation and enhancement of aromatic hydrocarbon production in catalytic fast pyrolysis of cellulose over different zeolites: effects of pore structure and acidity. *RSC Advances*. 2015. 5(80): 65408-65414.
13. Awayssa, O.R., Al-yassir, N., S, A., Abdullah Mohammed, and Al-khattaf, S.S. *Metal-modified zeolite for catalytic cracking of heavy oils and process for producing light olefins* King Fahd University of Petroleum and Minerals (Dhahran, SA). United States. 2015
14. Saeaeh, L. and Jitkarnka, S. Investigation of Nickel as a Metal Substitute of Palladium Supported on HBeta Zeolite for Waste Tire Pyrolysis. *Proceedings of World Academy of Science, Engineering and Technology*. World Academy of Science, Engineering and Technology. 2012.
15. Wu, H., Shen, Y., Ma, D., An, Q., Harada, N., and Yoshikawa, K. Fuel Oil Production from Two-Stage Pyrolysis-Catalytic Reforming of Brominated High Impact Polystyrene Using Zeolite and Iron Oxide Loaded Zeolite Catalysts. *Open Journal of Ecology*. 2015. 5(04): 136.
16. Escola, J., Aguado, J., Serrano, D., and Briones, L. Transportation fuel production by combination of LDPE thermal cracking and catalytic hydroreforming. *Waste Management*. 2014. 34(11): 2176-2184.
17. Pappa, G., Boukouvalas, C., Giannaris, C., Ntaras, N., Zografos, V., Magoulas, K., Lygeros, A., and Tassios, D. The selective dissolution/precipitation technique for polymer recycling: a pilot unit application. *Resources Conservation and Recycling*. 2001. 34(1): 33-44.

18. Wu, J., Chen, T., Luo, X., Han, D., Wang, Z., and Wu, J. TG/FTIR analysis on co-pyrolysis behavior of PE, PVC and PS. *Waste Management*. 2014. 34(3): 676-682.

19. Arandes, J.M., Ereña, J., Bilbao, J., López-Valerio, D., and De la Puente, G. Valorization of Polyolefins Dissolved in Light Cycle Oil over HY Zeolites under Fluid Catalytic Cracking Unit Conditions. *Industrial & Engineering Chemistry Research*. 2003. 42(17): 3952-3961.

20. Arandes, J.M., Ereña, J., Bilbao, J., López-Valerio, D., and de la Puente, G. Valorization of the Blends Polystyrene/Light Cycle Oil and Polystyrene−Butadiene/Light Cycle Oil over HZSM-5 Zeolites. *Industrial & Engineering Chemistry Research*. 2003. 42(16): 3700-3710.

21. Sagel, E., *Polyethylene Global Overview* Available from:<http://www.ptq.pemex.com/productosyservicios/eventosdescargas/Documents/Foro%20PEMEX%20Petroqu%C3%ADmica/2012/PEMEX%20PE.pdf>. [17 February 2014].

22. Anonymous, *Research and Markets: China's Ethylene Vinyl Acetate (EVA) Industry, 2013-2017,* Available from:<http://www.businesswire.com/news/home/20130423005779/en/Research-Markets-Chinas-Ethylene-Vinyl-Acetate-EVA#.UuITf1CwonI>. [23 April 2013].

23. Donaruma, L., Block, B., Loening, K., Plate, N., Tsuruta, T., Buschbeck, K.C., Powell, W., and Reedijk, J. Nomenclature for regular single-strand and quasi single-strand inorganic and coordination polymers (Recommendations 1984): International Union of Pure and Applied Chemistry (IUPAC) Macromolecular Division, Commission on Macromolecular Nomenclature Inorganic Chemistry Division, Commission on Nomenclature of Inorganic Chemistry. *Polymer Science USSR*. 1986. 28(5): 1240-1260.

24. Sartorius, I. Materials Case Study 4: Plastics. *OECD Global Forum on Environment*. OECD Environment Directorate, OECD, 2010. 2010.

25. Kumar, S., Panda, A.K., and Singh, R.K. A review on tertiary recycling of high-density polyethylene to fuel. *Resources Conservation and Recycling*. 2011. 55(11): 893-910.

26. Al-Salem, S.M., Lettieri, P., and Baeyens, J. The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and

chemicals. *Progress in Energy and Combustion Science*. 2010. 36(1): 103-129.

27. Al-Salem, S.M., Lettieri, P., and Baeyens, J. Recycling and recovery routes of plastic solid waste (PSW): a review. *Waste Management*. 2009. 29(10): 2625-2643.
28. Shah, S.H., Khan, Z.M., Raja, I.A., Mahmood, Q., Bhatti, Z.A., Khan, J., Farooq, A., Rashid, N., and Wu, D. Low temperature conversion of plastic waste into light hydrocarbons. *J Hazard Mater*. 2010. 179(1-3): 15-20.
29. Escola, J.M., Aguado, J., Serrano, D.P., García, A., Peral, A., Briones, L., Calvo, R., and Fernandez, E. Catalytic hydroreforming of the polyethylene thermal cracking oil over Ni supported hierarchical zeolites and mesostructured aluminosilicates. *Applied Catalysis B: Environmental*. 2011. 106(3-4): 405-415.
30. Marcilla, A., Beltran, M.I., and Navarro, R. Evolution of products during the degradation of polyethylene in a batch reactor. *Journal of Analytical and Applied Pyrolysis*. 2009. 86(1): 14-21.
31. Miskolczi, N. Co-pyrolysis of petroleum based waste HDPE, poly-lactic-acid biopolymer and organic waste. *Journal of Industrial and Engineering Chemistry*. (0).
32. Covarrubias, C., Gracia, F., and Palza, H. Catalytic degradation of polyethylene using nanosized ZSM-2 zeolite. *Applied Catalysis a-General*. 2010. 384(1-2): 186-191.
33. Lee, J.Y., Park, S.M., Saha, S.K., Cho, S.J., and Seo, G. Liquid-phase degradation of polyethylene (PE) over MFI zeolites with mesopores: Effects of the structure of PE and the characteristics of mesopores. *Applied Catalysis B: Environmental*. 2011. 108(1-2): 61-71.
34. Jan, M.R., Shah, J., and Gulab, H. Catalytic degradation of waste high-density polyethylene into fuel products using BaCO3 as a catalyst. *Fuel Processing Technology*. 2010. 91(11): 1428-1437.
35. Rasul Jan, M., Shah, J., and Gulab, H. Degradation of waste High-density polyethylene into fuel oil using basic catalyst. *Fuel*. 2010. 89(2): 474-480.
36. Shah, J., Jan, M.R., Mabood, F., and Jabeen, F. Catalytic pyrolysis of LDPE leads to valuable resource recovery and reduction of waste problems. *Energy Conversion and Management*. 2010. 51(12): 2791-2801.

37. de Marco, I., Caballero, B.M., López, A., Laresgoiti, M.F., Torres, A., and Chomón, M.J. Pyrolysis of the rejects of a waste packaging separation and classification plant. *Journal of Analytical and Applied Pyrolysis*. 2009. 85(1-2): 384-391.

38. Renzini, M.S., Lerici, L.C., Sedran, U., and Pierella, L.B. Stability of ZSM-11 and BETA zeolites during the catalytic cracking of low-density polyethylene. *Journal of Analytical and Applied Pyrolysis*. 2011. 92(2): 450-455.

39. Sharma, B.K., Moser, B.R., Vermillion, K.E., Doll, K.M., and Rajagopalan, N. Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags. *Fuel Processing Technology*. 2014. 122(0): 79-90.

40. Sarker, M., Rashid, M.M., and Molla, M. Waste polypropylene plastic conversion into liquid hydrocarbon fuel for producing electricity and energies. *Environ Technol*. 2012. 33(22-24): 2709-2721.

41. Ali, M.F., Ahmed, S., and Qureshi, M.S. Catalytic coprocessing of coal and petroleum residues with waste plastics to produce transportation fuels. *Fuel Processing Technology*. 2011. 92(5): 1109-1120.

42. Ates, F., Miskolczi, N., and Borsodi, N. Comparision of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I: product yields, gas and pyrolysis oil properties. *Bioresour Technol*. 2013. 133(0): 443-454.

43. Miskolczi, N., Ates, F., and Borsodi, N. Comparison of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part II: contaminants, char and pyrolysis oil properties. *Bioresour Technol*. 2013. 144(0): 370-379.

44. Adrados, A., De Marco, I., Lopez-Urionabarrenechea, A., Caballero, B.M., and Laresgoiti, M.F. Pyrolysis behavior of different type of materials contained in the rejects of packaging waste sorting plants. *Waste Management*. 2013. 33(1): 52-59.

45. Adrados, A., de Marco, I., Caballero, B.M., Lopez, A., Laresgoiti, M.F., and Torres, A. Pyrolysis of plastic packaging waste: A comparison of plastic residuals from material recovery facilities with simulated plastic waste. *Waste Management*. 2012. 32(5): 826-832.

46. Lopez, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., and Adrados, A. Pyrolysis of municipal plastic wastes: Influence of raw material composition. *Waste Management*. 2010. 30(4): 620-627.
47. Lopez, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., Adrados, A., and Torres, A. Pyrolysis of municipal plastic wastes II: Influence of raw material composition under catalytic conditions. *Waste Management*. 2011. 31(9-10): 1973-1983.
48. Miskolczi, N., Borsodi, N., Buyong, F., Angyal, A., and Williams, P.T. Production of pyrolytic oils by catalytic pyrolysis of Malaysian refuse-derived fuels in continuously stirred batch reactor. *Fuel Processing Technology*. 2011. 92(5): 925-932.
49. Lopez, A., de Marco, I., Caballero, B.M., Adrados, A., and Laresgoiti, M.F. Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. *Waste Management*. 2011. 31(8): 1852-1858.
50. Lopez-Urionabarrenechea, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., Adrados, A., and Aranzabal, A. Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. *Applied Catalysis B-Environmental*. 2011. 104(3-4): 211-219.
51. Lopez-Urionabarrenechea, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., and Adrados, A. Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor. *Chemical Engineering Journal*. 2011. 173(1): 62-71.
52. Lopez-Urionabarrenechea, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., and Adrados, A. Catalytic stepwise pyrolysis of packaging plastic waste. *Journal of Analytical and Applied Pyrolysis*. 2012. 96(0): 54-62.
53. Jung, S.H., Cho, M.H., Kang, B.S., and Kim, J.S. Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. *Fuel Processing Technology*. 2010. 91(3): 277-284.
54. Yuan, G., Chen, D., Yin, L., Wang, Z., Zhao, L., and Wang, J.Y. High efficiency chlorine removal from polyvinyl chloride (PVC) pyrolysis with a gas-liquid fluidized bed reactor. *Waste Management*. 2014. 34(6): 1045-1050.

55. Huang, W.C., Huang, M.S., Huang, C.F., Chen, C.C., and Ou, K.L. Thermochemical conversion of polymer wastes into hydrocarbon fuels over various fluidizing cracking catalysts. *Fuel*. 2010. 89(9): 2305-2316.

56. Donaj, P.J., Kaminsky, W., Buzeto, F., and Yang, W. Pyrolysis of polyolefins for increasing the yield of monomers' recovery. *Waste Management*. 2012. 32(5): 840-846.

57. Cho, M.H., Jung, S.H., and Kim, J.S. Pyrolysis of Mixed Plastic Wastes for the Recovery of Benzene, Toluene, and Xylene (BTX) Aromatics in a Fluidized Bed and Chlorine Removal by Applying Various Additives. *Energy & Fuels*. 2010. 24(2): 1389-1395.

58. Lopez-Urionabarrenechea, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., and Adrados, A. Dechlorination of fuels in pyrolysis of PVC containing plastic wastes. *Fuel Processing Technology*. 2011. 92(2): 253-260.

59. G.Yuana, D.Chena, Yina, L., Wang, Z., Zhaob, L., and Wang, J.Y. High Efficiency of HCl Removal from Waste Plastics Pyrolysis with a Gas-fluidized Reactor. *The 1st IWWG-ARB Symposium*. 18-21 March 2013. 2013.

60. Elordi, G., Olazar, M., Aguado, R., Lopez, G., Arabiourrutia, M., and Bilbao, J. Catalytic pyrolysis of high density polyethylene in a conical spouted bed reactor. *Journal of Analytical and Applied Pyrolysis*. 2007. 79(1-2): 450-455.

61. Elordi, G., Olazar, M., Lopez, G., Artetxe, M., and Bilbao, J. Product Yields and Compositions in the Continuous Pyrolysis of High-Density Polyethylene in a Conical Spouted Bed Reactor. *Industrial & Engineering Chemistry Research*. 2011. 50(11): 6650-6659.

62. Elordi, G., Olazar, M., Lopez, G., Amutio, M., Artetxe, M., Aguado, R., and Bilbao, J. Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor. *Journal of Analytical and Applied Pyrolysis*. 2009. 85(1-2): 345-351.

63. Castaño, P., Elordi, G., Olazar, M., Aguayo, A.T., Pawelec, B., and Bilbao, J. Insights into the coke deposited on HZSM-5, Hβ and HY zeolites during the cracking of polyethylene. *Applied Catalysis B: Environmental*. 2011. 104(1-2): 91-100.

64. Arabiourrutia, M., Elordi, G., Lopez, G., Borsella, E., Bilbao, J., and Olazar, M. Characterization of the waxes obtained by the pyrolysis of polyolefin

plastics in a conical spouted bed reactor. *Journal of Analytical and Applied Pyrolysis*. 2012. 94(0): 230-237.

65. Dimitrov, N., Krehula, L.K., Sirocic, A.P., and Hrnjak-Murgic, Z. Analysis of recycled PET bottles products by pyrolysis-gas chromatography. *Polymer Degradation and Stability*. 2013. 98(5): 972-979.
66. Liu, W.W., Hu, C.W., Yang, Y., Tong, D.M., Li, G.Y., and Zhu, L.F. Influence of ZSM-5 zeolite on the pyrolytic intermediates from the co-pyrolysis of pubescens and LDPE. *Energy Conversion and Management*. 2010. 51(5): 1025-1032.
67. Aguado, J., Serrano, D.P., San Miguel, G., Castro, M.C., and Madrid, S. Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system. *Journal of Analytical and Applied Pyrolysis*. 2007. 79(1-2): 415-423.
68. San Miguel, G., Serrano, D.P., and Aguado, J. Valorization of Waste Agricultural Polyethylene Film by Sequential Pyrolysis and Catalytic Reforming. *Industrial & Engineering Chemistry Research*. 2009. 48(18): 8697-8703.
69. Miskolczi, N., Buyong, F., Angyal, A., Williams, P.T., and Bartha, L. Two stages catalytic pyrolysis of refuse derived fuel: production of biofuel via syncrude. *Bioresource Technology*. 2010. 101(22): 8881-8890.
70. Serrano, D.P., Aguado, J., Escola, J.M., and Garagorri, E. Conversion of low density polyethylene into petrochemical feedstocks using a continuous screw kiln reactor. *Journal of Analytical and Applied Pyrolysis*. 2001. 58(0): 789-801.
71. Aguado, J., Serrano, D.P., Escola, J.M., and Garagorri, E. Catalytic conversion of low-density polyethylene using a continuous screw kiln reactor. *Catalysis Today*. 2002. 75(1-4): 257-262.
72. Fukushima, M., Wu, B.L., Ibe, H., Wakai, K., Sugiyama, E., Abe, H., Kitagawa, K., Tsuruga, S., Shimura, K., and Ono, E. Study on dechlorination technology for municipal waste plastics containing polyvinyl chloride and polyethylene terephthalate. *Journal of Material Cycles and Waste Management*. 2010. 12(2): 108-122.
73. Ludlow-Palafox, C. and Chase, H.A. Microwave-induced pyrolysis of plastic wastes. *Industrial & Engineering Chemistry Research*. 2001. 40(22): 4749-4756.

74. Undri, A., Rosi, L., Frediani, M., and Frediani, P. Efficient disposal of waste polyolefins through microwave assisted pyrolysis. *Fuel*. 2014. 116(0): 662-671.

75. Hussain, Z., Khan, K.M., Perveen, S., Hussain, K., and Voelter, W. The conversion of waste polystyrene into useful hydrocarbons by microwave-metal interaction pyrolysis. *Fuel Processing Technology*. 2012. 94(1): 145-150.

76. Hussain, Z., Khan, K.M., Basheer, N., and Hussain, K. Co-liquefaction of Makarwal coal and waste polystyrene by microwave-metal interaction pyrolysis in copper coil reactor. *Journal of Analytical and Applied Pyrolysis*. 2011. 90(1): 53-55.

77. Undri, A., Rosi, L., Frediani, M., and Frediani, P. Upgraded fuel from microwave assisted pyrolysis of waste tire. *Fuel*. 2014. 115(0): 600-608.

78. Undri, A., Meini, S., Rosi, L., Frediani, M., and Frediani, P. Microwave pyrolysis of polymeric materials: Waste tires treatment and characterization of the value-added products. *Journal of Analytical and Applied Pyrolysis*. 2013. 103(0): 149-158.

79. Undri, A., Sacchi, B., Cantisani, E., Toccafondi, N., Rosi, L., Frediani, M., and Frediani, P. Carbon from microwave assisted pyrolysis of waste tires. *Journal of Analytical and Applied Pyrolysis*. 2013. 104(0): 396-404.

80. Bai, F., Zhu, C.C., Liu, Y., Yuan, P.Q., Cheng, Z.M., and Yuan, W.K. Co-pyrolysis of residual oil and polyethylene in sub- and supercritical water. *Fuel Processing Technology*. 2013. 106(0): 267-274.

81. Tan, X.C., Zhu, C.C., Liu, Q.K., Ma, T.Y., Yuan, P.Q., Cheng, Z.M., and Yuan, W.K. Co-pyrolysis of heavy oil and low density polyethylene in the presence of supercritical water: The suppression of coke formation. *Fuel Processing Technology*. 2014. 118(0): 49-54.

82. de la Puente, G., Arandes, J.M., and Sedran, U.A. Recycled Plastics in FCC Feedstocks: Specific Contributions. *Industrial & Engineering Chemistry Research*. 1997. 36(11): 4530-4534.

83. de la Puente, G. Conversion of waste plastics into fuels Recycling polyethylene in FCC. *Applied Catalysis B: Environmental*. 2002. 36(4): 279-285.

84. Passamonti, F.J. and Sedran, U. Recycling of waste plastics into fuels. LDPE conversion in FCC. *Applied Catalysis B-Environmental*. 2012. 125(0): 499-506.

85. Marcilla, A., Garcia, A.N., and Hernandez, M.D. Thermal degradation of LDPE-vacuum gas oil mixtures for plastic wastes valorization. *Energy & Fuels*. 2007. 21(2): 870-880.

86. Vicente, G., Aguado, J., Serrano, D.P., and Sanchez, N. HDPE chemical recycling promoted by phenol solvent. *Journal of Analytical and Applied Pyrolysis*. 2009. 85(1-2): 366-371.

87. Papaspyrides, C.D., Poulakis, J.G., and Varelides, P.C. A Model Recycling Process for Low-Density Polyethylene. *Resources Conservation and Recycling*. 1994. 12(3-4): 177-184.

88. Huang, H., Wang, K., Wang, S., Klein, M.T., and Calkins, W.H. *Applications of the thermogravimetric analysis in the study of fossil fuels.* 1996.

89. Burke, J., *Solubility Parameters: Theory and Application,* Available from:<http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html>. [9 January 2016].

90. Chanda, M. and Roy, S.K. *Plastics Technology Handbook.* CRC Press. 2006.

91. Miller-Chou, B.A. and Koenig, J.L. A review of polymer dissolution. *Progress in Polymer Science*. 2003. 28(8): 1223-1270.

92. Sakata, Y., Uddin, M.A., Muto, A., Kanada, Y., Koizumi, K., and Murata, K. Catalytic degradation of polyethylene into fuel oil over mesoporous silica (KFS-16) catalyst. *Journal of Analytical and Applied Pyrolysis*. 1997. 43(1): 15-25.

93. Jalil, P.A. Investigations on polyethylene degradation into fuel oil over tungstophosphoric acid supported on MCM-41 mesoporous silica. *Journal of Analytical and Applied Pyrolysis*. 2002. 65(2): 185-195.

94. Uddin, M.A., Koizumi, K., Murata, K., and Sakata, Y. Thermal and catalytic degradation of structurally different types of polyethylene into fuel oil. *Polymer Degradation and Stability*. 1997. 56(1): 37-44.

95. Sakata, Y., Uddin, M.A., and Muto, A. Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts. *Journal of Analytical and Applied Pyrolysis*. 1999. 51(1-2): 135-155.

96. Manos, G., Yusof, I.Y., Papayannakos, N., and Gangas, N.H. Catalytic cracking of polyethylene over clay catalysts. Comparison with an ultrastable Y zeolite. *Industrial & Engineering Chemistry Research*. 2001. 40(10): 2220-2225.

97. Artetxe, M., Lopez, G., Amutio, M., Elordi, G., Bilbao, J., and Olazar, M. Cracking of High Density Polyethylene Pyrolysis Waxes on HZSM-5 Catalysts of Different Acidity. *Industrial & Engineering Chemistry Research*. 2013. 52(31): 10637-10645.

98. Van Grieken, R., Sotelo, J.L., Menéndez, J.M., and Melero, J.A. Anomalous crystallization mechanism in the synthesis of nanocrystalline ZSM-5. *Microporous and Mesoporous Materials*. 2000. 39(1-2): 135-147.

99. van Grieken, R., Serrano, D.P., Aguado, J., García, R., and Rojo, C. Thermal and catalytic cracking of polyethylene under mild conditions. *Journal of Analytical and Applied Pyrolysis*. 2001. 58-59(0): 127-142.

100. Karagöz, S., Karayildirim, T., Uçar, S., Yuksel, M., and Yanik, J. Liquefaction of municipal waste plastics in VGO over acidic and non-acidic catalysts☆. *Fuel*. 2003. 82(4): 415-423.

101. Cardona, S.C. and Corma, A. Tertiary recycling of polypropylene by catalytic cracking in a semibatch stirred reactor - Use of spent equilibrium FCC commercial catalyst. *Applied Catalysis B-Environmental*. 2000. 25(2-3): 151-162.

102. Marcilla, A., Gomez-Siurana, A., and Valdes, F. Catalytic cracking of low-density polyethylene over H-Beta and HZSM-5 zeolites: Influence of the external surface. Kinetic model. *Polymer Degradation and Stability*. 2007. 92(2): 197-204.

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

104. Botas, J.A., Serrano, D.P., García, A., de Vicente, J., and Ramos, R. Catalytic conversion of rapeseed oil into raw chemicals and fuels over Ni- and Mo-modified nanocrystalline ZSM-5 zeolite. *Catalysis Today*. 2012. 195(1): 59-70.

105. Botas, J.A., Serrano, D.P., García, A., and Ramos, R. Catalytic conversion of rapeseed oil for the production of raw chemicals, fuels and carbon nanotubes

over Ni-modified nanocrystalline and hierarchical ZSM-5. *Applied Catalysis B: Environmental*. 2014. 145(0): 205-215.

106. Iliopoulou, E.F., Stefanidis, S.D., Kalogiannis, K.G., Delimitis, A., Lappas, A.A., and Triantafyllidis, K.S. Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite. *Applied Catalysis B-Environmental*. 2012. 127(0): 281-290.

107. Iliopoulou, E.F., Stefanidis, S., Kalogiannis, K., Psarras, A.C., Delimitis, A., Triantafyllidis, K.S., and Lappas, A.A. Pilot-scale validation of Co-ZSM-5 catalyst performance in the catalytic upgrading of biomass pyrolysis vapours. *Green Chemistry*. 2014. 16(2): 662-674.

108. Huang, W., Gong, F., Fan, M., Zhai, Q., Hong, C., and Li, Q. Production of light olefins by catalytic conversion of lignocellulosic biomass with HZSM-5 zeolite impregnated with 6wt.% lanthanum. *Bioresour Technol*. 2012. 121(0): 248-255.

109. Shah, J., Jan, M.R., and Adnan. Catalytic activity of metal impregnated catalysts for degradation of waste polystyrene. *Journal of Industrial and Engineering Chemistry*. 2014. 20(5): 3604-3611.

110. Khan, M.I., Ahmad, I., Khan, H., Ishaq, M., Khan, R., Gul, K., and Ahmad, W. Catalytic Performance of Metal Impregnated Carbon (Darco) in Conversion of Polypropylene and High-Density Polyethylene into Useful Products. *Fullerenes, Nanotubes and Carbon Nanostructures*. 2014. 23(7): 627-639.

111. Marcilla, A., Gomez-Siurana, A., and Berenguer, D. Study of the early deactivation in pyrolysis of polymers in the presence of catalysts. *Journal of Analytical and Applied Pyrolysis*. 2007. 79(1-2): 443-449.

112. Marcilla, A., Beltran, M.I., and Navarro, R. Study of the deactivation process of HZSM5 zeolite during polyethylene pyrolysis. *Applied Catalysis a-General*. 2007. 333(1): 57-66.

113. Salmiaton, A. and Garforth, A.A. Multiple use of waste catalysts with and without regeneration for waste polymer cracking. *Waste Management*. 2011. 31(6): 1139-1145.

114. Lerici, L.C., Renzini, M.S., Sedran, U., and Pierella, L.B. Tertiary Recycling of Low-Density Polyethylene by Catalytic Cracking over ZSM-11 and BETA

Zeolites Modified with Zn2+: Stability Study. *Energy & Fuels*. 2013. 27(4): 2202-2208.

115. Ibáñez, M., Artetxe, M., Lopez, G., Elordi, G., Bilbao, J., Olazar, M., and Castaño, P. Identification of the coke deposited on an HZSM-5 zeolite catalyst during the sequenced pyrolysis–cracking of HDPE. *Applied Catalysis B: Environmental*. 2014. 148-149(0): 436-445.

116. Singhal, R., Singhal, C., and Upadhyayula, S. Thermal-catalytic degradation of polyethylene over silicoaluminophosphate molecular sieves—A thermogravimetric study. *Journal of Analytical and Applied Pyrolysis*. 2010. 89(2): 313-317.

117. Marcilla, A., Gomez-Siurana, A., and Valdes, F. Catalytic pyrolysis of LDPE over H-beta and HZSM-5 zeolites in dynamic conditions - Study of the evolution of the process. *Journal of Analytical and Applied Pyrolysis*. 2007. 79(1-2): 433-442.

118. Abbas-Abadi, M.S., McDonald, A.G., Nekoomanesh, M., and Haghighi, H.Y. Estimation of pyrolysis product of LDPE degradation using different process parameters in a stirred reactor. *Polyolefins Journal*. 2015. 2(1): 39-47.

119. Zhang, X.S., Lei, H.W., Yadavalli, G., Zhu, L., Wei, Y., and Liu, Y.P. Gasoline-range hydrocarbons produced from microwave-induced pyrolysis of low-density polyethylene over ZSM-5. *Fuel*. 2015. 144(0): 33-42.

120. Kumar, S. and Singh, R.K. Optimization of process parameters by response surface methodology (RSM) for catalytic pyrolysis of waste high-density polyethylene to liquid fuel. *Journal of Environmental Chemical Engineering*. 2014. 2(1): 115-122.

121. Mo, Y., Zhao, L., Wang, Z., Chen, C.L., Tan, G.Y., and Wang, J.Y. Enhanced styrene recovery from waste polystyrene pyrolysis using response surface methodology coupled with Box-Behnken design. *Waste Management*. 2014. 34(4): 763-769.

122. Mante, O.D., Agblevor, F.A., and McClung, R. A study on catalytic pyrolysis of biomass with Y-zeolite based FCC catalyst using response surface methodology. *Fuel*. 2013. 108(0): 451-464.

123. Roozbehani, B., Sakaki, S.A., Shishesaz, M., Abdollahkhani, N., and Hamedifar, S. Taguchi method approach on catalytic degradation of

polyethylene and polypropylene into gasoline. *Clean Technologies and Environmental Policy*. 2015. 17(7): 1873-1882.

124. Pinto, F., Paradela, F., Gulyurtlu, I., and Ramos, A.M. Prediction of liquid yields from the pyrolysis of waste mixtures using response surface methodology. *Fuel Processing Technology*. 2013. 116(0): 271-283.

125. Rice, F.O. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. I. Saturated Hydrocarbons. *Journal of the American Chemical Society*. 1931. 53(5): 1959-1972.

126. Rice, F.O., Johnston, W.R., and Evering, B.L. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. Ii. Experimental Evidence of the Decomposition of Organic Compounds into Free Radicals. *Journal of the American Chemical Society*. 1932. 54(9): 3529-3543.

127. Rice, F.O. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. III. The Calculation of the Products Formed from Paraffin Hydrocarbons. *Journal of the American Chemical Society*. 1933. 55(7): 3035-3040.

128. Rice, F.O. and Glasebrook, A.L. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VII. The Ethylidene Radical. *Journal of the American Chemical Society*. 1934. 56(3): 741-743.

129. Rice, F.O. and Johnston, W.R. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. V. The Strength of Bonds in Organic Molecules. *Journal of the American Chemical Society*. 1934. 56(1): 214-219.

130. Rice, F.O. and Herzfeld, K.F. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VI. The Mechanism of Some Chain Reactions. *Journal of the American Chemical Society*. 1934. 56(2): 284-289.

131. Rice, F.O. and Whaley, F.R. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VIII. A Comparison of the Thermal and Electrical Decomposition of Organic Compounds into Free Radicals. *Journal of the American Chemical Society*. 1934. 56(6): 1311-1313.

132. Rice, F.O. and Glasebrook, A.L. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. X. The Identification of

Methyl Groups as Dimethyl Ditelluride. *Journal of the American Chemical Society*. 1934. 56(11): 2472-2472.

133. Rice, F.O. and Rodowskas, E.L. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. XIII. The Decomposition of Ethyl Nitrite. *Journal of the American Chemical Society*. 1935. 57(2): 350-352.

134. Rice, F.O. and Evering, B.L. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. IX. The Combination of Methyl Groups with Metallic Mercury. *Journal of the American Chemical Society*. 1934. 56(10): 2105-2107.

135. Rice, F.O. and Glasebrook, A.L. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. XI. The Methylene Radical. *Journal of the American Chemical Society*. 1934. 56(11): 2381-2383.

136. Rice, F.O. and Dooley, M.D. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. IV. The Dehydrogenation of Paraffin Hydrocarbons and the Strength of the C—C Bond. *Journal of the American Chemical Society*. 1933. 55(10): 4245-4247.

137. Rice, F.O. and Teller, E. The Role of Free Radicals in Elementary Organic Reactions. *The Journal of Chemical Physics*. 1938. 6(8): 489.

138. Greensfelder, B.S., Voge, H.H., and Good, G.M. Catalytic and Thermal Cracking of Pure Hydrocarbons: Mechanisms of Reaction. *Industrial & Engineering Chemistry*. 1949. 41(11): 2573-2584.

139. Voge, H.H. and Good, G.M. Thermal Cracking of Higher Paraffins. *Journal of the American Chemical Society*. 1949. 71(2): 593-597.

140. Brems, A., Baeyens, J., Beerlandt, J., and Dewil, R. Thermogravimetric pyrolysis of waste polyethylene-terephthalate and polystyrene: A critical assessment of kinetics modelling. *Resources Conservation and Recycling*. 2011. 55(8): 772-781.

141. Nyakuma, B.B., Johari, A., and Ahmad, A. Analysis of the Pyrolytic Fuel Properties of Empty Fruit Bunch Briquettes. *Journal of Applied Sciences*. 2012. 12(24): 2527-2533.

142. Minowa, T., Kondo, T., and Sudirjo, S.T. Thermochemical liquefaction of Indonesian biomass residues. *Biomass & Bioenergy*. 1998. 14(5-6): 517-524.

143. Aguado, J., Serrano, D.P., Escola, J.M., and Briones, L. Deactivation and regeneration of a Ni supported hierarchical Beta zeolite catalyst used in the hydroreforming of the oil produced by LDPE thermal cracking. *Fuel*. 2013. 109(0): 679-686.

144. Dueso, C., Abad, A., García-Labiano, F., de Diego, L.F., Gayán, P., Adánez, J., and Lyngfelt, A. Reactivity of a NiO/Al2O3 oxygen carrier prepared by impregnation for chemical-looping combustion. *Fuel*. 2010. 89(11): 3399-3409.

145. Hajheidary, M., Ghashghaee, M., and Karimzadeh, R. Olefins production from LPG via dehydrogenative cracking over three ZSM-5 catalysts. *Journal of Scientific & Industrial Research*. 2013. 72(12): 760-766.

146. Brunauer, S., Emmett, P.H., and Teller, E. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*. 1938. 60(2): 309-319.

147. Stuart, B. Infrared Spectroscopy, in *Kirk-Othmer Encyclopedia of Chemical Technology*: John Wiley & Sons, Inc.; 2000.

148. Lundstedt, T., Seifert, E., Abramo, L., Thelin, B., Nystrom, A., Pettersen, J., and Bergman, R. Experimental design and optimization. *Chemometrics and Intelligent Laboratory Systems*. 1998. 42(1-2): 3-40.

149. Zhou, L.M., Wang, Y.P., Huang, Q.W., and Cai, J.Q. Thermogravimetric characteristics and kinetic of plastic and biomass blends co-pyrolysis. *Fuel Processing Technology*. 2006. 87(11): 963-969.

150. Uçar, S., Özkan, A.R., and Karagöz, S. Co-pyrolysis of waste polyolefins with waste motor oil. *Journal of Analytical and Applied Pyrolysis*. 2016. 119: 233-241.

151. Saad, J.M. and Williams, P.T. Pyrolysis-Catalytic-Dry Reforming of Waste Plastics and Mixed Waste Plastics for Syngas Production. *Energy & Fuels*. 2016. 30(4): 3198-3204.

152. Fu, P., Hu, S., Xiang, J., Li, P.S., Huang, D., Jiang, L.C., Zhang, A.Y., and Zhang, J. FTIR study of pyrolysis products evolving from typical agricultural residues. *Journal of Analytical and Applied Pyrolysis*. 2010. 88(2): 117-123.

153. Smith, A.L. *Applied infrared spectroscopy: fundamentals, techniques, and analytical problem-solving.* Wiley. 1979.

154. Volland, W. Organic compound identification using infrared spectroscopy. *Bellevue Community College, Washington*. 1999.

155. Kalashnikov, V. Shear - rate dependent viscosity of dilute polymer solutions. *Journal of Rheology (1978-present)*. 1994. 38(5): 1385-1403.

156. Huang, H., Ye, X., Huang, W., Chen, J., Xu, Y., Wu, M., Shao, Q., Peng, Z., Ou, G., Shi, J., Feng, X., Feng, Q., Huang, H., Hu, P., and Leung, D.Y.C. Ozone-catalytic oxidation of gaseous benzene over MnO2/ZSM-5 at ambient temperature: Catalytic deactivation and its suppression. *Chemical Engineering Journal*. 2015. 264(0): 24-31.

157. Fodor, D., Krumeich, F., Hauert, R., and van Bokhoven, J.A. Differences between individual ZSM-5 crystals in forming hollow single crystals and mesopores during base leaching. *Chemistry*. 2015. 21(16): 6272-6277.

158. van Koningsveld, H., van Bekkum, H., and Jansen, J.C. On the location and disorder of the tetrapropylammonium (TPA) ion in zeolite ZSM-5 with improved framework accuracy. *Acta Crystallographica Section B Structural Science*. 1987. 43(2): 127-132.

159. Díaz, E., Muñoz, E., Vega, A., and Ordóñez, S. Enhancement of the CO2Retention Capacity of Y Zeolites by Na and Cs Treatments: Effect of Adsorption Temperature and Water Treatment. *Industrial & Engineering Chemistry Research*. 2008. 47(2): 412-418.

160. Yuan, D.H., He, D.W., Xu, S.T., Song, Z.J., Zhang, M.Z., Wei, Y.X., He, Y.L., Xu, S.L., Liu, Z.M., and Xu, Y.P. Imidazolium-based ionic liquids as novel organic SDA to synthesize high-silica Y zeolite. *Microporous and Mesoporous Materials*. 2015. 204(0): 1-7.

161. Baur, W. On Cation and Water Positions In Faujasite. *American Mineralogist*. 1964. 49(5-6): 697-704.

162. Aziz, M.A.A., Jalil, A.A., Triwahyono, S., and Saad, M.W.A. CO2 methanation over Ni-promoted mesostructured silica nanoparticles: Influence of Ni loading and water vapor on activity and response surface methodology studies. *Chemical Engineering Journal*. 2015. 260(0): 757-764.

163. Luengnaruemitchai, A. and Kaengsilalai, A. Activity of different zeolite-supported Ni catalysts for methane reforming with carbon dioxide. *Chemical Engineering Journal*. 2008. 144(1): 96-102.

164. Millini, R., Perego, C., Parker, W., Flego, C., and Girotti, G. Stability upon thermal treatment of coked zeolite beta. *Studies in Surface Science and Catalysis*. 2004. 154: 1214-1221.

165. Millini, R., Perego, C., Parker, W.O., Flego, C., and Girotti, G. Stability upon thermal treatment of coked zeolite beta, in *Studies in Surface Science and Catalysis*: Elsevier. 1214-1221; 2004.

166. Pena, M.A., Pawelec, B., Terreros, P., Fierro, J.L.G., Lezaun, J., Gomez, J.P., Jimenez, J.M., and Vic, S. Partial oxidation of methane to syngas over Ni-loaded ultrastable HY zeolite catalysts. *Natural Gas Conversion Iv*. 1997. 107: 441-446.

167. Sarkar, B., Tiwari, R., Singha, R.K., Suman, S., Ghosh, S., Acharyya, S.S., Mantri, K., Konathala, L.N.S., Pendem, C., and Bal, R. Reforming of methane with CO2 over Ni nanoparticle supported on mesoporous ZSM-5. *Catalysis Today*. 2012. 198(1): 209-214.

168. Vitale, G., Molero, H., Hernandez, E., Aquino, S., Birss, V., and Pereira-Almao, P. One-pot preparation and characterization of bifunctional Ni-containing ZSM-5 catalysts. *Applied Catalysis A: General*. 2013. 452(0): 75-87.

169. Zhang, Q., Wang, T., Li, B., Jiang, T., Ma, L., Zhang, X., and Liu, Q. Aqueous phase reforming of sorbitol to bio-gasoline over Ni/HZSM-5 catalysts. *Applied Energy*. 2012. 97(0): 509-513.

170. Mohan, V., Raghavendra, C., Pramod, C.V., Raju, B.D., and Rama Rao, K.S. Ni/H-ZSM-5 as a promising catalyst for vapour phase hydrogenation of levulinic acid at atmospheric pressure. *RSC Advances*. 2014. 4(19): 9660.

171. Vichaphund, S., Aht-ong, D., Sricharoenchaikul, V., and Atong, D. Catalytic upgrading pyrolysis vapors of Jatropha waste using metal promoted ZSM-5 catalysts: An analytical PY-GC/MS. *Renewable Energy*. 2014. 65(0): 70-77.

172. Elordi, G., Olazar, M., Castaño, P., Artetxe, M., and Bilbao, J. Polyethylene Cracking on a Spent FCC Catalyst in a Conical Spouted Bed. *Industrial & Engineering Chemistry Research*. 2012. 51(43): 14008-14017.

173. Rahimi, N. and Karimzadeh, R. Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. *Applied Catalysis a-General*. 2011. 398(1-2): 1-17.

174. Qiu, Y., Zhao, G., Liu, G., Wang, L., and Zhang, X. Catalytic cracking of supercritical n-dodecane over wall-coated nano-Ag/HZSM-5 zeolites. *Industrial & Engineering Chemistry Research*. 2014. 53(47): 18104-18111.

175. Lu, J.Y., Zhao, Z., Xu, C.M., Duan, A.J., and Zhang, P. CrHZSM-5 zeolites - Highly efficient catalysts for catalytic cracking of isobutane to produce light olefins. *Catalysis Letters*. 2006. 109(1-2): 65-70.

176. Lu, J., Zhao, Z., Xu, C., Zhang, P., and Duan, A. FeHZSM-5 molecular sieves – Highly active catalysts for catalytic cracking of isobutane to produce ethylene and propylene. *Catalysis Communications*. 2006. 7(4): 199-203.

177. Burange, A.S., Gawande, M.B., Lam, F.L.Y., Jayaram, R.V., and Luque, R. Heterogeneously catalyzed strategies for the deconstruction of high density polyethylene: plastic waste valorisation to fuels. *Green Chemistry*. 2015. 17(1): 146-156.

178. Aguado, J., Serrano, D.P., and Escola, J.M. Fuels from Waste Plastics by Thermal and Catalytic Processes: A Review. *Industrial & Engineering Chemistry Research*. 2008. 47(21): 7982-7992.

179. Syamsiro, M., Cheng, S., Hu, W., Saptoadi, H., Pratama, N.N., Trisunaryanti, W., and Yoshikawa, K. Liquid and Gaseous Fuel from Waste Plastics by Sequential Pyrolysis and Catalytic Reforming Processes over Indonesian Natural Zeolite Catalysts. *Waste Technology*. 2014. 2(2): 44-51.

180. Marcilla, A., Gomez, A., Menargues, S., Garcia-Martinez, J., and Cazorla-Amoros, D. Catalytic cracking of ethylene-vinyl acetate copolymers: comparison of different zeolites. *Journal of Analytical and Applied Pyrolysis*. 2003. 68-9(0): 495-506.

181. Serrano, D.P., Escola, J.M., Briones, L., Medina, S., and Martínez, A. Hydroreforming of the oils from LDPE thermal cracking over Ni–Ru and Ru supported over hierarchical Beta zeolite. *Fuel*. 2015. 144(0): 287-294.

182. Friedel, C. and Crafts, J.M. Organic chemistry. *Journal of the Chemical Society*. 1877. 32(0): 725.

183. Lee, K.-H. Effects of the types of zeolites on catalytic upgrading of pyrolysis wax oil. *Journal of Analytical and Applied Pyrolysis*. 2012. 94(0): 209-214.

184. Liu, W.-W., Hu, C.-W., Yang, Y., Tong, D.-M., Zhu, L.-F., Zhang, R.-N., and Zhao, B.-H. Study on the effect of metal types in (Me)-Al-MCM-41 on the mesoporous structure and catalytic behavior during the vapor-catalyzed

co-pyrolysis of pubescens and LDPE. *Applied Catalysis B: Environmental*. 2013. 129(0): 202-213.

185. Cheng, Y.-T. and Huber, G.W. Production of targeted aromatics by using Diels–Alder classes of reactions with furans and olefins over ZSM-5. *Green Chemistry*. 2012. 14(11): 3114.
186. Onwudili, J.A., Insura, N., and Williams, P.T. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. *Journal of Analytical and Applied Pyrolysis*. 2009. 86(2): 293-303.
187. Wu, C. and Williams, P.T. Pyrolysis–gasification of post-consumer municipal solid plastic waste for hydrogen production. *International Journal of Hydrogen Energy*. 2010. 35(3): 949-957.
188. Bauer, F. and Karge, H.G. Characterization of Coke on Zeolites, in *Characterization II*: Springer Berlin Heidelberg. 249-364; 2007.
189. Murata, K., Khongwong, W., Larpkattaworn, S., Liu, Y., Inaba, M., and Takahara, I. Evaluation of PtPd-modified Zeolite Catalysts (ZSM-5, Beta, USY) for Pyrolysis of Jatropha Waste. *Journal of the Japan Petroleum Institute*. 2014. 57(3): 133-145.
190. Serrano, D.P., Aguado, J., Escola, J.M., Rodriguez, J.M., and Peral, A. Catalytic properties in polyolefin cracking of hierarchical nanocrystalline HZSM-5 samples prepared according to different strategies. *Journal of Catalysis*. 2010. 276(1): 152-160.
191. Last, P. Catalytic transformation of the gases evolved during the thermal decomposition of HDPE using acid-activated and pillared clays. *Journal of Materials Chemistry*. 1999. 9(3): 813-818.
192. Miskolczi, N., Angyal, A., Bartha, L., and Valkai, I. Fuels by pyrolysis of waste plastics from agricultural and packaging sectors in a pilot scale reactor. *Fuel Processing Technology*. 2009. 90(7–8): 1032-1040.
193. Hujuri, U., Ghoshal, A.K., and Gumma, S. Temperature-dependent pyrolytic product evolution profile for low-density polyethylene from gas chromatographic study. *Waste Management*. 2010. 30(5): 814-820.
194. Zhou, H., Wu, C., Onwudili, J.A., Meng, A., Zhang, Y., and Williams, P.T. Polycyclic aromatic hydrocarbons (PAH) formation from the pyrolysis of

different municipal solid waste fractions. *Waste Management*. 2015. 36: 136-146.

195. Elordi, G., Olazar, M., Lopez, G., Castaño, P., and Bilbao, J. Role of pore structure in the deactivation of zeolites (HZSM-5, Hβ and HY) by coke in the pyrolysis of polyethylene in a conical spouted bed reactor. *Applied Catalysis B: Environmental*. 2011. 102(1-2): 224-231.
196. Zhang, H., Shao, S., Xiao, R., Shen, D., and Zeng, J. Characterization of coke deposition in the catalytic fast pyrolysis of biomass derivates. *Energy & Fuels*. 2013. 28(1): 52-57.
197. Fuentes-Ordóñez, E.G., Salbidegoitia, J.A., González-Marcos, M.P., and González-Velasco, J.R. Mechanism and kinetics in catalytic hydrocracking of polystyrene in solution. *Polymer Degradation and Stability*. 2016. 124: 51-59.
198. Wang, Y., Huang, Q., Zhou, Z.Y., Yang, J.Z., Qi, F., and Pan, Y. Online Study on the Pyrolysis of Polypropylene over the HZSM-5 Zeolite with Photoionization Time-of-Flight Mass Spectrometry. *Energy & Fuels*. 2015. 29(2): 1090-1098.
199. Wu, C.J. and Hamada, M.S. *Experiments: planning, analysis, and optimization.* John Wiley & Sons. 2011.
200. Montgomery, D.C. *Design and analysis of experiments.* Wiley New York. 1984.
201. Muhammad, C., Onwudili, J.A., and Williams, P.T. Thermal Degradation of Real-World Waste Plastics and Simulated Mixed Plastics in a Two-Stage Pyrolysis-Catalysis Reactor for Fuel Production. *Energy & Fuels*. 2015. 29(4): 2601-2609.
202. Abbas-Abadi, M.S., Haghighi, M.N., and Yeganeh, H. Evaluation of pyrolysis product of virgin high density polyethylene degradation using different process parameters in a stirred reactor. *Fuel Processing Technology*. 2013. 109(0): 90-95.
203. Panda, A.K., Singh, R.K., and Mishra, D.K. Thermolysis of waste plastics to liquid fuel A suitable method for plastic waste management and manufacture of value added products-A world prospective. *Renewable & Sustainable Energy Reviews*. 2010. 14(1): 233-248.