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NAME: Mr. Piriya Pinthong

THIS THESIS HAS BEEN ACCEPTED BY

THESIS ADVISOR
(Associate Professor Apinya Duangchan, Ph.D.)

THESIS CO-ADVISOR
(Assistant Professor Siripon Anantawaraskul, Ph.D.)

DEPARTMENT HEAD
(Associate Professor Phungphai Phanawadee, Ph.D.)

APPROVED BY THE GRADUATE SCHOOL ON

DEAN
(Associate Professor Gunjana Theeragool, D.Agr.)

THESIS

CO-PYROLYSIS OF RICE HUSK, POLYETHYLENE AND POLYPROPYLENE MIXTURES: A KINETIC STUDY

PIRIYA PINTHONG

A Thesis Submitted in Partial Fulfillment of
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Co-pyrolysis behavior of rice husk, waste plastics and their blends was studied by thermogravimetric analyzer (TGA). The data obtained from TGA can describe the decomposition behavior of materials and synergistic effect. They can also be used to determine the kinetic parameters (activation energy and pre-exponential factor).

The activation energy (E) and pre-exponential factor (A) of waste plastics (HDPE, LDPE and PP) decomposition were in ranges of 279.0-455.1 kJ/mol and 4.95×10^{19}-1.48×10^{31} min^{-1}, respectively. The activation energy of plastic decomposition reaction reduced when plasics were mixed with rice husk. The activation energy of the mixture was in range of 221.2-317.3 kJ/mol while the pre-exponential factor (A) was in range of 2.11×10^{15}-7.18×10^{21} min^{-1}.

Waste plastics (WPL) and their blends with rice husk (RH) at different WPL/RH ratios of 30/70, 50/50 and 70/30 had synergy at 485°C about 23%, 10.97%, 9.18% and 7.15%, respectively. The WPL/RH mixture of 30/70 showed the highest synergy in conversion (1.46%). Main product from pyrolysis at 485°C of all mixtures was wax. The WPL/RH mixture of 30/70 which provided the highest synergy in conversion was chosen to be pyrolyzed with H-ZSM-5 catalyst. Liquid product from the catalytic pyrolysis contained almost no wax had higher heating value than the wax product (46.31 MJ/kg > 44.74 MJ/kg). The liquid product was distilled and yielded gasoline 54.54%, kerosene 24.24%, diesel 15.15% and residue 16.06% by volume.

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Piriya Pinthong
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CO-PYROLYSIS OF RICE HUSK, POLYETHYLENE AND POLYPROPYLENE MIXTURES: A KINETIC STUDY

INTRODUCTION

The depletion of fossil fuels is a big problem facing the world at this time. As fossil fuels are coming to a shortage, measures are to be taken in order to conserve the irreplaceable energy resources. Alternative energy sources are taking into account. Biomass is one of the most promising materials that can be directly converted into liquid fuels. Among the various conversion technologies, pyrolysis of biomass offers a convenient way to produce liquid fuels.

Rice husk, a renewable by-product of rice milling operations, is an energy source that can be utilized to meet the increasing demands for energy. Its utilization can also help rice millers meet increasing costs of rice husk disposal because of increasing restrictions on disposal (Mansaray, 1998). There are large amounts of rice husk in Thailand because there are many rice mill industries in this country. Annually, about 20 million tons of rice are produced. Accordingly, tremendous amounts of rice husk, residues from processing of rice, are available as energy sources. Despite extensive utilization of rice husk by the Thai milling companies and industrial sectors, significant amounts of these biomass fuels are being unused and eventually lost. Annual losses of rice husk in Thailand are estimated to be 2.3–3.7 million tones. So, it’s of interest to change rice husk, which is agricultural residue, to more valuable products, such as bio-oil or other chemicals.

Polymer waste is an important problem of environmental protection. It is known that polyolefin can be readily thermally decomposed to gaseous and liquid hydrocarbons. The pyrolysis of this kind of polymer in an inert atmosphere or under vacuum at elevated temperatures gives heavy hydrocarbons as a major reaction product. Mainly light paraffins and olefins are obtained during polymer thermolysis at higher temperatures (above 700°C) (Sharypov, 2003).

Pyrolysis is a thermochemical process that can be described as the direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid and gas products. Many kinds of biomass species have been subjected to pyrolysis conditions to produce fuels, solvents, chemicals and other products (Wang, 2008). Sharypov et al. (2003) studied co-pyrolysis of wood biomass and polymer mixture. It was shown that co-pyrolysis of different types of natural and synthetic polymer mixtures in an inert atmosphere has led to high yield of light distillate fraction and benzene soluble products.

Thermogravimetric analysis (TGA) is one of the most common techniques used to investigate thermal events and kinetics during pyrolysis of solid raw materials such as coal, biomass and plastic. It provides a measurement of weight loss of the sample as a function of time and temperature (Zhou, 2006). So, thermogravimetric analysis technique could be used to predict the thermal decomposition behavior and investigate the kinetics of rice husk or plastic or the mixture of rice husk and plastic.

In this work, kinetics of co-pyrolysis reaction was studied by using thermogravimetric analyzer (TGA) under inert atmosphere (N_2 gas) to determine the kinetic parameters (activation energy, pre-exponential factor and order of reaction). The thermal decomposition behaviors were identified. Furthermore, co-pyrolysis of the mixture of rice husk (RH)/plastics mixture (HDPE, LDPE and PP) were investigated and the pyrolysis products were analyzed. The properties of liquid products were characterized such as by determining heating value, and distillation fraction.

OBJECTIVES

1. To investigate the decomposition behavior of rice husk (RH), waste polyethylene (PE) and polypropylene (PP) and their blends.

2. To study the kinetics of co-pyrolysis process of rice husk and waste plastics by calculating the kinetics parameters (activation energy and pre-exponential factor).

3. To study the co-pyrolysis process of rice husk, waste polyethylene (PE) and polypropylene (PP) and their blends.

Working Scopes

1. Wastes of high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) were used as plastics-mixture at a constant ratio.

2. Rice husk (RH)/plastics-mixture ratios were 100/0, 70/30, 50/50, 30/70 and 0/100 (by wt%).

3. Pyrolysis processes were performed in a semi-batch reactor under nitrogen atmosphere at a temperature range between 400 and 500°C and a heating rate of 2.5^{o}C/min.

Impact of the result

The TGA data can describe the decomposition behavior of materials in a reactor. The obtained kinetics parameters can be applied in pyrolysis reactor design. This research produces bio-oil which can be used as an alternative energy. The experimental data can be applied to agricultural and municipal solid waste treatment. Value is added to rice husk and waste plastics.

LITERATURE REVIEW

1. Biomass

Biomass is anything living matter on earth. These are the substances in which solar energy is stored. Plants produce biomass continuously by the process of photosynthesis (Goyal, 2008).

Biomass resources can be divided into two broad categories, i.e., natural and derived materials. Biomass resources include wood and wood wastes, agricultural crops and their waste by-products, municipal solid waste, animal wastes, waste from food processing and aquatic plants and algae. Biomass resource can be subdivided into three categories (Demirbas, 2001).

Wastes: agricultural production wastes, agricultural processing wastes, crop residues, mill wood wastes, urban wood-wastes and urban organic wastes.

Forest products: wood, logging residues, trees, shrubs and wood residues, sawdust, bark, etc., from forest clearings.

Energy crops: short rotation woody crops, herbaceous woody crops, grasses, starch crops (corn, wheat and barley), sugar crops (cane and beet), oilseed crops (soya bean, sunflower and safflower).

1.1. Biomass constituents

Utility of biomass as feedstock for conversion depends upon the chemical constituents and physical properties. Biomass contains varying amounts of cellulose, hemi-cellulose and lignin.

Cellulose is a polymer, consisting of linear chains of 1,4-D-glucopyranose units, in which the units are linked 1–4 in the alpha-configuration, with an average molecular weight of around 100,000 as shown in Figure 1.

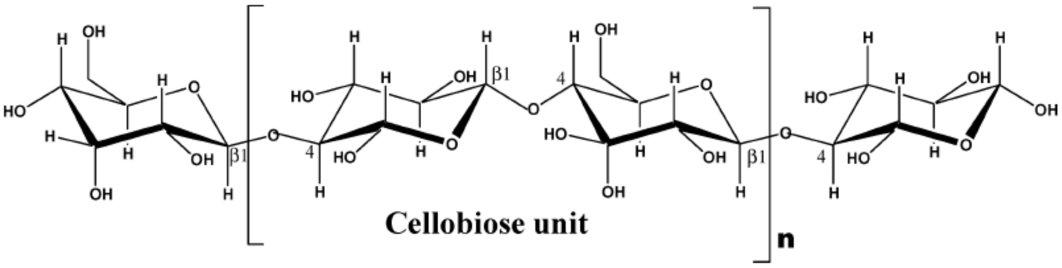

Figure 1 Chemical structure of cellulose

Source: Mohan *et al.* (2006)

Hemi-celluloses are complex polysaccharides present in the cell wall, which consist of branched structures and vary with biomasses. It is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methylglucoronic and galaturonic acids, with an average molecular weight of 30,000.

Lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of the certain biomass, especially woody species, and are often adjacent to cellulose fibers to form a ligno-cellulosic complex (Beis, 2002). Lignin is regarded as a group of amorphous, high molecular weight, chemically related compounds. The building blocks of lignin are believed to be a three-carbon chain attached to rings of six carbon atoms, called phenyl-propanes (see Figure 2).

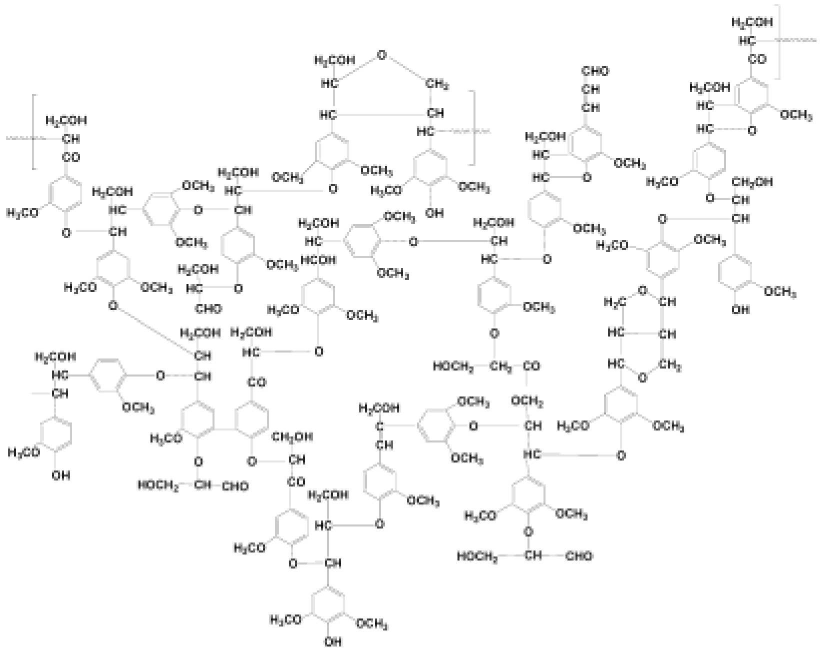

Figure 2 Partial structure of a hardwood lignin molecule from European beech

Source: Mohan *et al.* (2006)

In biomass, cellulose is generally the largest fraction followed by hemi-cellulose, lignin, ash, etc. (Bridgewater, 1999; Ana Rita, 1996).

2. Biomass conversion process

Biomass can be converted to useful products by two main processes:

(a) Thermo-chemical processes

(b) Bio-chemical processes

In this work, only thermo-chemical process was focused

2.1 Thermo-chemical processes

The thermo-chemical conversion processes have two basic approaches. The first approach is the gasification of biomass and its conversion to hydrocarbons. The second approach is to liquefy biomass directly by high-temperature pyrolysis, high-pressure liquefaction, ultra-pyrolysis, or supercritical extraction. These processes convert waste biomass into energy rich useful products. Choice of conversion process depends upon the type and quantity of biomass feedstock, the desired form of the energy, i.e., end user requirements, environmental standards, economic conditions and project specific factors.

Different thermo-chemical conversion processes include combustion, gasification, liquefaction, hydrogenation and pyrolysis. Although pyrolysis is still under developing stage but during current energy scenario, pyrolysis has received special attention as it can convert biomass directly into solid, liquid and gaseous products by thermal decomposition of biomass in the absence of oxygen. Pyrolysis offers efficient utilization of particular importance for agriculture countries with vastly available biomass by-products. In this work, the focus has been made on pyrolysis process only.

3. Pyrolysis

It is thermo-chemical conversion process and is found to be best suited for conversion of biomass to liquid fuel. Pyrolysis is thermal destruction of biomass in the absence of air/oxygen. Pyrolysis of biomass starts at 350–550^{o}C and goes up to 700^{o}C. This leads to the production of useful liquid oil, gases and solid products. Different conditions lead to formation of products in different proportions.

3.1. Pyrolysis process types

3.1.1. Slow pyrolysis

Biomass is pyrolysed at slow heating rates (5–7 K/min). This leads to less liquid and gaseous product and more of char production. Significant amount of work has been done on this process.

Zendersons *et al.* (1999) conducted slow pyrolysis of sugarcane bagasse for char production and obtained 23–28% yield of charcoal.

In Turkey, Putun *et al.* (2001) conducted fixed bed pyrolysis of Euphorbia rigida, sunflower presses, bagasse, and hazelnut shell, at different temperatures and heating rate of 7 K/min. Product yield was found to increase in all the three cases when the pyrolysis temperature was increased from 673 to 973 K. Similar results were obtained on increasing the N_2 flow rate.

Slow pyrolysis of cottonseed cake at heating rate of $7^{o}C$/min in a tubular reactor was reported by Ozbay *et al.* (2001). Pyrolysis experiments were conducted in two reactors, Heinz retort and a well-swept tubular reactor. From results, it was seen that with the increase in the temperature up to $600^{o}C$ the oil yield increased but decreased at around $750^{o}C$. Char yield showed continuous decrease. Oil yield was maximum at N_2 flow rate of 100 cm^3/min.

Onay and Kockar (2004) conducted slow pyrolysis experiments of rapeseed in a Heinz retort and a tubular reactor with variable temperatures, nitrogen flows and particle sizes. Results showed that the increase in temperature up to $550^{o}C$ increased the oil yield and later reduced beyond this temperature. The char yield decreased and gas yield increased with rising temperature. For particle size $0.6<dp<0.85$ the oil yield was maximum. Char was found to be the least with the size of $0.85<dp<1.25$.

Fixed bed slow pyrolysis experiments of safflower seed with a heating rate of 5°C/min were reported by Beis *et al.* (2002). Pyrolysis final temperature, sweep gas flow and particle size were the variable parameters during the study. Results showed that oil yield was highest at 550°C for all particle sizes and flow rates. Gas yield was also found highest at 700°C. In all cases char yield decreased with an increase in the temperature.

3.1.2. Fast pyrolysis.

Initially pyrolysis was done with slow heating rates. This in turn produces more char. The higher yield of desirable liquid product can be obtained by fast pyrolysis. It involves rapid heating of biomass but not as fast as flash pyrolysis. Heating rate is somewhere about 300°C/min. Generally, fast pyrolysis is used to obtain high-grade bio oil. Fast pyrolysis is successful with most of fluidized bed reactors as it offers high heating rates, rapid de-volatilization, easy control, easy product collection, etc. (Lou, 2004).

Various reactors like entrained flow reactor, wire mesh reactor, vacuum furnace reactor, vortex reactor, rotating reactor, circulating fluidized bed reactor, etc. were designated for performing fast pyrolysis. Many researchers have contributed in the field of fast pyrolysis of biomass using various reactors.

3.2. Pyrolysis reactors

Pyrolysis reactor designs includes fixed beds, moving beds, suspended and fluidized beds, entrained feed solid reactor, inclined rotating kilns, etc. Some of the reactors used consist of circulating fluid bed reactor, ablative pyrolysis reactor, bubbling fluid bed reactor, rotating cone reactor, vacuum pyrolysis reactor, wire mesh reactor, ultra pyrolysis entrained flow reactor, etc.

3.3. Pyrolysis reaction mechanism (Savage, 2000)

Hydrocarbon pyrolysis mechanisms usually comprise a set of reversible free-radical reactions that are drawn from a relatively small number of reaction families. These reaction families are displayed in figure 3. They include homolytic dissociation and its reverse, radical recombination; radical disproportionation and its reverse, molecular disproportionation; b-scission and its reverse, radical addition to an unsaturated carbon; isomerization; and hydrogen abstraction. The foregoing reaction families provide opportunities for both making and breaking chemical bonds. Consequently, thermal hydrocarbon chemistry can involve the degradation of large molecules into smaller ones, but it can also involve molecular growth and the production of heavier molecules.

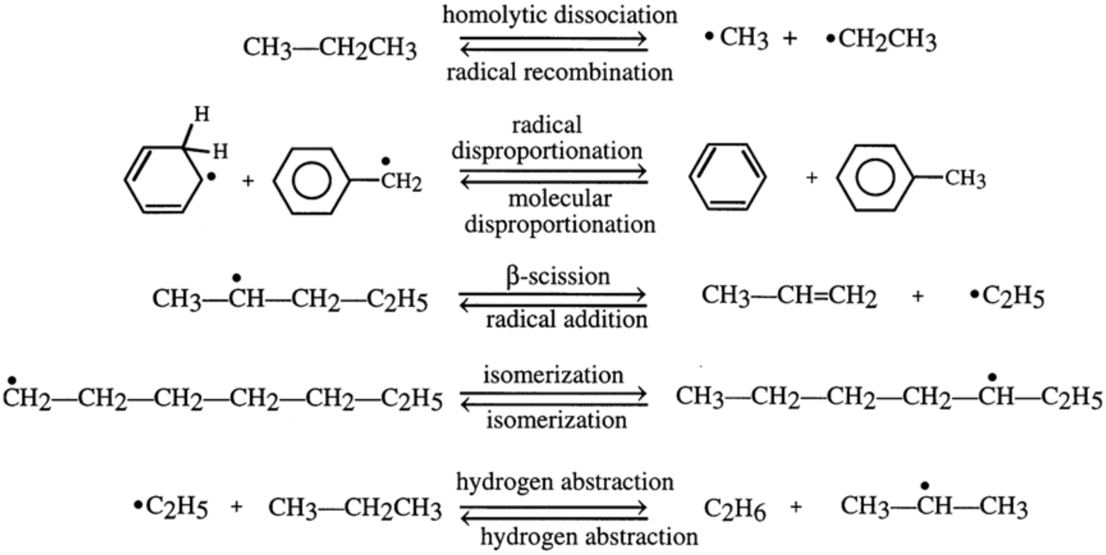

Figure 3 Main reaction families for hydrocarbon pyrolysis

Source: Savage (2006)

When multiple paths are available for a given type of bond-breaking reaction, the path that involves cleavage of the weakest chemical bond is expected to be the fastest path. In this light, note that C-H bonds are typically stronger than C-C bonds, and that other factors being equal the relative strength of C-H and C-C bonds is in the order primary (1°) > secondary (2°) > tertiary (3°). The presence of a double bond or an aromatic ring can also influence the strengths of the C-H and C-C bonds.

4. Pyrolysis product composition

4.1. Pyrolysis oil composition

Oil obtained from pyrolysis of biomass contains several organic as well as inorganic species. Some of the organic groups present in the bio-oil are acids, esters, alcohols, ketones, aldehydes, phenols, alkenes, aromatics, nitrogen compounds, furans, sugars and miscellaneous oxygenate compounds.

Moreover, inorganic species are present in following forms in the bio-oil: (i) associated with counter ions, (ii) connected to organic acids, (iii) related to various enzymatic compounds. Inorganics present in the bio oil comprises of Ca, Si, K, Fe, Al, Na, S, P, Mg, Ni, Cr, Zn, Li, Ti, Mn, Ln, Ba, V, Cl, etc. (Goyal, 2008).

4.2. Pyrolysis gas composition

Pyrolysis gas comprises of CO, CO_2 and CH_4. The other components present are H_2, propane, propylene, butane, butenes, C_5, ethane, etc.

4.3. Pyrolysis char composition

Char contains elemental carbon along with hydrogen. In addition, char also comprises various inorganic species.

5. Pyrolysis products application

5.1. Uses of bio-oil

The bio-oil obtained from pyrolysis can have the following industrial uses: combustion fuel used for power generation, production of chemicals and resins, a transportation fuel which could be a good substitute for fossil fuels, binders for palletizing and briquetting of combustible organic waste materials and preservatives, e.g., wood preservative. A suitable blend of a pyrolysis liquid with the diesel oil may be used as diesel engine fuels. Bio-oils can be used in making adhesives, the oil obtained from sewage sludge pyrolysis can be used directly in diesel fuel engines.

5.2. Uses of char

The char could be used as a solid fuel in boilers. This can be converted into brickets alone or mixed with biomass and can be used as high efficiency fuel in boilers. The char could be used for the production of activated carbon. Possibility of using this carbon feedstock for making carbon-nano-tubes may be explored. It can be used further for the gasification process to obtain hydrogen rich gas by thermal cracking.

5.3. Uses of gas

Pyrolysis gas containing significant amount of carbon dioxide along with methane, might be used as a fuel for industrial combustion purposes.

6. Rice husk

Rice husks (or rice hulls) are the hard protecting coverings of rice grains. In addition to protecting rice during the growing season, rice hulls can be put to use as building material, fertilizer, insulation material, or fuel.

Rice hulls are the coating for the seeds, or grains, of the rice plant. To protect the seed during the growing season, the hull is made of hard materials, including opaline silica and lignin. The hull is mostly indigestible to humans. During the milling process, the hulls are removed from the grain to create white rice. The very high content in amorphous silica of the hulls confer to them and to their ash (SiO_2 ~ 20 wt.%) after combustion very valuable properties.

There are many applications of rice husk such as use as a pet food fiber, a building material, fertilizer, use in industry and use as fuel.

Zeng *et al.* (2006) focuses on studying the conversion of rice husks and sawdust into liquid fuel. Rice husks, sawdust and their mixture are pyrolyzed at temperatures between 420 and 540^{o}C, and the main product of liquid fuel is obtained. The experimental result shows that the yield of liquid fuel depends on various factors such as feedstock and temperature. The maximum yields for rice husks, sawdust and their mixture are 56%, 61% and 60% at 465, 490 and 475^{o}C, respectively. Analyses with GC–MS and other apparatus show that the liquid fuel is a complicated compound with low caloric value and can be directly used as a fuel oil for combustion in a boiler or a furnace without any upgrading. Alternatively, the fuel can be refined to be used by vehicles.

Worasuwannarak *et al.* (2007) investigated the pyrolysis behaviors of rice straw, rice husk, and corncob with the TG-MS technique, while paying close attention to the gas formation during the pyrolysis. The weight decreasing profiles and the gas formation rates were significantly different among the samples although their elemental compositions were almost the same. It was found that H_2O is the main product formed for all the samples. The differences in the gas formation rates were found to be due to their differences in the composition of hemicellulose, cellulose, and lignin. There were significant interactions between cellulose and lignin during the pyrolysis. The interactions between cellulose and lignin during the pyrolysis contributed to a decrease in tar yields but an increase in char yields. From the gas formation data and FTIR analyses of the chars, it may be concluded that the suppression of tar formation during the pyrolysis of biomass was brought about by the cross-linking reactions between lignin and cellulose to form H_2O and ester groups during the pyrolysis.

Ji-lu (2007) studied pyrolysis of rice husk. The fast pyrolysis process was performed in the experimental device which mainly consists of a hopper, two screw feeders, an electric heater, a fluidized-bed reactor, two cyclones, a condenser and an oil pump. The nitrogen gas was pre-heated to the temperature range of 450-550^{o}C before entering into fluidized-bed reactor. Rice husks were fed at the rate of 7.32 kg/h and pyrolysed at temperature between 420^{o}C and 540^{o}C in a fluidized-bed reactor. The hot gas can be quickly cooled into liquid in the condenser. The maximum bio-oil yield of 56 wt% was observed at 465^{o}C. Bio-oil from rice husks was analyzed by GC-MS for its chemical composition. Furthermore, the heating value, stability, miscibility and corrosivity were investigated. The results showed that the bio-oil is a complicated organic compound which consists mainly of water, acid and heterocyclic substances. Bio-oil is completely immiscible in diesel. The corrosivity is very mild toward copper and stainless steel. The obtained bio-oil can be directly used as fuel oil for combustion in a boiler or a furnace without any upgrading.

Tsai *et al.* (2007) prepared a series of pyrolysis oils and chars from agricultural by-product rice husk by the lab-scale fast pyrolysis system using induction heating. The effects of process parameters such as pyrolysis temperature, heating rate, holding time, nitrogen gas flow rate, condensation temperature and particle size on the pyrolysis product yields and their chemical compositions were examined. The maximum oil yield of over 40% was obtained at the proper pyrolysis conditions. The chemical characterization by elemental, calorific, spectroscopic and chromatographic studies showed that the pyrolysis oils derived from the fast pyrolysis of rice husk contained considerable amounts of carbonyl groups and/or oxygen content, resulting in low pH and low heating values.

7. Plastics

Plastic is a general common term for a wide range of synthetic or semisynthetic organic solid materials suitable for the manufacture of industrial products. Plastics are typically polymers of high molecular weight, and may contain other substances to improve performance and/or reduce costs.

7.1. Polyethylene

Polyethylene (PE), sometimes known as polythene, was discovered in 1933 by Reginald Gibson and Eric Fawcett at the British industrial giant imperial chemical industries (ICI). This material evolved into two forms, low density polyethylene (LDPE), and high density polyethylene (HDPE).

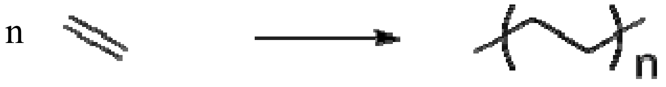

Figure 4 Polymerization reaction of ethylene

PEs are cheap, flexible, durable, and chemically resistant. LDPE is used to make films and packaging materials, while HDPE is used for containers, plumbing, and automotive fittings. While PE has low resistance to chemical attack, it was found later that a PE container could be made much more robust by exposing it to fluorine gas, which modified the surface layer of the container into the much tougher polyfluoroethylene.

7.2. Polypropylene

Polyethylene would lead after the war to an improved material, polypropylene (PP), which was discovered in the early 1950s by Giulio Natta. It is common in modern science and technology that the growth of the general body of knowledge can lead to the same inventions in different places at about the same time, but polypropylene was an extreme case of this phenomenon, being separately invented about nine times. The ensuing litigation was not resolved until 1989.

Polypropylene managed to survive the legal process and two American chemists working for Phillips Petroleum, J. Paul Hogan and Robert Banks, are now generally credited as the "official" inventors of the material. Polypropylene is similar to its ancestor, polyethylene, and shares polyethylene's low cost, but it is much more robust. It is used in everything from plastic bottles to carpets to plastic furniture, and is very heavily used in automobiles.

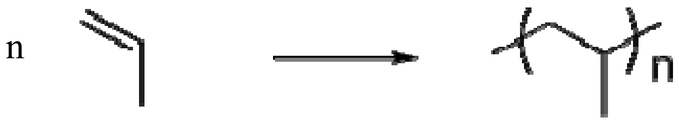

Figure 5 Polymerization reaction of propylene

Experiments of waste polymers cracking in a continuous flow tube reactor were carried out (Walendziewski, 2005). The main components of the reactor unit were a screw extruder as a waste plastics feeder and a tube cracking reactor equipped with an internal screw mixer. Cracking process was realized at the temperature range 420–480^{o}C and raw material feeding rate from 0.3 up to 2.4 kg/h. The principal process products, gaseous and liquid hydrocarbon fractions, are similar to the refinery cracking products. They are unstable due to the high olefins content (especially from polystyrene cracking) and their chemical composition and properties strongly depend on the applied feed composition, i.e. shares of polyethylene, polypropylene and polystyrene. The material balance experiments showed that the main products, liquid or solid materials in ambient temperature, contain typically 20–40% of gasoline fractions and 60–80% of light gas oil fractions. The solid carbon residues are similar to coal cokes and contain even of 50% mineral components. Their calorific values attain 20 MJ/kg and they are solid fuels of quality similar to brown coals.

Three plastic fractions from a commercial waste electrical and electronic equipment (WEEE) processing plant were collected and investigated for the possibility of recycling them by batch pyrolysis (Williams and Slaney, 2007). The first plastic was from equipment containing cathode ray tubes (CRTs), the second plastic was from refrigeration equipment, and the third plastic was from mixed WEEE. Initially, the decomposition of each of the plastics was investigated using a TGA linked to a FT-IR spectrometer which showed that the CRT plastic decomposed to form aliphatic and aromatic compounds, the refrigerator plastic decomposed to form aldehydes, CO_2, aromatic, and aliphatic compounds, and the mixed WEEE plastic decomposed to form aromatic and aliphatic compounds, CO_2, and CO. Each plastic mixture was also pyrolysed in a batch reactor to determine the halogen and metal content of the pyrolysis products, additionally, characterisation of the pyrolysis oils was carried out by GC–MS and the pyrolysis gases by GC–FID and GC–TCD. It was found that the halogen content of the oils was relatively low but the halogen and metal content of the chars was high. The pyrolysis oils were found to contain valuable chemical products and the pyrolysis gases were mainly halogen free, making them suitable as a fuel

Pinto (1999) study the pyrolysis of plastic mixture municipal solid waste (MSW). A typical plastic composition in Portuguese municipal solid waste may contain about 68% PE, 16% PP and 16% PS. This mixture guaranteed the production of an end product with more than 30% of aromatic content and calorific value around 45 MJ/kg. If higher calorific value or octane number is eventually required, the input mixture should be optimised, with the addition of more PS or PP, to increase the aromatic or the alkene contents, respectively.

8. Co-pyrolysis of biomass and plastics

Sharypov *et al.* (2002) investigated the co-pyrolysis of wood biomass and synthetic polymers under inert atmosphere in autoclave conditions. Beech wood, pine wood, cellulose, hydrolytic lignin, medium density polyethylene, isotactic and atactic polypropylene were selected as starting materials. Co-pyrolysis of the different types of natural and synthetic polymer mixtures in an inert atmosphere has led to high yield of light distillate fraction and benzene soluble products. The optimum temperature for biomass/plastic mixture conversion which corresponds to the maximum yield of light liquids was 400°C.

Paradela *et al.* (2009) study the recovery of three types of waste by the process of pyrolysis: biomass, plastics and used tyres by pyrolysis. The effects of experimental conditions in products yield and composition were studied. The increase of reaction time increased alkane content both in gas phase from 53% to 70% v/v and in liquid fraction from 48% to 60% w/w. The rise of reaction temperature led to a decrease of liquid yield (from 82% to 73% w/w), which was followed by the increase of solids and gases. The increase of reaction temperature also allowed the increase of the alkane content in gas phase from 39% to 70% v/v. The parameter that most affected products yield and composition was plastics content on the wastes initial mixture. The enhancement of this parameter increased liquid yield from 33% to 92% w/w, at the expense of solids and gases contents and also decreased aromatic contents from 52% to 28% w/w.

9. Thermogravimetric analysis and kinetic study

To illuminate the synergistic effect between the biomass and plastic samples, the difference of weight loss (ΔW) was defined,

$$\Delta W = W_{blend} - (x_1 W_1 + x_2 W_2) \qquad (1)$$

where W_{blend} is the weight loss of blend, x_i is the weight fraction of each material in the blend and W_i is the weight loss of each material in the same operational conditions.

Obviously, ΔW describes the ‘extent’ of synergistic effect during co-pyrolysis (Zhuo *et al.*, 2006).

5.1 Kinetics analysis

The kinetic parameters, activation energy and pre-exponential factor, of biomass and plastic pyrolysis were determined by the integral method. Many investigators assumed that solid fuel pyrolysis is a first order reaction. So the biomass and plastic pyrolysis reaction equation may simply be expressed as the following formula (Zhuo *et al.*, 2006)

$$\frac{dx}{dt} = A\exp(-\frac{E}{RT})(1-x) \qquad (2)$$

where A is pre-exponential factor, E is activation energy, T is temperature, t is time, x is weight loss fraction or pyrolysis conversion which can be calculated by

$$x = \frac{W_0 - W_t}{W_0 - W_f} \qquad (3)$$

where W_0 is the original mass of the test sample; W_t is the mass at time t or T and W_f is final mass at the end of pyrolysis.

For a constant heating rate H during pyrolysis, H=dT/dt, rearranging equation 2 and integrating give

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HE}(1-\frac{2RT}{E})\right] - \frac{E}{RT} \qquad (4)$$

Since it may be shown that for most values of E and for the temperature range of the pyrolysis, the expression ln[AR/HE(1−2RT/E)] in equation 4 is essentially constant, if the left side of equation 4 is plotted versus 1/T, a straight line may be obtained if the process can be assumed as a first order reaction. From the slope, −E/R, the activation energy E can be determined, and by taking the temperature at which W_t

= $(W_0 + W_f)/2$ in the place of T in the intercept term of equation 4, the pre-exponential factor A can also be determined.

Zhuo *et al.* (2006) investigated co-pyrolysis behaviours of plastic/biomass by using a thermogravimetric analyser under nitrogen atmosphere at heating rate of 20°C/min from room temperature to 650°C. The biomass sample selected was Chinese pine wood sawdust (SW), while high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene were selected as plastic samples. Results obtained from this comprehensive investigation indicated that plastic was decomposed in the temperature range 438–521°C, while the thermal degradation temperature of biomass is 292–480°C. The difference of weight loss (ΔW) between experimental and theoretical ones, calculated as algebraic sums of those from each separated component, is about 6–12% at 530–650°C. These experimental results indicate a significant synergistic effect during plastic and biomass co-pyrolysis at the high temperature region. The results of kinetic analyses show that first order reactions together with Arrhenius law account for the different subintervals of weight loss found for materials and their blends quite satisfactorily. For SW, HDPE and LDPE, the pyrolysis process can be described by one first order reaction. However, for PP or SW/plastic blends, this process can be described by two or three consecutive first order reactions respectively.

Cai *et al.* (2008) investigated co-pyrolytic behaviours of different plastics (high density polyethylene, low density polyethylene and polypropylene), low volatile coal and their blends with the addition of the plastic of 5 wt% using a thermogravimetric analyzer. The results indicated that plastic was decomposed in the temperature range 438–521°C, while the thermal degradation temperature of coal was 174–710°C. The overlapping degradation temperature interval between coal and plastic was favorable for hydrogen transfer from plastic to coal. The difference of weight loss (ΔW) between experimental and theoretical ones, calculated as an algebraic sum of those from each separated component, was 2.0–2.7% at 550–650 °C. These experimental results indicated a synergistic effect during plastic and coal co-pyrolysis at the high temperature region. In addition, a kinetic analysis was performed to fit thermogavimetric data, the estimated kinetic parameters (activation energies and pre-exponential factors) for coal, plastic and their blends, were found to be in the range of 35.7–572.8 kJ/mol and $27–1.7\times10^{38}$ min^{-1}, respectively.

MATERIALS AND METHODS

Materials

The materials which were used in this study are rice husk and waste plastics including polypropylene (PP), high density polyethylene (HDPE) and low density polyethylene (LDPE). Rice husk (obtained from rice mill in Phra Nakhorn Si Ayutthaya, Thailand) was dried at 110°C for 2 hours and then crushed and sieved. The fraction of particle diameter less than 0.2 mm was used in this study. Waste plastics were collected as following, PP from plastic cup, LDPE from a plastic wrap of a pack of drinking water bottles "Nestle" brand and HDPE from the cap of a plastic bottle of drinking water "Crystal" brand. All waste plastics were scrubbed by a file into small pieces which diameters are not greater than 1 mm. Waste plastics were blended at the HDPE/LDPE/PP ratio of 50/30/20 according to the ratio of waste plastics in Thailand (Bangsantia, 2007).

Methods

1. Thermogravimetric analysis

Thermogravimetric analysis was carried out in a thermogravimetric analyzer (TGA) model SDT 2960 PN 925605.001, Perkin Elmer. The amount of sample was approximately 10 mg. Samples of rice husk and plastic blends were prepared by mixing rice husk with plastics mixtures at various ratios. Under N_2 gas flow rate of 100 ml/min, samples were heated from room temperature to 700°C at a heating rate of 20°C/min.

2. Kinetic analysis

Kinetic of co-pyrolysis reaction was analyzed by using thermogravimetric (TGA). Kinetic parameter was determined by using thermogravimetric (TGA) data and Arrhenius's equation. First, conversion (x) was calculated at constant temperature following equation 3. Kinetic parameters were determined by equation 4.

$$x = \frac{W_0 - W_t}{W_0 - W_f} \tag{3}$$

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HE}(1-\frac{2RT}{E})\right] - \frac{E}{RT} \tag{4}$$

From equation 4, kinetic parameter (E and A) is obtained if the left side of equation 4 is plotted versus 1/T, a straight line may be obtained if the process is assumed as a first order reaction. This equation was used under the assumption of constant heating rate and negligible heat transfer limitation. From the slope, −E/R, the activation energy E can be determined, and by taking the temperature at which $W_t = (W_0 + W_f)/2$ in place of T in the intercept term of equation 4, the pre-exponential factor A can also be determined. One-step integral method is a method to determine decomposition rate of reactions in pyrolysis by applying equations 3 and 4 to the whole pyrolysis temperature range (room temperature to 700°C). It was observed that the plot of $\ln[-\ln(1-x)/T^2]$ versus $1/T^2$ showed multi-step reactions. Therefore, multi-step integral method was used to determine the reaction rate of each step. Multi-step integral method is a method to determine the kinetic parameters for each step (temperature range). Conversion was re-calculated for each temperature range and equation 4 was applied for each step.

3. Co-pyrolysis process

Pyrolysis experiments were carried out in nitrogen atmosphere. In this study, 316 stainless steel pyrolysis reactor (700 ml) was heated by a furnace with auto-tuning PID temperature controller using a K-type thermocouple placed on the furnace as shown in Figure 6. The desired flow rate of the carrier gas (N_2) was adjusted and maintained by using a needle valve.

First of all, rice husk and plastics-mixture was mixed and placed in the pyrolysis reactor and occupied about 1/3 of reactor volume or approximately 50 g. The flow rate of N_2 gas was adjusted to 300-400 ml/min and then heated by electric resistance up to 400-500°C. The temperature was measured using calibrated thermocouples. When temperature inside the reactor reached 400-500°C, rice husk and plastics-mixture were pyrolyzed and vaporized. Then the vapor entered the tube reactor (Figure 6) at 400-500°C. The condensable vapor products were condensed with the help of a condenser which maintained temperature around 25°C attached to the reactor outlet and the liquid product leaving the condenser was collected in a flask which was cooled in an ice bath at a temperature about -5°C.

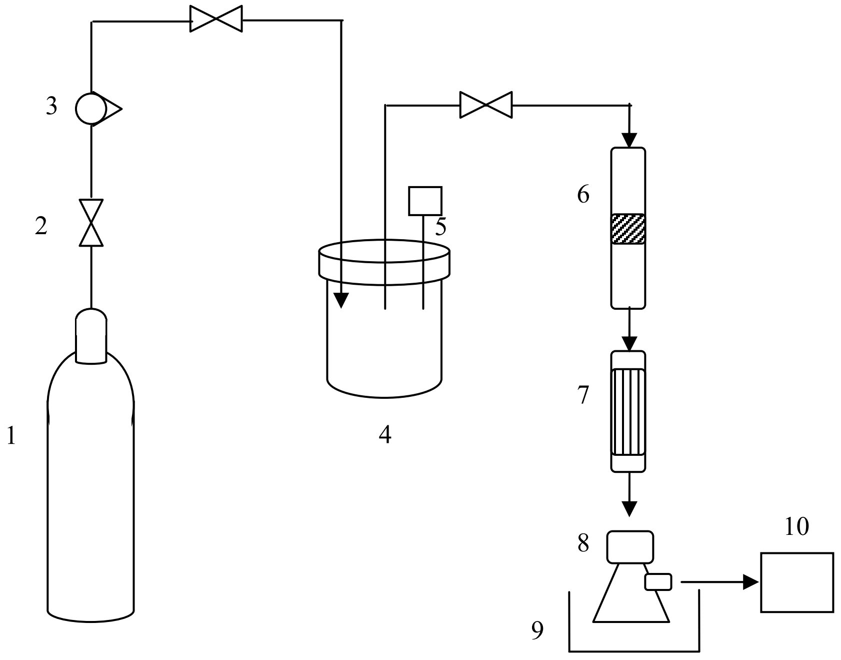

Figure 6 Schematic diagram of experimental setup for co-pyrolysis process : (1) nitrogen cylinder, (2) valve, (3) pressure gauge, (4) pyrolysis reactor, (5) thermocouple, (6) tube reactor, (7) condenser, (8) condensate collector, (9) ice bath, (10) gas product collector or ventilation hood.

4. Product Analysis and Characterization

Yield of each pyrolysis product can be calculated by following formula:

$$\% \text{ yield of liquid product} = \frac{\text{wt. of liquid product}}{\text{wt. of initial pyrolysis material}} \times 100\% \qquad (5)$$

$$\% \text{ yield of solid product} = \frac{\text{wt. of solid product}}{\text{wt. of initial pyrolysis material}} \times 100\% \qquad (6)$$

$$\% \text{ yield of gas product} = 100 - (\% \text{ yield of liq. prod.}) - (\% \text{ yield of solid prod.}) \qquad (7)$$

Liquid product obtained from pyrolysis process was analyzed its heating value by bomb calorimeter. The distillation fraction was analysed following ASTM D-86. Gas products were analyzed by gas chromatograph (Varian, CP3800) connected with Rt®-Q-Bond capillary column and FID detector. The injection port temperature was 220^{o}C. The column temperature was initially at 40^{o}C and increased at a rate of 10^{o}C/min to temperature of 240^{o}C. Total time was 20 min.

RESULTS AND DISCUSSION

1. Thermogravimetric analysis of rice husk, waste plastics and their mixtures by thermogravimetric analyzer (TGA)

Pyrolysis of material and their blends were observed by thermogravimetric analyzer (TGA). The TGA and DTA profiles of rice husk are shown in Figure 7.

First, decomposition temperature range of rice husk was 70-100°C which was vaporization of moisture. Moisture content of rice husk was found to be approximately 10%. The second range of rice husk decomposition was 270-380°C (weight loss around 55%). After 400°C, a slow rate of weight loss occurred until 700°C, the residue was around 40%.

Rice husk mainly consists of three basic constituents of biomass; hemicelluloses (decomposed at 220-350°C), cellulose (decomposed at 325-375°C) and lignin (decomposed at 200-700°C) (Uzun, 2007).

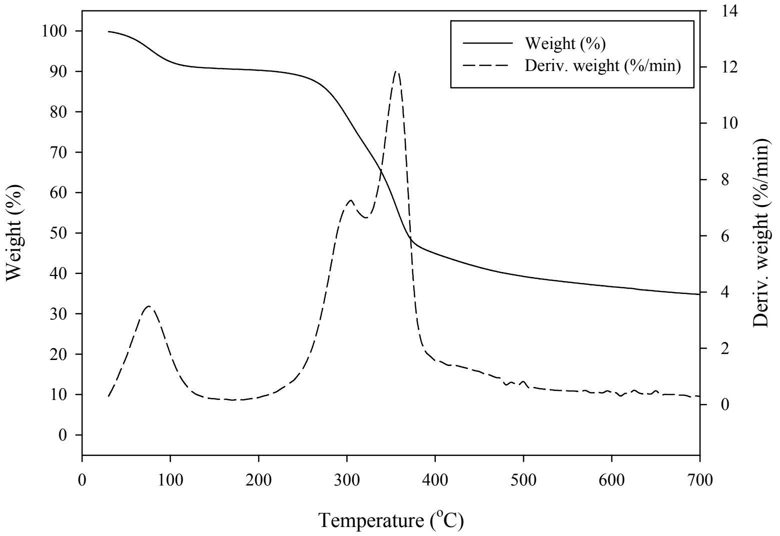

Figure 7 TGA and DTA profiles of rice husk pyrolysis, under N_2 atmosphere, heating rate of 20°C/min.

The TGA profiles of plastics pyrolysis are shown in Figures 8 to 10. HDPE, LDPE and PP decomposed at 465-510°C (Figure 8), 445-505°C (Figure 9) and 425-490°C (Figure 10), respectively. These three types of plastics almost completely decomposed (residue <1%) at 700°C.

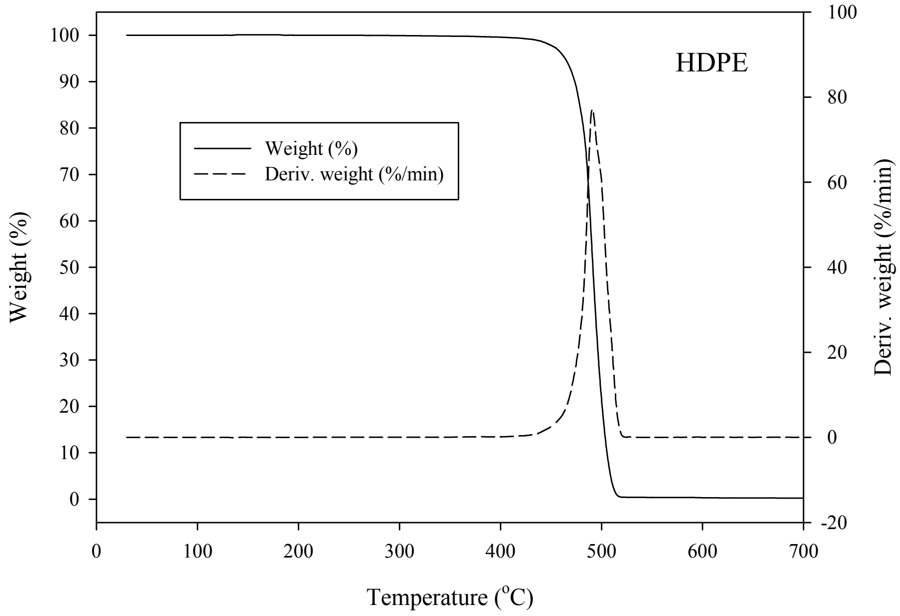

Figure 8 TGA and DTA profiles of HDPE pyrolysis, under N_2 atmosphere, heating rate of 20°C/min.

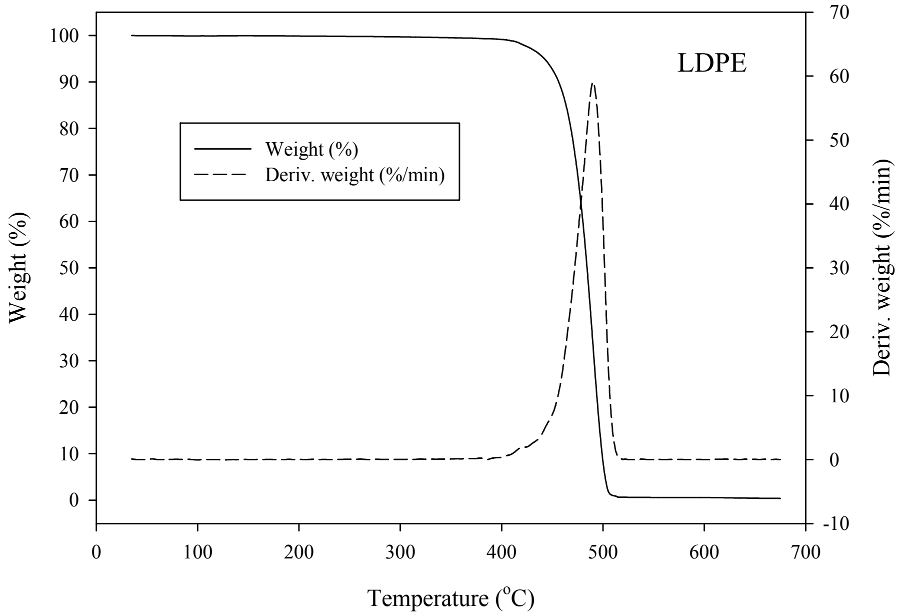

Figure 9 TGA and DTA profiles of LDPE pyrolysis, under N_2 atmosphere, heating rate of 20°C/min.

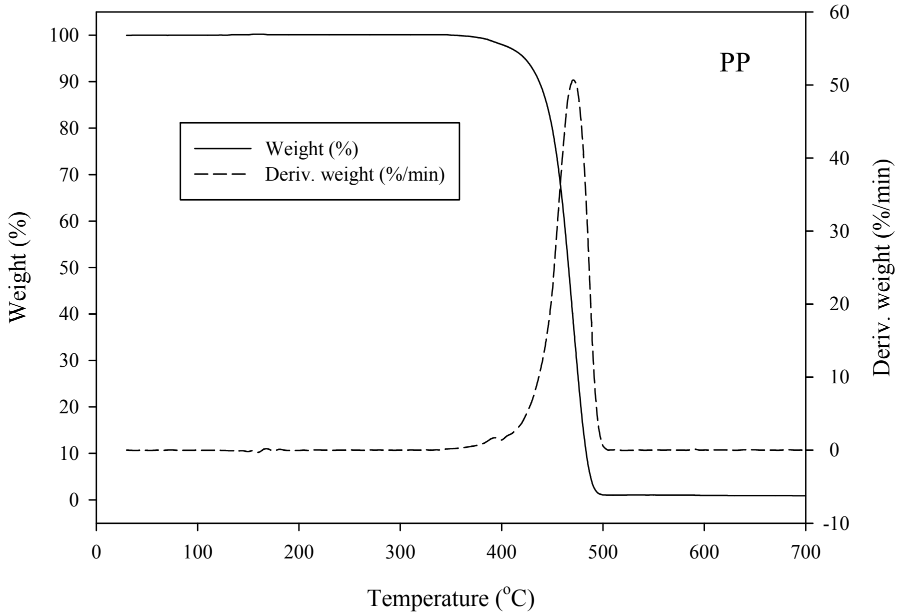

Figure 10 TGA and DTA profiles of PP pyrolysis, under N_2 atmosphere, heating rate of 20°C/min.

TGA profiles of rice husk with the three types of plastics were compared and the result is shown in Figure 11. When temperature increased, weight loss increased for all samples. Rice husk decomposed at lower temperature (270°C) than plastics (HDPE, LDPE and PP) which started to decompose at >400°C. HDPE, LDPE and PP started to decompose at 465°C, 445°C and 425°C, respectively. When the decomposition of the three types of plastics were compared, it was found that PP decomposed easier than LDPE and HDPE. Finally, all plastics decomposed almost 100% (residue <1%) but rice husk decomposed approximately 65%.

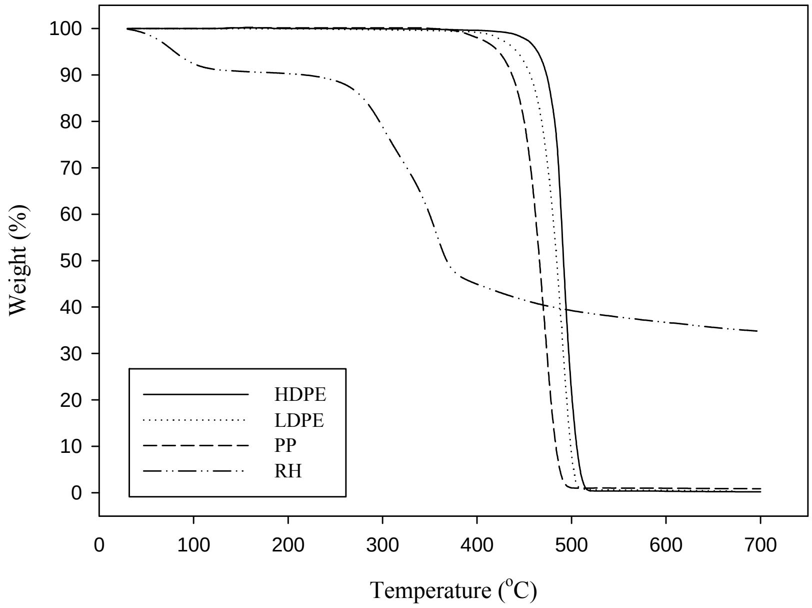

Figure 11 TGA and DTA profiles of rice husk (RH) and waste plastic (HDPE, LDPE and PP) pyrolysis, under N_2 atmosphere, heating rate of 20°C/min.

In the case of rice husk/plastic mixtures, TGA profile shows two regions of thermal decomposition that consist of the profile of rice husk and plastic as shown in Figures 12 to 15.

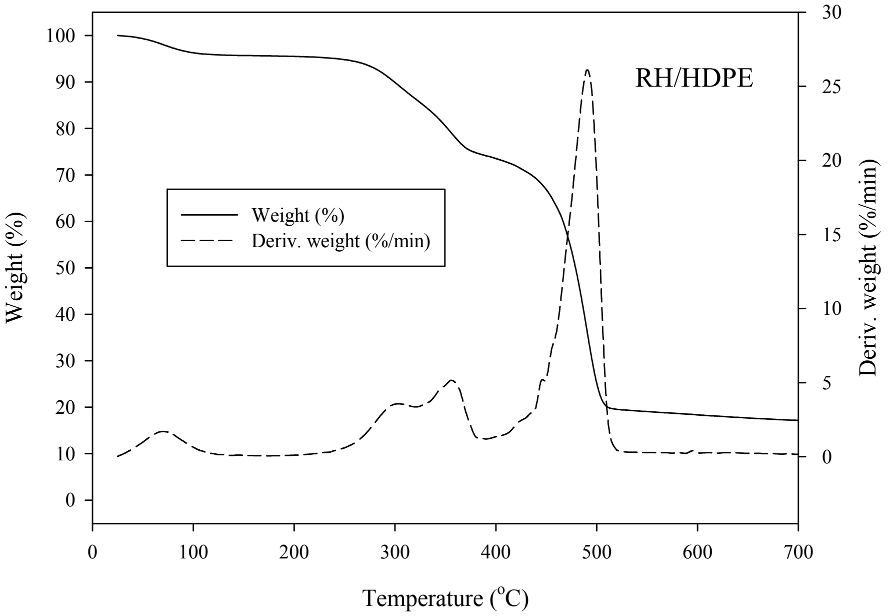

Figure 12 TGA and DTA profiles of rice husk (RH) and HDPE mixtures co-pyrolysis under N_2 atmosphere, heating rate of 20°C/min.

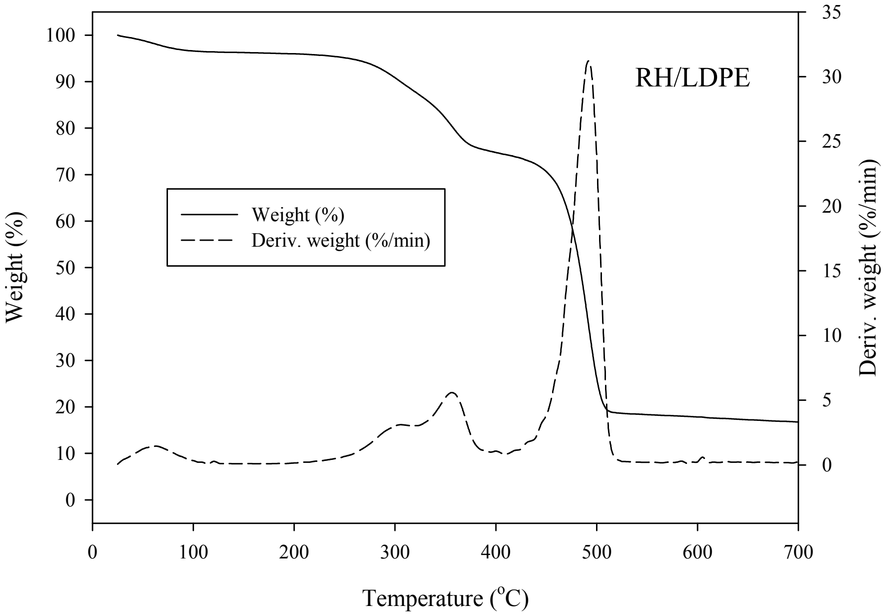

Figure 13 TGA and DTA profiles of rice husk (RH) and LDPE mixtures co-pyrolysis under N_2 atmosphere, heating rate of 20°C/min.

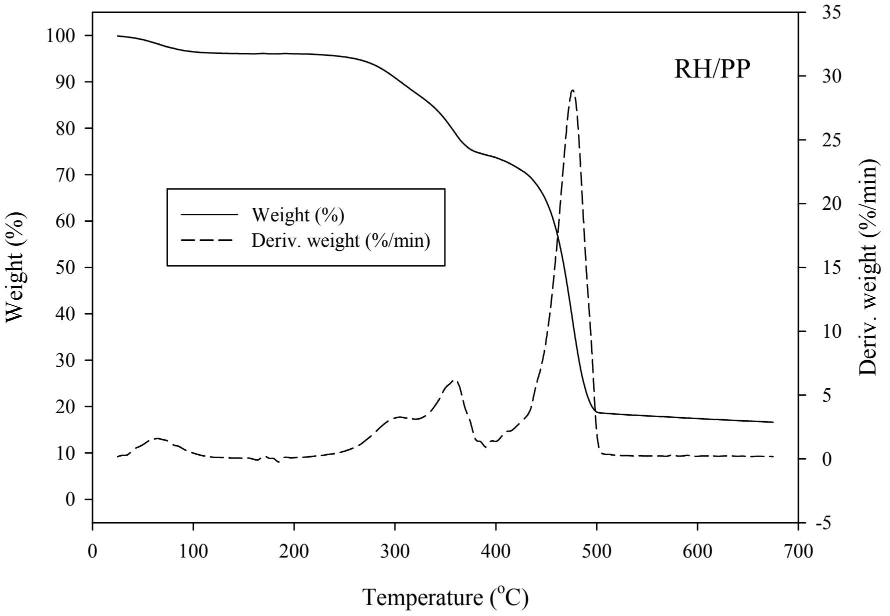

Figure 14 TGA and DTA profiles of rice husk (RH) and PP mixtures co-pyrolysis under N_2 atmosphere, heating rate of 20°C/min.

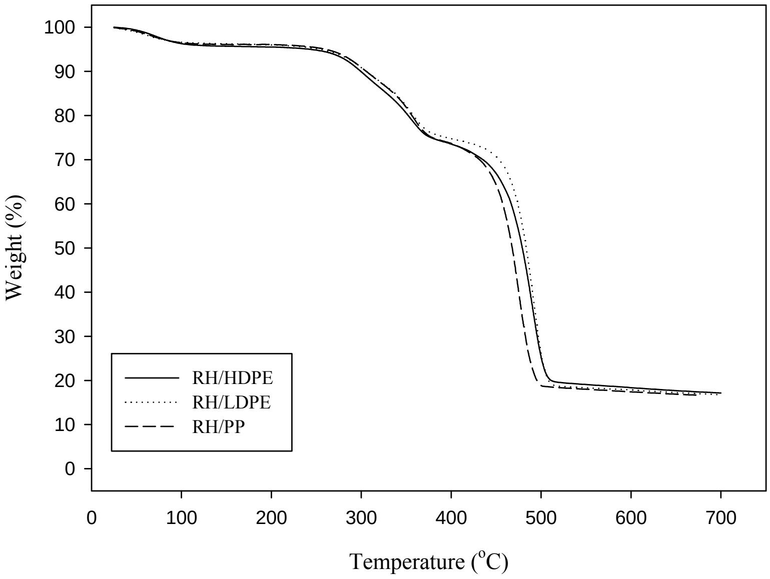

Figure 15 TGA and DTA profiles of rice husk (RH)/plastic mixtures co-pyrolysis under N_2 atmosphere, heating rate of 20°C/min.

When these three types of RH/plastic mixtures were compared, it was found that the first decomposition temperature range was in the same range (around 70-400°C) which was moisture vaporization and rice husk decomposition range. The second range was plastic decomposition. The RH/PP decomposed at the temperature range 450-500°C which was lower than those of the RH/HDPE and RH/LDPE mixtures. The RH/HDPE and RH/LDPE decomposed at nearly the same temperature range (480-500°C). All the three mixtures had weight loss around 85%. The residues were approximately 15% for all types of RH/plastic mixtures.

Three types of waste plastics (HDPE, LDPE and PP) were mixed at ratio of HDPE/LDPE/PP = 50/30/20 by wt% and pyrolyzed in thermogravimetric analyzer. This mixture was defined as WPL. The result is shown in Figure 16. One range of decomposition was found. Waste plastics rapidly decomposed at the temperature range of 440-500°C. After 500°C, weight loss was around 99% and residue was 1.3%.

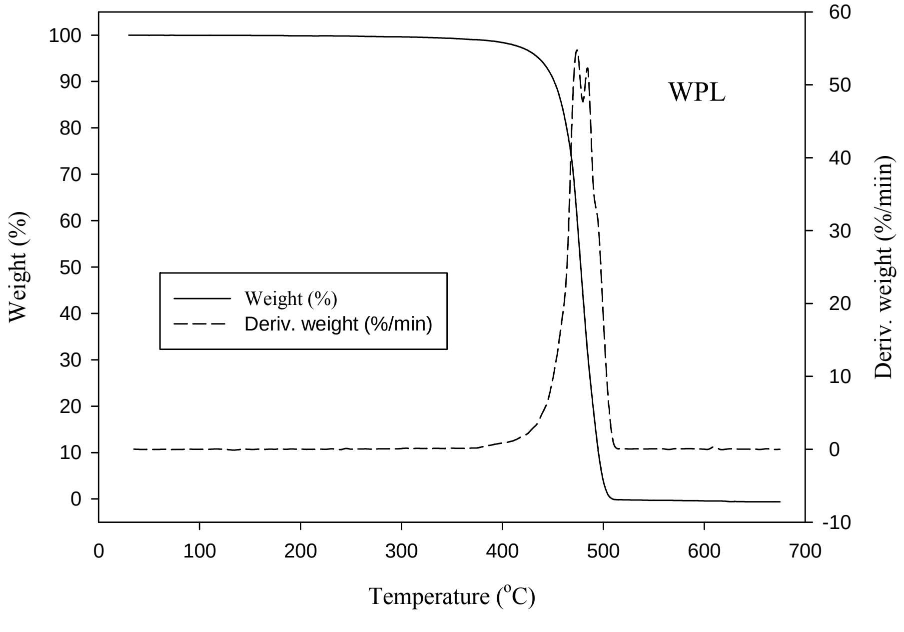

Figure 16 TGA and DTA profiles of waste plastics mixture or WPL (HDPE/LDPE/PP = 50/30/20 by weight) co-pyrolysis under N_2 atmosphere, heating rate of 20°C/min.

Rice husk and waste plastics mixture were blended at ratio of 30/70, 50/50 and 70/30 (by wt%) to investigate co-pyrolysis behavior in thermogravimetric analyzer. The TGA and DTA results showed that there were two ranges of decomposition in 30/70 mixture as shown in Figure 17. First range was rice husk decomposition which decomposed at the temperature range of 290-390°C. The second range was 400-505°C which was waste plastics decomposition range. No weight loss above 500°C and residue was 6.6%.

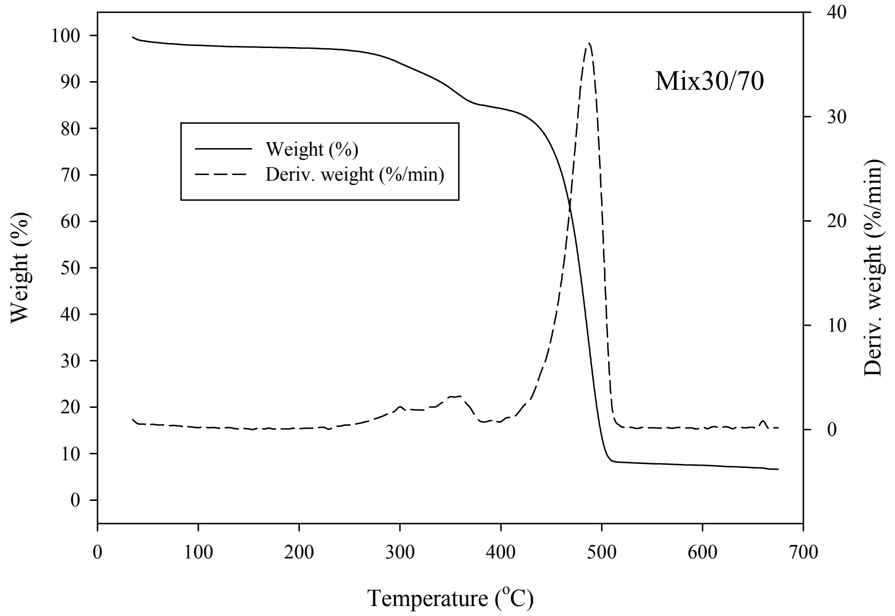

Figure 17 TGA and DTA profiles of rice husk and waste plastics mixture co-pyrolysis at the ratio of 30/70 (wt%) under N_2 atmosphere, heating rate of 20°C/min.

In case of 50/50 and 70/30 mixtures, three ranges of decomposition were found as shown in Figures 18 and 19. The first range was found at the temperature range around 50-100°C which was moisture vaporization. The second range was 290-390°C which was rice husk decomposition. The last range was 400-505°C which was waste plastics decomposition range. Waste plastics in the mixture rapidly decomposed from 400°C to 500°C and no weight loss above 500°C was observed. The residues of

50/50 and 70/30 mixtures were 16.95% and 21.35%, respectively. As known that residue was from rice husk, the more fraction of rice husk, the more residue occurred.

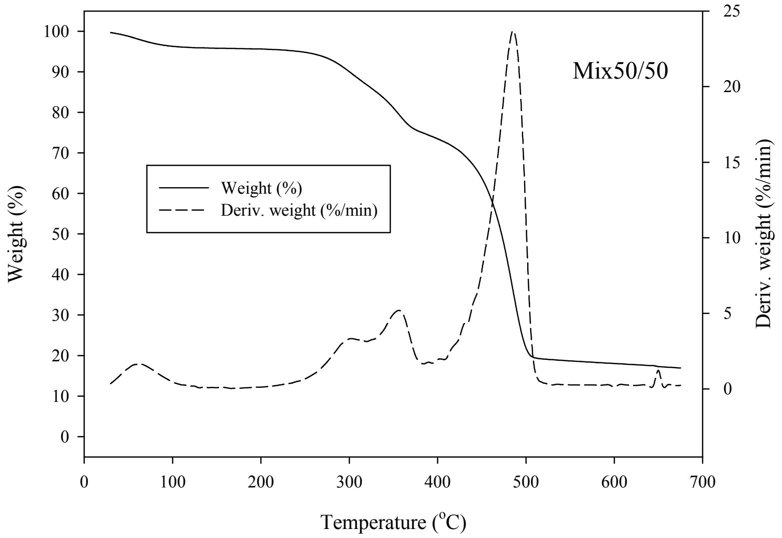

Figure 18 TGA and DTA profiles of rice husk and waste plastics mixture co-pyrolysis at the ratio of 50/50 (wt%) under N_2 atmosphere, heating rate of 20°C/min.

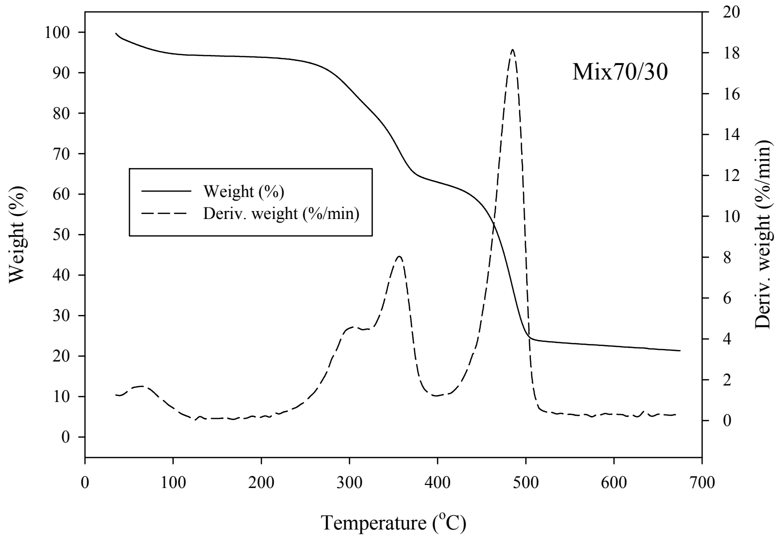

Figure 19 TGA and DTA profiles of rice husk and waste plastics mixture co-pyrolysis at the ratio of 70/30 (wt%) under N_2 atmosphere, heating rate of 20°C/min.

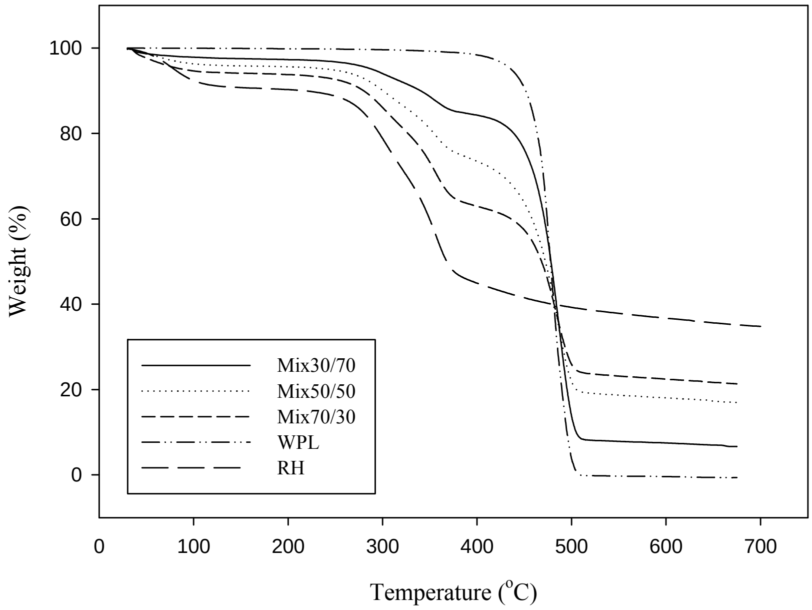

Figure 20 TGA and DTA profiles of rice husk, waste plastics mixture and RH/WPL mixtures co-pyrolysis under N_2 atmosphere, heating rate of 20°C/min.

The decomposition profile of rice husk, waste plastics mixture and their blends were compared and the results are shown in Figure 20. It was found that each profile of RH/WPL mixture consists of rice husk and waste plastics decomposition profiles. Weight loss of each mixture depends on rice husk and waste plastics content. The residues of 30/70, 50/50 and 70/30 mixtures were 6.65, 16.95 and 21.35%, respectively.

2. Kinetics analysis

Kinetic parameters, activation energy and pre-exponential factor, were calculated by

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right]=\ln\left[\frac{AR}{HE}(1-\frac{2RT}{E})\right]-\frac{E}{RT} \qquad (4)$$

From equation 4, if the left hand side of equation 4 is plotted versus 1/T. From the slope (-E/RT), the activation energy can be estimated, and by taking the temperature at which $W_t = (W_o + W_f)/2$ in the place of T in the intercept term of equation 4, the pre-exponential factor A can also be estimated. For the consecutive first order reaction, equation 4 is applied separately to each stage. The conversion (x) has to be recalculated in each stage. From the slope of each line, the value of E and A can be obtained for each stage.

Figure 21 shows the plot of $\ln(-\ln(1-x)/T^2)$ versus 1/T for rice husk pyrolysis. Two independent first order reactions were observed for this pyrolysis process. equation 2 was applied to each stage of reaction.

$$\frac{dx}{dt} = A\exp(-\frac{E}{RT})(1-x) \tag{2}$$

To determine two kinetic parameters (A and E), the conversion (x) had to be recalculated for each reaction.

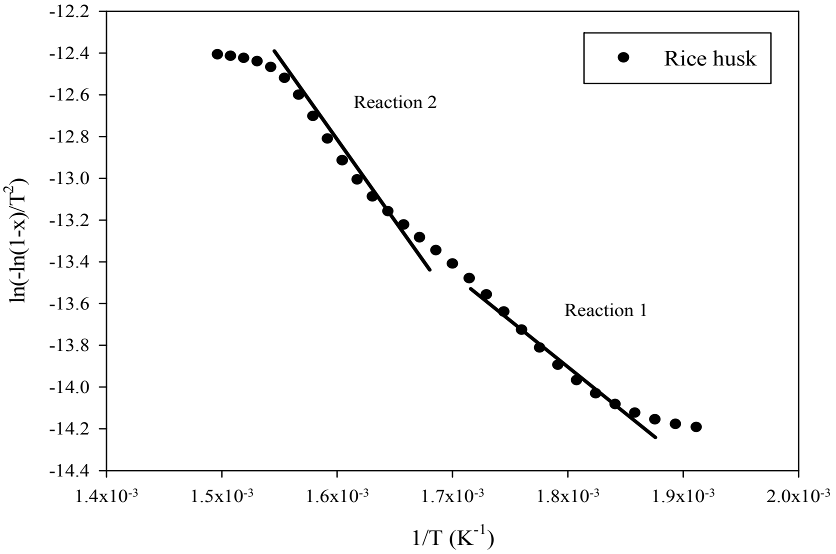

Figure 21 Plot of $\ln(-\ln(1-x)/T^2)$ vs 1/T of rice husk pyrolysis calculated by one-step integral method.

The plot of ln(-ln(1-x)/T^2) versus 1/T for waste plastics (HDPE, LDPE and PP) are shown in Figures 22 to 24. The single first order reaction was used to describe these pyrolysis processes. In case of rice husk and waste plastic co-pyrolysis, three independent first order reactions were used to describe these co-pyrolysis processes as shown in Figures 25 to 27. Equation 2 was applied to each stage of reaction and the conversions (x) of each reaction were recalculated to determine the kinetic parameter.

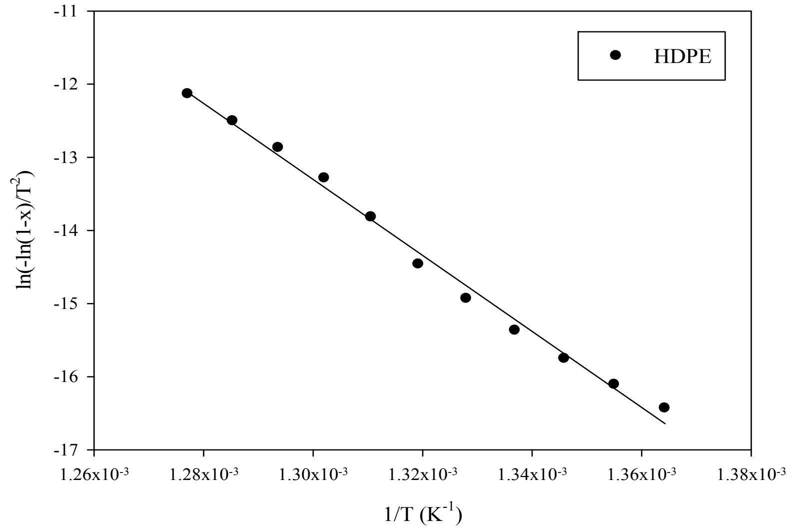

Figure 22 Plot of ln(-ln(1-x)/T^2) vs 1/T of HDPE pyrolysis calculated by one-step integral method.

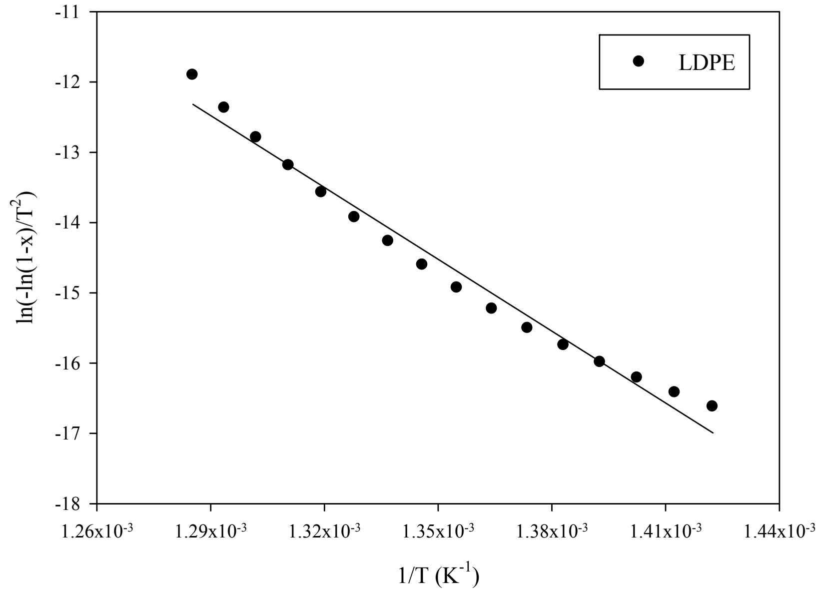

Figure 23 Plot of $\ln(-\ln(1-x)/T^2)$ vs 1/T of LDPE pyrolysis calculated by one-step integral method.

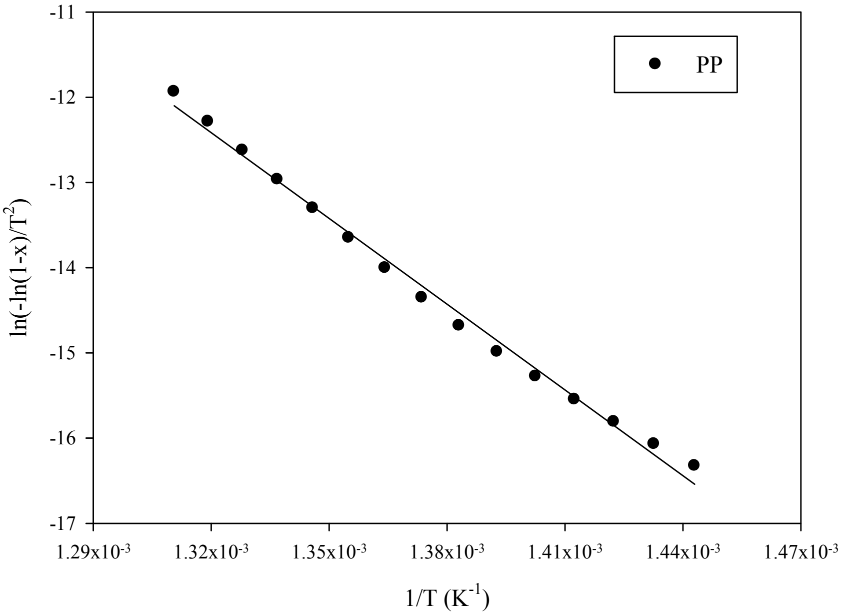

Figure 24 Plot of $\ln(-\ln(1-x)/T^2)$ vs 1/T of PP pyrolysis calculated by one-step integral method.

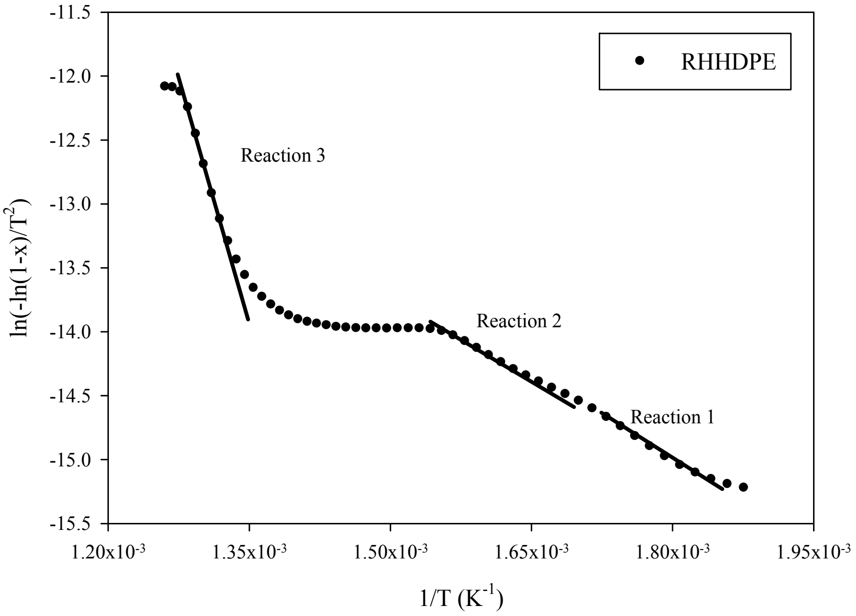

Figure 25 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and HDPE at the ratio of 1:1 (by weight) pyrolysis calculated by one-step integral method.

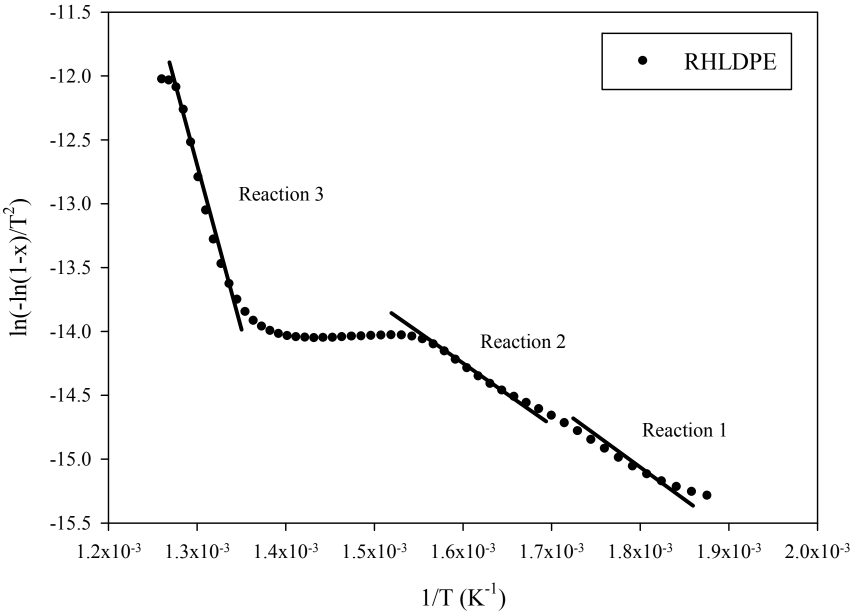

Figure 26 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and LDPE at the ratio of 1:1 (by weight) pyrolysis calculated by one-step integral method.

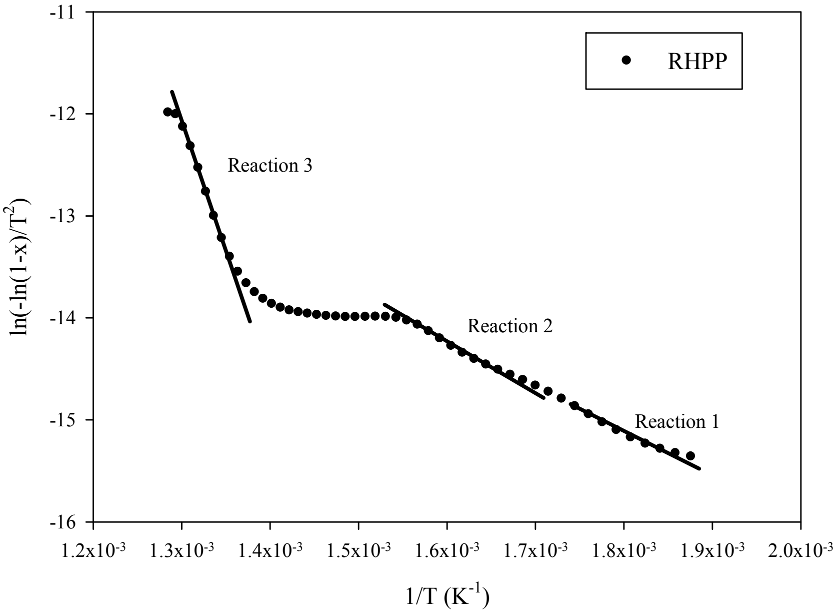

Figure 27 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and PP at the ratio of 1:1 (by weight) pyrolysis calculated by one-step integral method.

For the mixture of waste plastics HDPE, LDPE and PP co-pyrolysis, the plots of ln(-ln(1-x)/T^2) versus 1/T showed a single first order reaction as shown in Figure 28. In case of rice husk and waste plastics mixture co-pyrolysis at various ratios, three independent first order reactions were described these co-pyrolysis processes as shown in Figures 29 to 31. To determine the kinetic parameters, the conversions (x) of each reaction had to be recalculated.

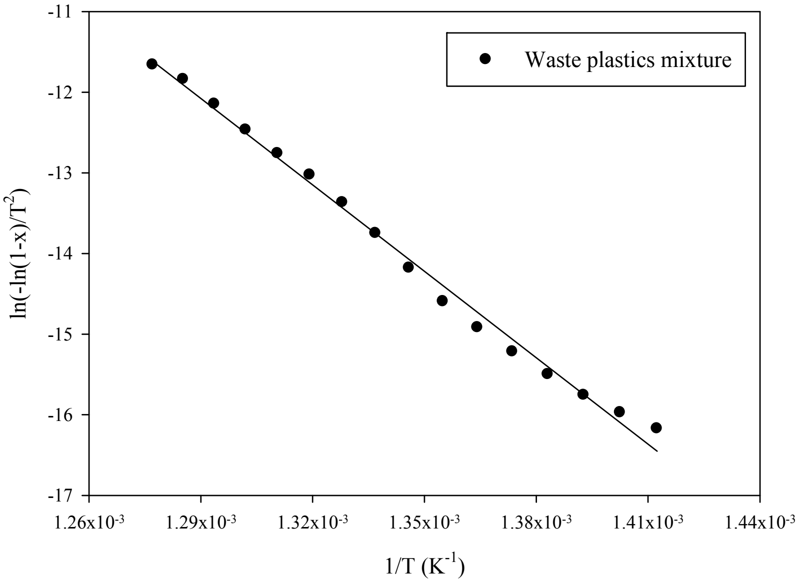

Figure 28 Plot of ln(-ln(1-x)/T^2) vs 1/T of waste plastics mixture (HDPE, LDPE and PP at the ratio of 50/30/20 by weight) pyrolysis calculated by one-step integral method.

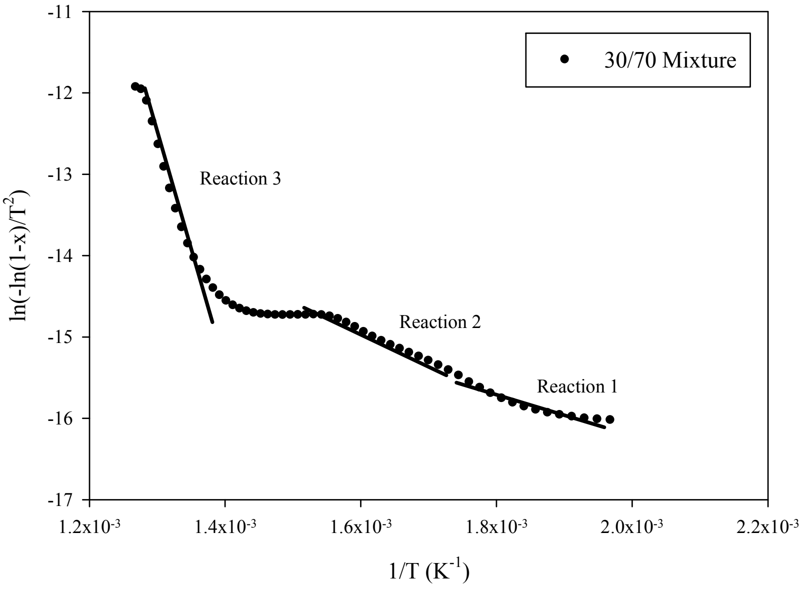

Figure 29 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and waste plastics mixture at the ratio of 30/70 (by weight) pyrolysis calculated by one-step integral method.

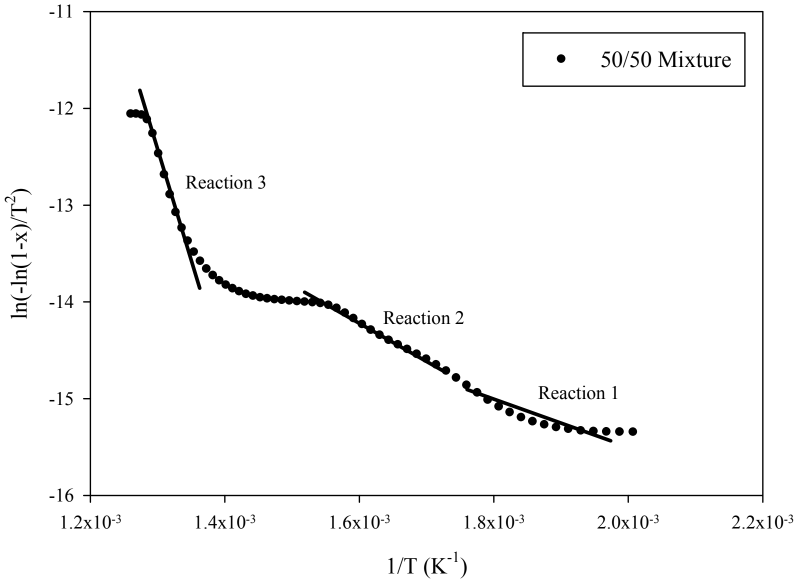

Figure 30 Plot of $\ln(-\ln(1-x)/T^2)$ vs 1/T of rice husk and waste plastics mixture at the ratio of 50/50 (by weight) pyrolysis calculated by one-step integral method.

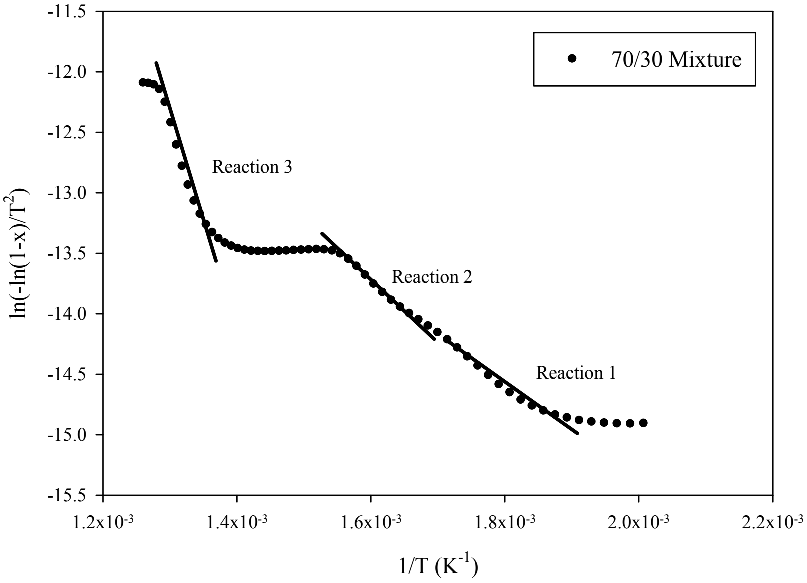

Figure 31 Plot of $\ln(-\ln(1-x)/T^2)$ vs 1/T of rice husk and waste plastics mixture at the ratio of 70/30 (by weight) pyrolysis calculated by one-step integral method.

When the conversions (x) were recalculated, each reaction for each pyrolysis process was separated as shown in Figures 32 to 42. Rice husk and each type of waste plastic were discussed first. The kinetic parameter A and E were calculated. Activation energy (E) can be calculated from the slope of each plot. The results are compared with the work of Junqing et al. (2008) and shown in Table 1.

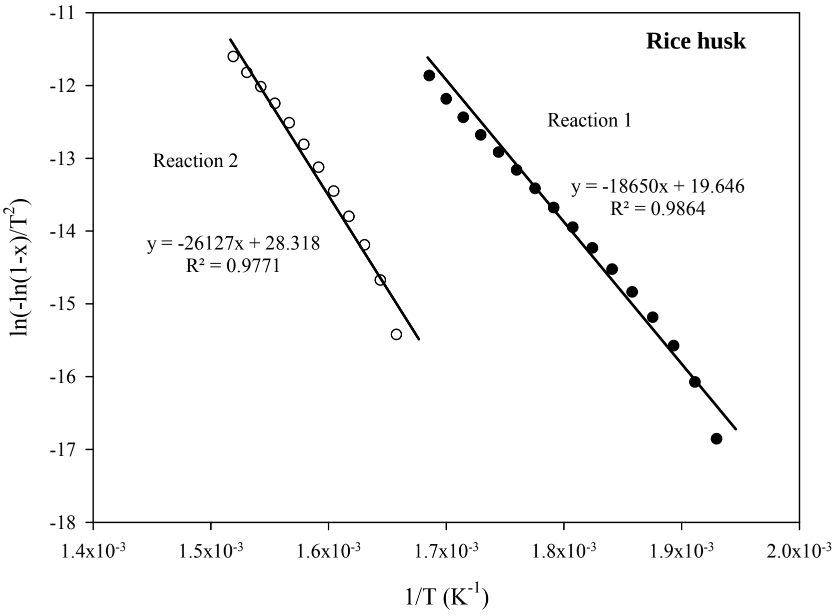

Figure 32 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk pyrolysis calculated by multi-step integral method.

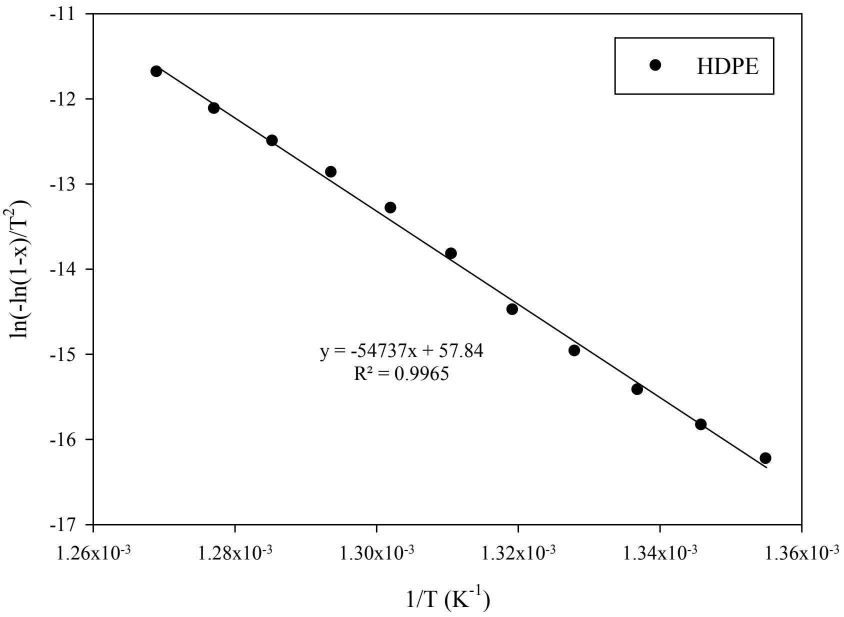

Figure 33 Plot of ln(-ln(1-x)/T^2) vs 1/T of HDPE pyrolysis calculated by multi-step integral method.

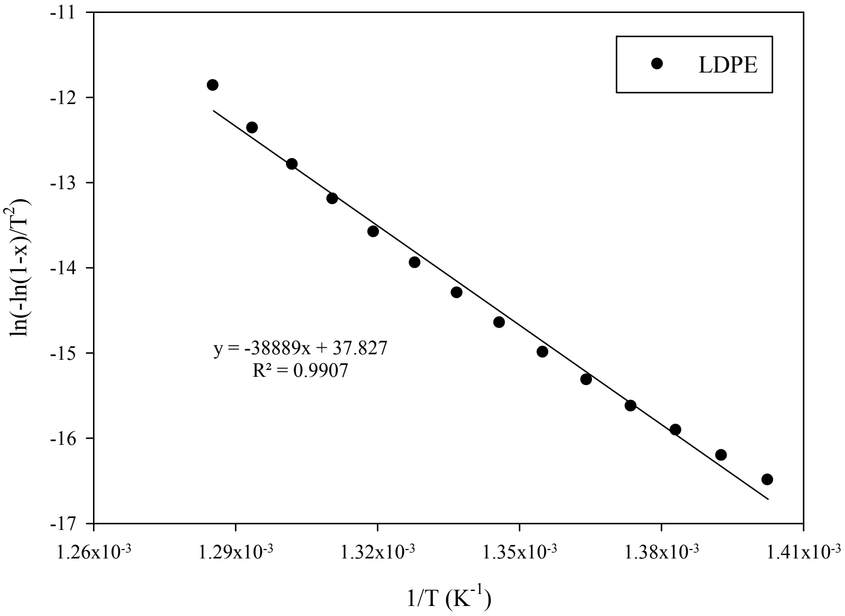

Figure 34 Plot of ln(-ln(1-x)/T^2) vs 1/T of LDPE pyrolysis calculated by multi-step integral method.

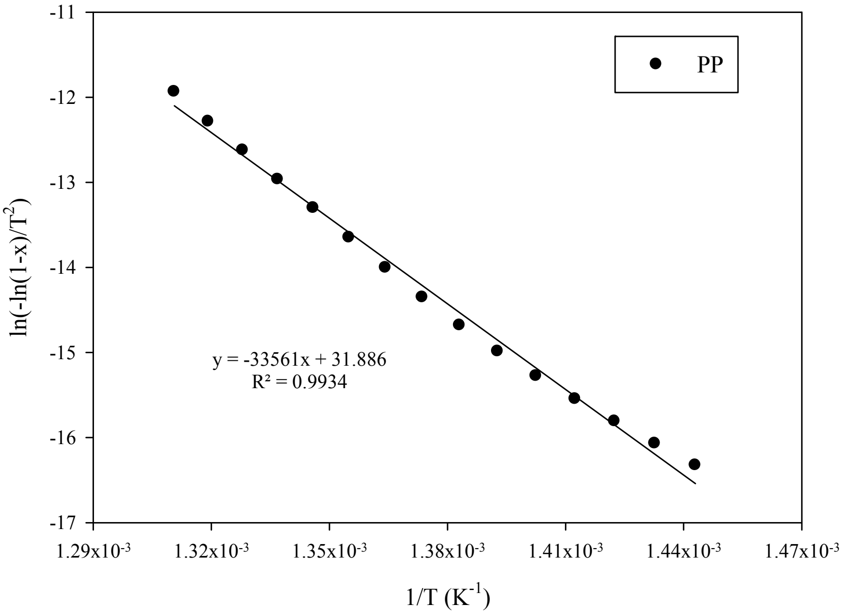

Figure 35 Plot of ln(-ln(1-x)/T^2) vs 1/T of PP pyrolysis calculated by multi-step integral method.

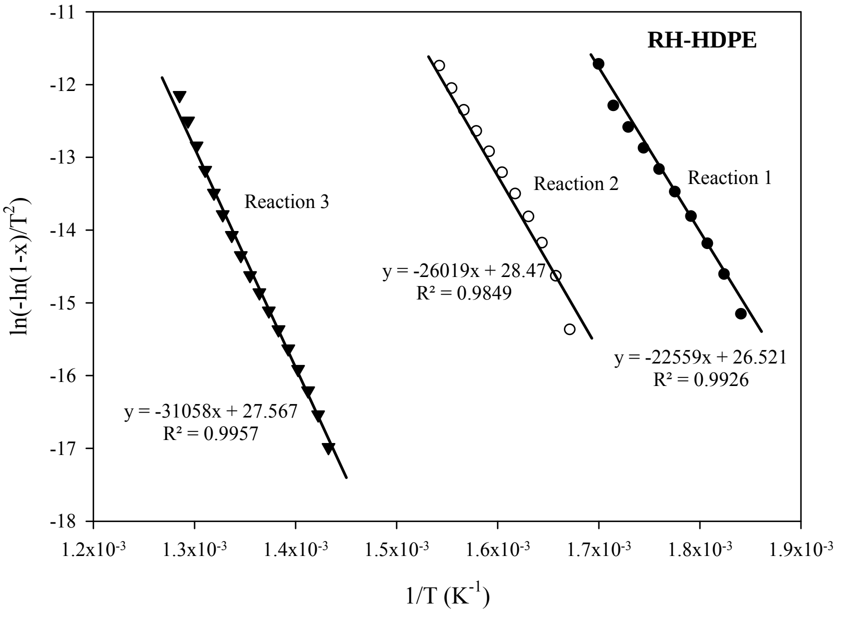

Figure 36 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and HDPE at the ratio of 1:1 (by weight) pyrolysis calculated by multi-step integral method.

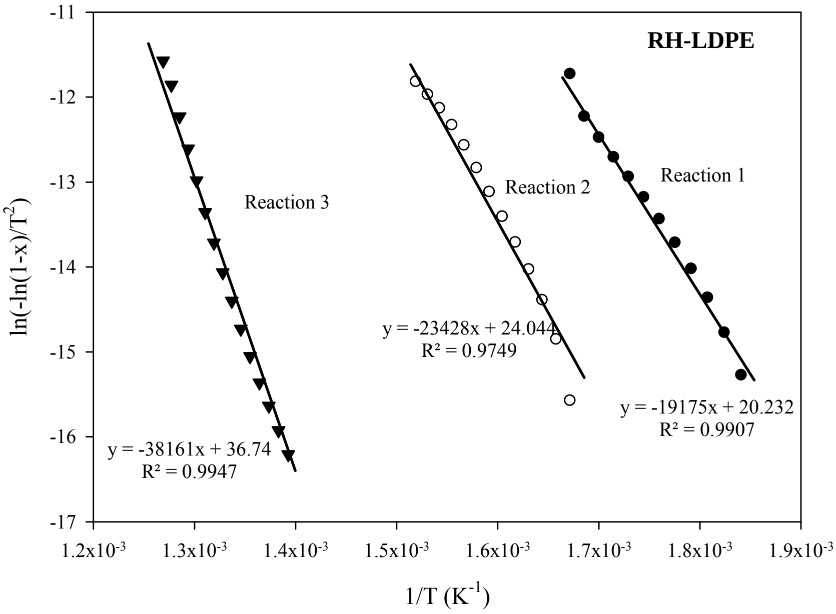

Figure 37 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and LDPE at the ratio of 1:1 (by weight) pyrolysis calculated by multi-step integral method.

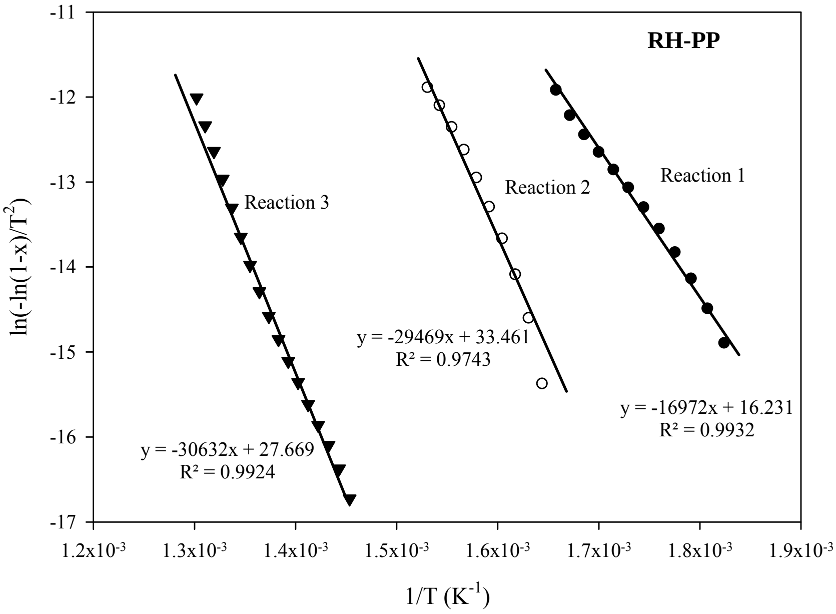

Figure 38 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and PP at the ratio of 1:1 (by weight) pyrolysis calculated by multi-step integral method.

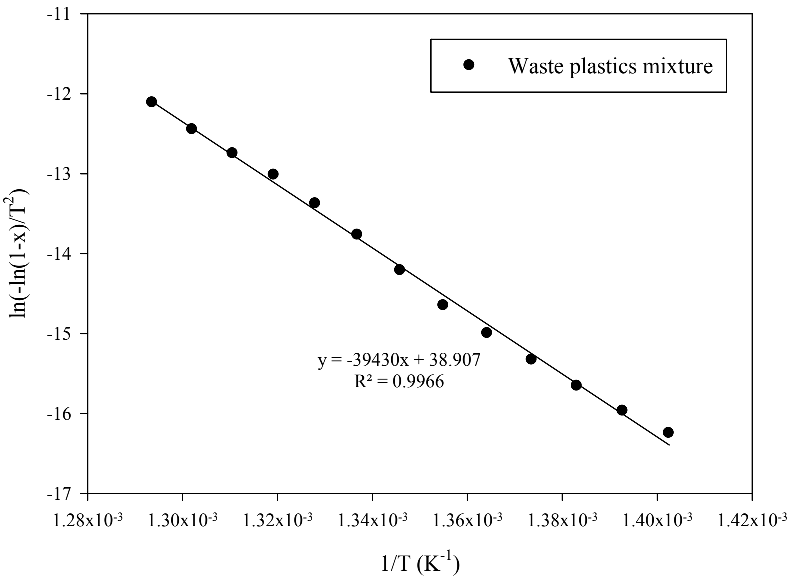

Figure 39 Plot of ln(-ln(1-x)/T^2) vs 1/T of waste plastics mixture (HDPE, LDPE and PP at the ratio of 50/30/20 by weight) pyrolysis calculated by multi-step integral method.

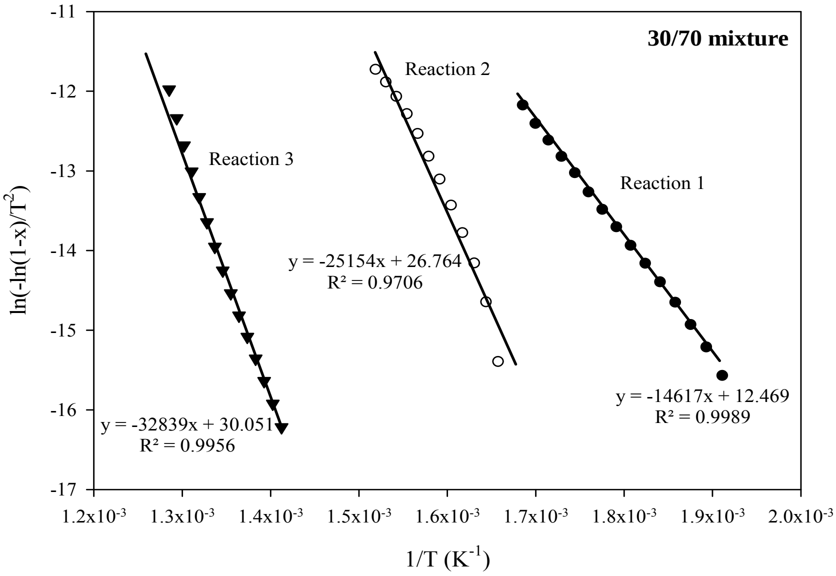

Figure 40 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and waste plastics mixture at the ratio of 30/70 (by weight) pyrolysis calculated by multi-step integral method.

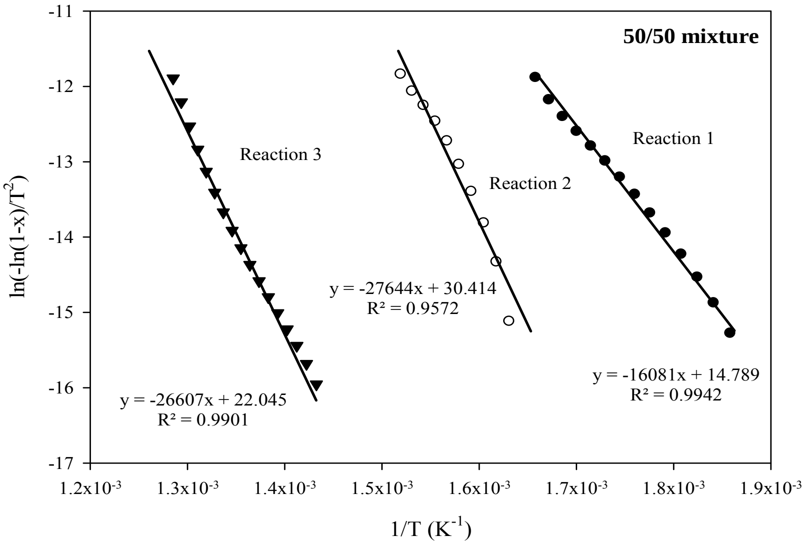

Figure 41 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and waste plastics mixture at the ratio of 50/50 (by weight) pyrolysis calculated by multi-step integral method.

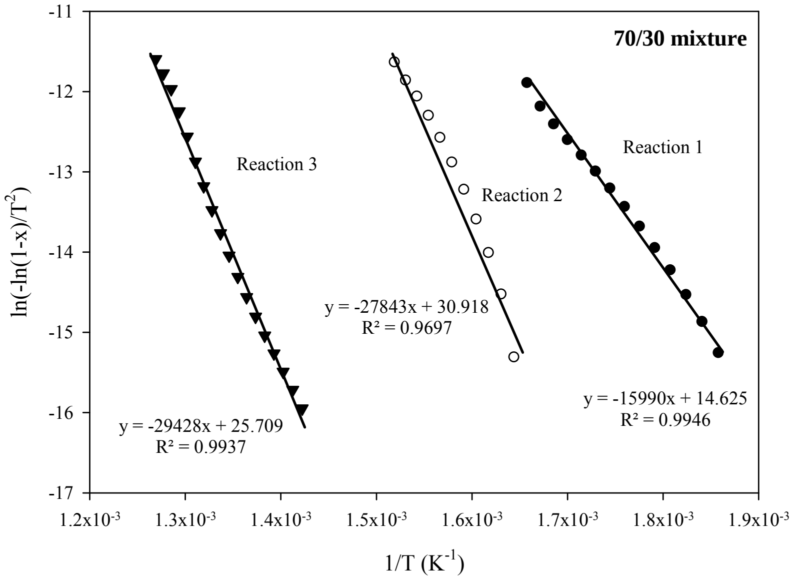

Figure 42 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and waste plastics mixture at the ratio of 70/30 (by weight) pyrolysis calculated by multi-step integral method.

From Table 1, the results showed that activation energy of HDPE (455.1 kJ/mol) was greater than LDPE (323.3 kJ/mol), PP (279.0 kJ/mol) and rice husk (155.1 and 217.2 kJ/mol), respectively. When these activation energies were compared with those of Junqing et al. (2008), it was found that activation energy of HDPE was nearly the same. The activation energies of LDPE and PP were slightly different, this may come from the difference of raw materials. Waste plastics were used in this study but Junqing et al. (2008) used virgin plastics. For pre-exponential factor (A), the same trend as activation energy was found. Pre-exponential factor (A) of HDPE (1.48×10^{31}) was greater than LDPE (2.17×10^{22}), PP (4.95×10^{19}) and rice husk (1.35×10^{14} and 1.09×10^{18}), respectively. Furthermore, the trend was different to that of Junqing et al. (2008), this may come from the difference of raw materials.

Table 1 Kinetic parameters for pyrolysis of rice husk and waste plastics (HDPE, LDPE and PP)

Sample	**This study**		**R^2**	**Junqing *et al.*, (2008)**	
	E (kJ/mol)	**A (min^{-1})**		**E (kJ/mol)**	**A (min^{-1})**
HDPE	455.1	1.48×10^{31}	0.9965	457.2	3.50×10^{30}
LDPE	323.3	2.17×10^{22}	0.9907	300.4	2.20×10^{20}
PP	279.0	4.95×10^{19}	0.9934	319.7	5.90×10^{21}
Rice husk	155.1	1.35×10^{14}	0.9864	-	-
	217.2	1.09×10^{18}	0.9771	-	-

In case of rice husk/plastic mixtures, kinetic parameters are shown in Table 2. It was found that activation energy and pre-exponential factor of co-pyrolysis reaction decreased in the range of plastics decomposition reaction as show in Tables 3 and 4. These results may be caused by the interaction between rice husk and waste plastics during decomposition reaction.

Table 2 Kinetic parameters for pyrolysis of rice husk, waste plastics mixture (WPL) and their blends.

Sample	E (kJ/mol)	A (min^{-1})	R^2
RH/HDPE	187.6	1.57×10^{17}	0.9926
	216.3	1.26×10^{18}	0.9849
	258.2	6.12×10^{17}	0.9957
RH/LDPE	159.4	2.50×10^{14}	0.9907
	194.8	1.37×10^{16}	0.9749
	317.3	7.18×10^{21}	0.9947
RH/PP	141.1	4.08×10^{12}	0.9932
	245.0	2.10×10^{20}	0.9743
	254.7	6.69×10^{17}	0.9924
WPL	327.8	6.47×10^{22}	0.9966
30/70	121.5	8.25×10^{10}	0.9989
	209.1	2.22×10^{17}	0.9706
	273.0	7.74×10^{18}	0.9956
50/50	133.7	9.17×10^{11}	0.9942
	229.8	9.37×10^{18}	0.9572
	221.2	2.11×10^{15}	0.9901
70/30	132.9	7.74×10^{11}	0.9946
	231.5	1.56×10^{19}	0.9697
	244.7	9.07×10^{16}	0.9937

Table 3 Comparison of kinetic parameters in plastic decomposition range for pyrolysis of rice husk, waste plastics (HDPE, LDPE and PP) and their blends

Sample	E (kJ/mol)	A (min^{-1})
HDPE	455.08	1.48×10^{31}
RH/HDPE	258.22	6.12×10^{17}
LDPE	323.32	2.17×10^{22}
RH/LDPE	317.27	7.18×10^{21}
PP	279.03	4.95×10^{19}
RH/PP	254.67	6.69×10^{17}

Table 4 Comparison of kinetic parameters in WPL decomposition range for pyrolysis of rice husk and WPL blends

Sample	E (kJ/mol)	A (min^{-1})
WPL	327.82	6.47×10^{22}
30/70	273.02	7.74×10^{18}
50/50	221.21	2.11×10^{15}
70/30	244.66	9.07×10^{16}

3. Synergistic effect analysis of rice husk and waste plastics mixtures by thermogravimetric analyzer (TGA)

To investigate the synergistic effect between the biomass and plastic samples, the difference of weight loss (ΔW), $\Delta W=W_{blend}-(x_1W_1+x_2W_2)$ was defined, where W_{blend} is the weight loss of blend, x_i is the weight fraction of each material in the blend and W_i is the weight loss of each material in the same operational conditions. Obviously, ΔW describes the ‘extent’ of synergistic effect during co-pyrolysis (Zhou, 2006).

From thermogravimetric analysis of co-pyrolysis study, the result has shown that the mixture of RH/HDPE has negative values of ΔW at 100-456°C and has a great difference of positive weight loss (ΔW) about 14% at temperature approximately 485°C and no difference of weight loss at temperature above 500°C as shown in Figure 43. The mixture of RH/PP has negative value of ΔW at the temperature range 100-500°C but positive ΔW (about 2% of weight loss) at 500°C and above. For the mixture of RH/LDPE, the difference of weight loss of the mixture is negative at the temperature range 100-700°C. This can be explained that all plastics first softened and melted at about 100°C (decompose temperature was 425-500°C) and were in a molten state that inhibited the diffusion of the volatile matter of rice husk. Therefore, the negative values of weight loss (-ΔW) were observed. When temperature increased up to 450-480°C, PP started to decompose. The reaction between radicals of rice husk and PP occurred and formed more non-volatile molecules than those from the individuals at this temperature, so ΔW in this range was also negative. Above 500°C, non-volatile molecules can decompose and vaporize and more rice husk reacted with radicals from PP and formed volatile molecules, so ΔW was positive above 500°C. For RH/HDPE, ΔW was first negative and then positive when HDPE decomposed (about 465°C) and the highest positive ΔW was founded at 485°C. HDPE decomposed and provided hydrogen radical which can transfer to rice husk radical and formed volatile molecules. For RH/LDPE, ΔW was first negative and when LDPE decomposed (about 445°C), ΔW was still negative until the end of reaction (700°C). This indicated that the reaction of rice husk and LDPE radicals formed non-volatile molecules which cannot decompose under 700°C. This can be explained by the reactions of LDPE and rice husk. Cracking of LDPE provided branch radicals. When these radicals reacted with rice husk, the more bulky molecules which were non-volatile were formed.

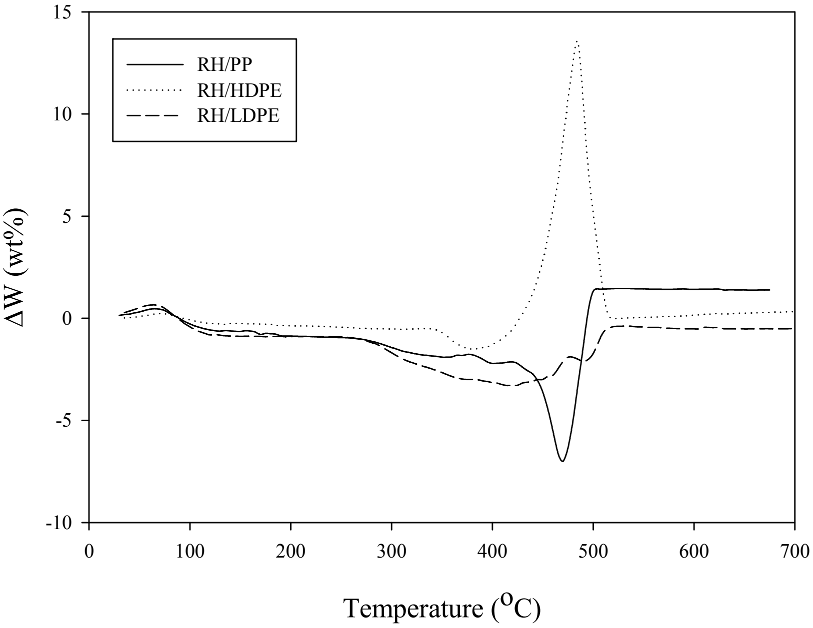

Figure 43 Variations of ΔW with temperature for the mixture of each waste plastic types and rice husk.

In case of waste plastics mixture (WPL), a great difference of weight loss was found about 23% at temperature 485°C and no different weight loss at the temperature above 500°C as shown in Figure 44. It was shown that there was interaction between each type of plastics in pyrolysis process. Three mixtures of rice husk and WPL showed the highest different weight loss at the same temperature (485°C). At 485°C, the highest different weight loss was found in 30/70 mixture (10.97%). For 50/50 and 70/30 mixtures, different weight losses were 9.18% and 7.15%, respectively. These results showed that there were interaction between rice husk and waste plastics in pyrolysis process at this temperature or it might be the interaction of each type of waste plastics. To further investigate this synergistic effect and interaction, co-pyrolysis process in a semi-batch reactor were performed.

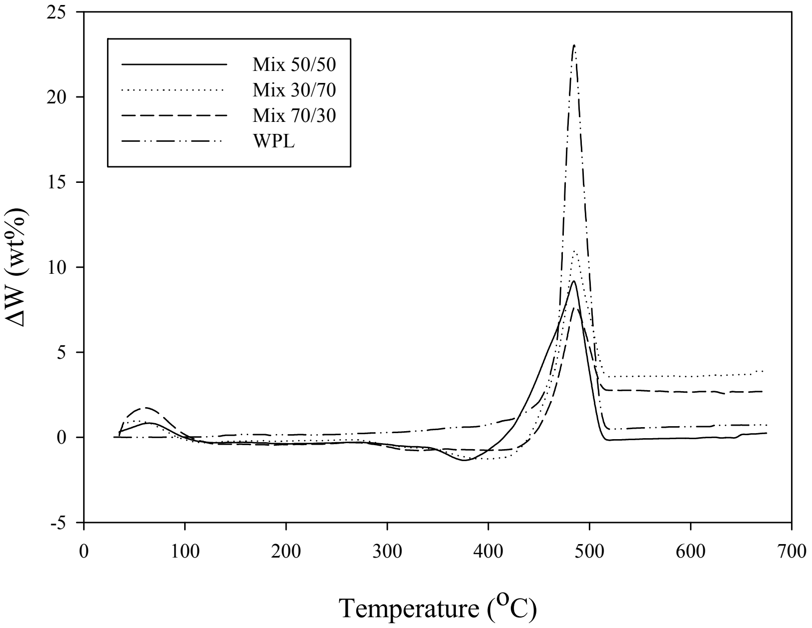

Figure 44 Variations of ΔW with temperature for rice husk and WPL mixtures.

4. Analysis and characterization of product obtained from rice husk and waste plastics mixture co-pyrolysis in a semi-batch reactor and synergistic effect.

The pyrolysis and co-pyrolysis processes of rice husk, waste plastics mixture and their blends were performed in a semi-batch reactor. The main product of waste plastics pyrolysis was wax (76.77 wt%) as shown in Figure 45. For rice husk pyrolysis, the main product was liquid (30.75 wt%). The content of wax in received product decreased when the amount of waste plastic mixture decreased. In contrast, liquid product increased. The solid residue of rice husk pyrolysis (40.55 wt%) was greater than those of waste plastics mixture and their blends. No wax was found in rice husk pyrolysis product.

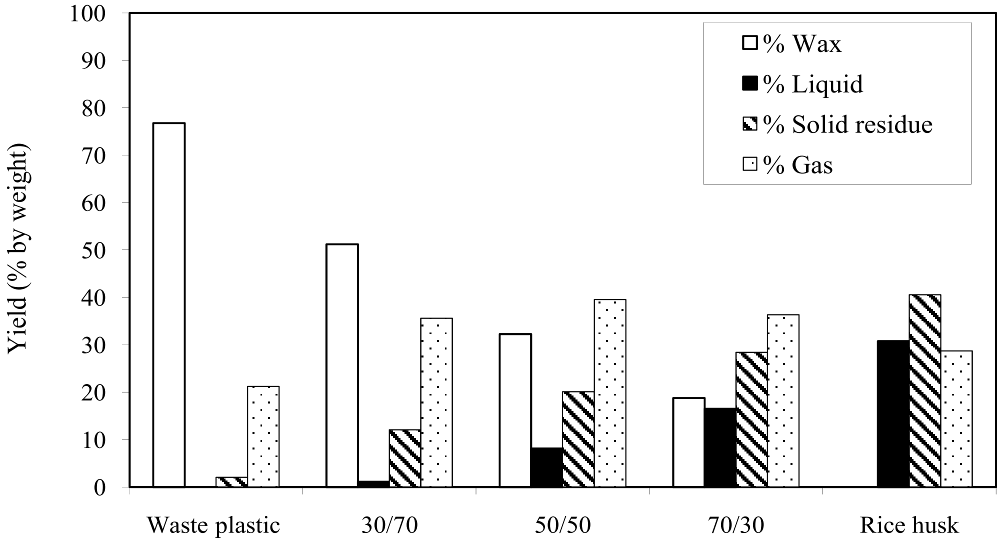

Figure 45 Yields of co-pyrolysis products of rice husk and waste plastics mixture.

Products obtained from pyrolysis and co-pyrolysis was calculated to determine the synergistic effect and the results are shown in Figure 46. It was found that the mixture of 30/70 (rice husk/WPL) showed the highest positive synergistic effect on conversion. It was about 1.49%, while 1.21% and 0.60% were observed in the mixtures of 50/50 and 70/30, respectively. These results showed that there were interaction between rice husk and waste plastics mixture co-pyrolysis which lead to higher decomposition of rice husk and waste plastics mixture than the individual one.

For wax and liquid product, the negative synergistic effects were found for all mixtures. The mixture of 30/70 showed lowest synergistic effect of production. it was about -2.55%, while -6.10% and -4.28% were found in the mixture of 50/50 and 70/30, respectively. In case of liquid product, the mixture of 30/70 was more negative (-8.07%) than 50/50 (-7.24%) and 70/30 (-5.01%), respectively. The results showed that co-pyrolysis of rice husk and waste plastics mixture reduced the production of wax and liquid product but increased the conversion.

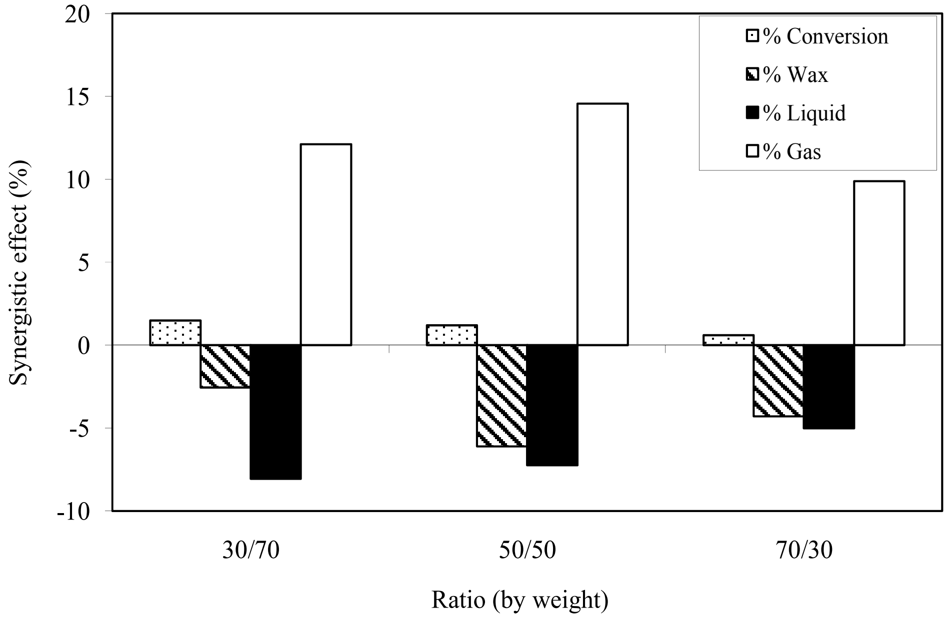

Figure 46 Synergistic effect of conversion and co-pyrolysis products of rice husk and waste plastics mixture at each ratio of rice husk/WPL.

From the above result, co-pyrolysis of 30/70 mixture was chosen to study catalytic reaction due to the highest synergistic effect on conversion and the most negative synergistic effect on wax production. A zeolite, H-ZSM-5, is widely used as a cracking catalyst in petroleum industry (Marcilla, 2003; Wang, 2004; Corma, 2007; Danuthai, 2009). The catalyst used in this study was H-ZSM-5 due to the catalytic cracking activity of the catalyst. The analysis of products obtained from catalytic co-pyrolysis is shown in Figure 47.

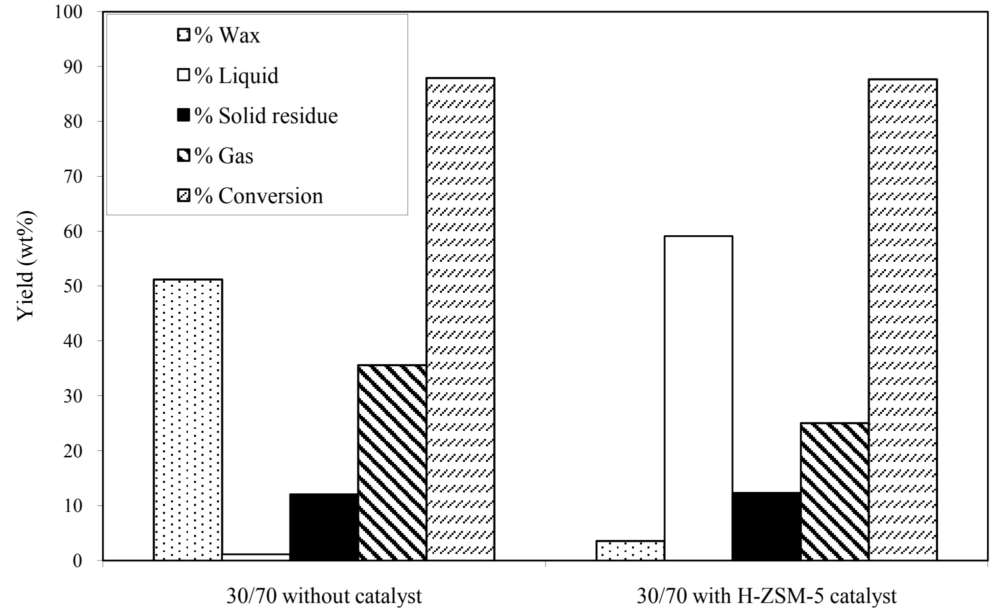

Figure 47 Yields of co-pyrolysis products of rice husk and waste plastics mixture at the ratio of 30/70 (by wt%) with and without H-ZSM-5 catalyst.

The result shows that, when H-ZSM-5 was used, wax was reduced by converting to liquid product. Liquid product consists of organic and aqueous phases. The organic phase was distilled and characterized. Gas product of catalytic co-pyrolysis slightly decreased from 35.58% in non-catalytic co-pyrolysis to 25.01%. Solid residue and conversion of catalytic co-pyrolysis and non-catalytic co-pyrolysis were about the same (12% for residue and 87% for conversion).

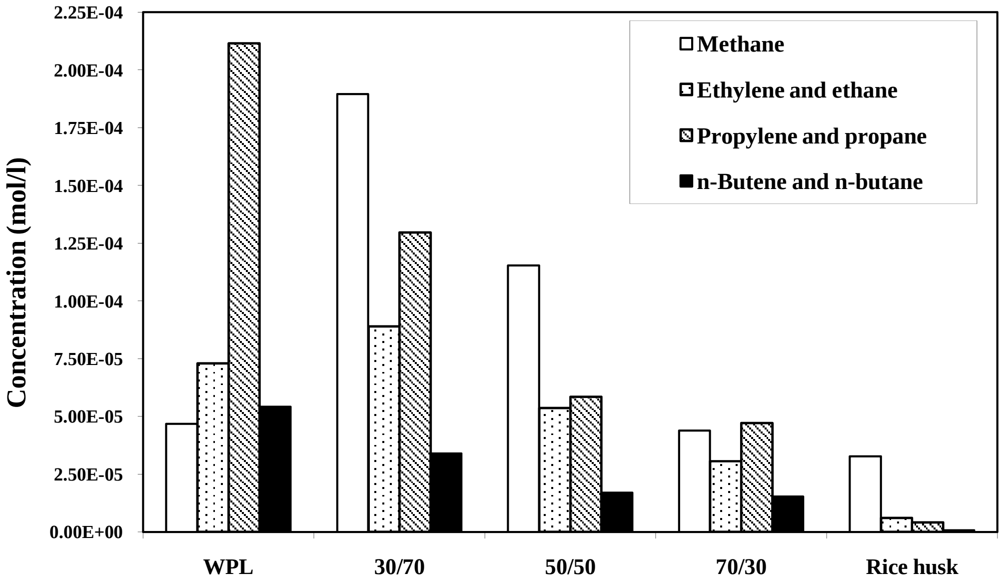

Figure 48 Concentration of hydrocarbon species in gaseous product from co-pyrolysis products of rice husk, waste plastics mixture and their blends.

Gaseous products were characterized by gas chromatograph. The result showed that gaseous product from waste plastics mixture pyrolysis had greatest amount of propylene + propane and n-butene + n-butane, 2.12×10^{-4} and 5.42×10^{-5} mole/l, respectively. The concentration of propylene + propane and n-butene + n-butane decreased when waste plastics were mixed with rice husk. The highest concentrations of methane and ethylene + ethane gas found in 30/70 mixture were around 1.90×10^{-4} and 8.94×10^{-5} mole/l, respectively. Pyrolysis gas of rice husk showed the lowest concentration of hydrocarbon gas due to the nature of raw material. Rice husk mainly consists of carbon, hydrogen and oxygen while plastics mainly consist of hydrogen and carbon. From this reason, pyrolysis gas of waste plastic mixture and their blends showed higher concentration of hydrocarbon gas than pyrolysis gas of rice husk.

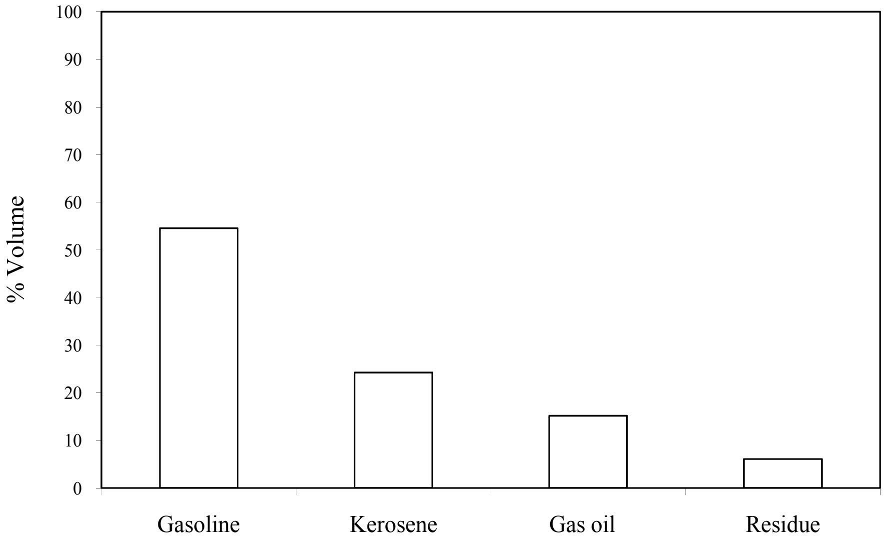

Figure 49 The yield of distillation product from co-pyrolysis product of rice husk and waste plastics mixture at ratio 30:70 with H-ZSM-5 catalyst.

The organic phase of liquid products from co-pyrolysis of rice husk and waste plastics mixture at ratio 30:70 (by wt%) with H-ZSM-5 catalyst was separated and distilled. Liquid product contains 54.54% (by volume) of gasoline (IBP-200^{o}C), 24.24% kerosene (201-250^{o}C), 15.15% diesel (251-370^{o}C) and residue 16.06% (>370^{o}C).

Furthermore, wax-like liquid which was produced from co-pyrolysis process was measured the heating value by bomb calorimeter. The results are shown in Figure 50. The wax product of waste plastics mixture showed the highest heating value of 46.66 MJ/kg. In case of non-catalytic co-pyrolysis, wax-like product of 30/70 mixture showed higher heating value (44.74MJ/kg) than 50/50 (43.15MJ/kg) and 70/30 (40.28MJ/kg), respectively. When H-ZSM-5 catalyst was used in 30/70 mixture co-pyrolysis, wax-like product was converted into liquid product and its heating value increased from 44.74 to 46.31 MJ/kg. Due to the cracking activity of H-ZSM-5 catalyst, almost all wax-like product converted into liquid product. This liquid product is preferred to be used as a fuel.

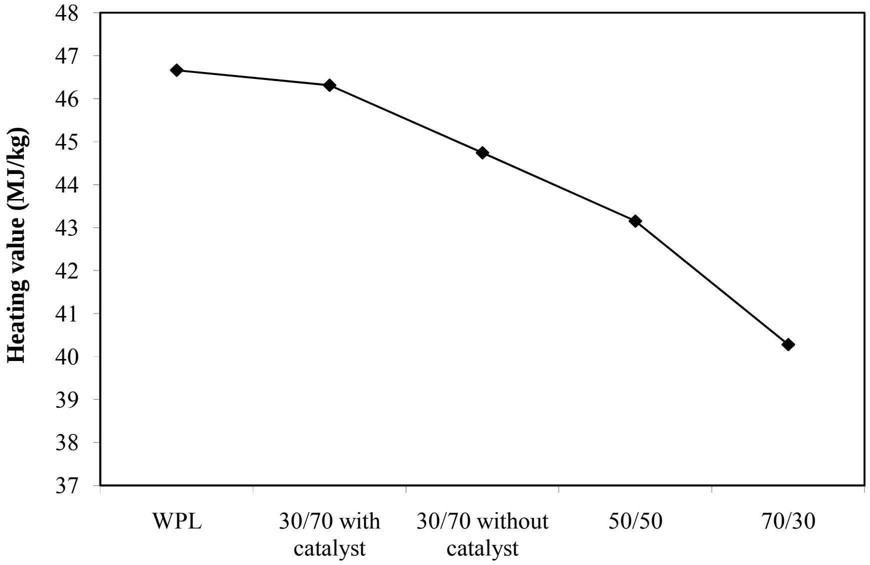

Figure 50 The heating values of wax-like and liquid products from co-pyrolysis of rice husk and waste plastics mixture at different ratios.

Table 5 Heating values of rice husk and bio-oil from rice husk

	Heating value (MJ/kg)	
Sample	**this study**	**Tsai et al. (2007)**
Rice husk	17.62	16.79
Bio-oil from rice husk	4.26	7.11

The heating values of rice husk and bio-oil from rice husk are shown in Table 5. Heating values of rice husk and bio-oil from rice husk in this study are slightly difference from those of Tsai et al. (2007). The heating value of bio-oil from rice husk was very low when compared with wax-like liquid product from plastics pyrolysis. The oxygen content in rice husk leads to the formation of oxygenated compound in bio-oil. The heating value of oxygenated compound was low, so the very low heating value of bio-oil from rice husk was obtained.

CONCLUSIONS

Co-pyrolysis behaviors of rice husk, waste plastics and their blend were studied. Pyrolysis processes were performed in a thermogravimetric analyzer (TGA) to investigate the decomposition behavior. The data obtained from TGA describe the decomposition behavior of materials, synergistic effect and also was used to determine the kinetic parameters (activation energy and pre-exponential factor) by assumption of first order reaction. Furthermore, the results from TGA were compared with experiments of co-pyrolysis in a semi-batch reactor.

For thermogravimetric analysis, rice husk decomposed at lower temperature than all types of plastic (270-380^{o}C), and weight loss was around 55wt%. Beyond 400^{o}C, a slow rate of weight loss occurred until 700^{o}C, the residue was around 40%. PP decomposed easier than LDPE and HDPE, respectively. HDPE, LDPE and PP decomposed at 465-510^{o}C, 445-505^{o}C and 425-490^{o}C, respectively. These three types of plastics almost completely decomposed (residue <1%). Three types of rice husk and waste plastic blends with weight ratio 1/1 (RH/HDPE, RH/LDPE and RH/PP) showed the same profile in rice husk decomposition range (270-380^{o}C) but differed in plastic decomposition range. This range in RH/PP blend was 450-500^{o}C. RH/HDPE and RH/LDPE decomposed at nearly the same temperature range (480-500^{o}C). All the three mixtures had residues around 15%. For the mixture of waste plastics (WPL), rapidly decomposition at the temperature range of 440-500^{o}C was founded and residue was 1.303%. Decomposition profile of the mixtures of rice husk and WPL consists of rice husk and WPL decomposition profiles at 270-380^{o}C and 440-500^{o}C, respectively.

Kinetic parameters (E and A) were calculated from the plot of $\ln(-\ln(1-x)/T^2)$ versus 1/T. the result showed that activation energy of HDPE (455.1 kJ/mol) was greater than those of LDPE (323.3 kJ/mol), PP (279.0 kJ/mol) and rice husk (155.1 and 217.2 kJ/mol). For pre-exponential factor (A), the similar trend as activation energy was found. Pre-exponential factor (A) of HDPE (1.48×10^{31}) was greater than those of LDPE (2.17×10^{22}), PP (4.95×10^{19}) and rice husk (1.35×10^{14} and 1.09×10^{18}). The activation energy of plastic decomposition reaction reduced when they were mixed with rice husk. In Decomposition reaction of plastics mixture, the activation energy was in range of 221.2-317.3 kJ/mol while pre-exponentail factor (A) was in range of 2.11×10^{15}-7.18×10^{21} min^{-1}.

For synergistic effect investigation, RH/HDPE had synergy at 485°C of 14% while RH/PP had synergy of 2% at above 500°C but no synergy in RH/LDPE blend was observed at any temperature. WPL and their blends with rice husk at different ratios of 30/70, 50/50 and 70/30 had synergy at 485°C about 23%, 10.97%, 9.18% and 7.15%, respectively. All of these mixtures were pyrolyzed in a semi-batch reactor.

The mixture of 30/70 showed the highest synergy in conversion (1.46%) when pyrolyzed in a semi-batch reactor (1.49%), while 1.21% and 0.60% were observed in the mixtures of 50/50 and 70/30, respectively. Main product of all mixtures was wax. So, the mixture of 30/70 was chosen to be pyrolyzed with catalyst due to the highest synergy in conversion. Catalyst used was H-ZSM-5. After catalytic co-pyrolysis process was performed, all wax was almost converted into liquid product which had heating value greater than the wax product (46.31 MJ/kg > 44.74 MJ/kg). Furthermore, Liquid product was distilled to four fractions, gasoline, kerosene, diesel and residue. It was found that fractions obtained were gasoline 54.54% (by volume), kerosene 24.24%, diesel 15.15% and residue 16.06%.

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APPENDICES

Appendix A

The experimental results of co-pyrolysis products

Appendix Table A1 The product yield received from rice husk, waste plastics mixture pyrolysis and co-pyrolysis of their blends

Sample	**RH (g)**	**Waste plastics (g)**			**Total (g)**	**Products (g)**		
		HDPE (50%)	LDPE (30%)	PP (20%)		**Wax**	**Liquid**	**Solid residue**
WPL	0	25	15.04	10.02	50.06	38.43	0	1.01
30/70	15.05	17.62	10.45	7.11	50.23	25.71	0.58	6.07
50/50	25.02	12.49	7.5	5.05	50.06	16.16	4.07	10.05
70/30	35.77	7.35	4.46	3.35	50.93	9.55	8.41	14.46
Rice husk	60.07	0	0	0	60.07	0	18.47	24.36

Appendix Table A2 Percentage of product yield received from rice husk, waste plastics mixture pyrolysis and co-pyrolysis of their blends

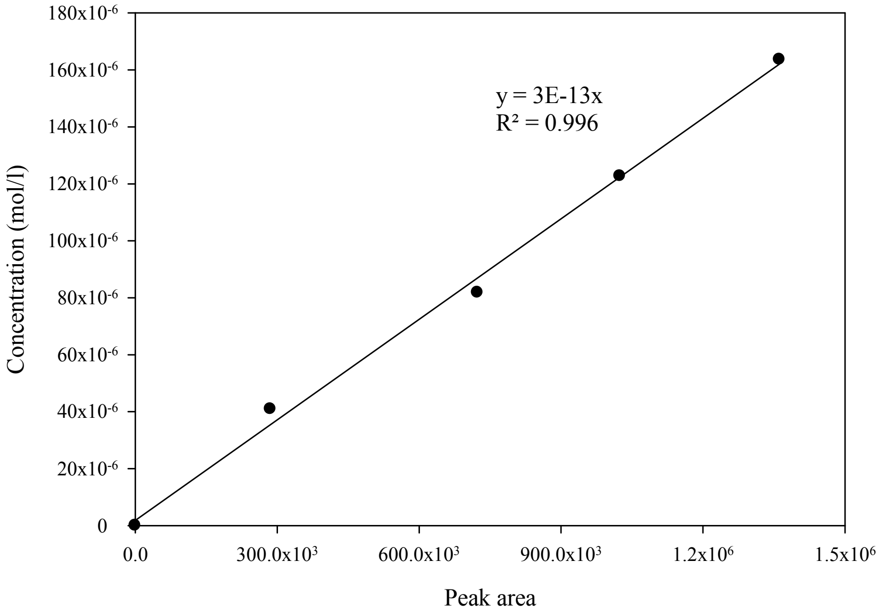
	Products (%wt)				
Sample	**Wax**	**Liquid**	**Solid residue**	**Gas**	**% Conversion**
WPL	76.77	0.00	2.02	21.21	97.98
30/70	51.18	1.15	12.08	35.58	87.92
50/50	32.28	8.13	20.08	39.51	79.92
70/30	18.75	16.51	28.39	36.34	71.61
Rice husk	0.00	30.75	40.55	28.70	59.45

Appendix Table A3 Percentage of synergistic effect of product yield received from rice husk and waste plastics mixture co-pyrolysis

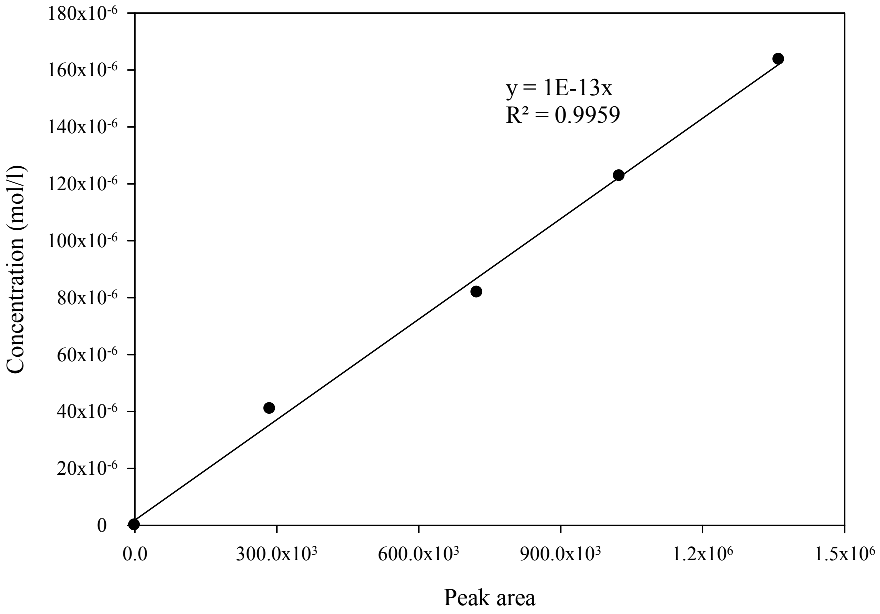
	Synergistic effect (%)			
Sample	**Conversion**	**Wax**	**Liquid**	**Gas**
30/70	1.49	-2.55	-8.07	12.12
50/50	1.21	-6.10	-7.24	14.56
70/30	0.60	-4.28	-5.01	9.89

Appendix B

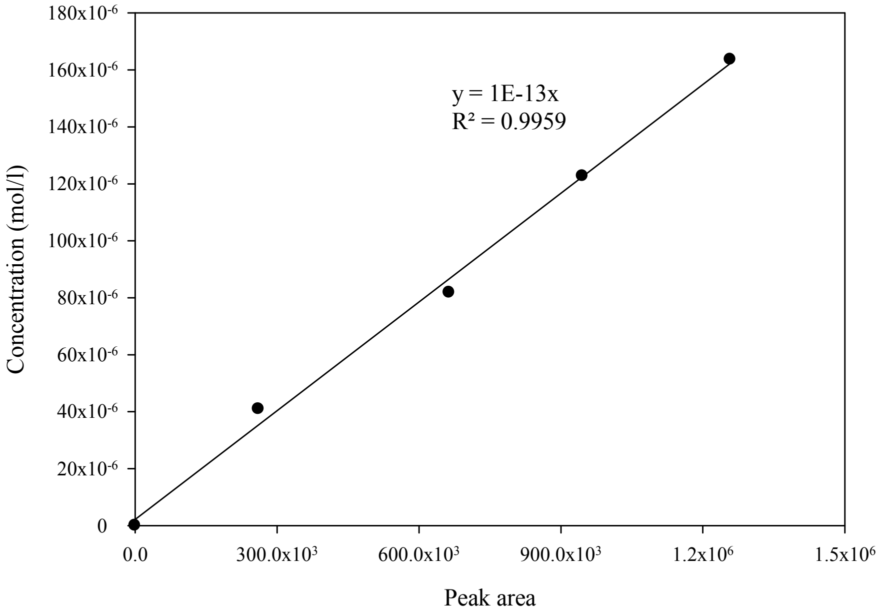
Characterization of gaseous product



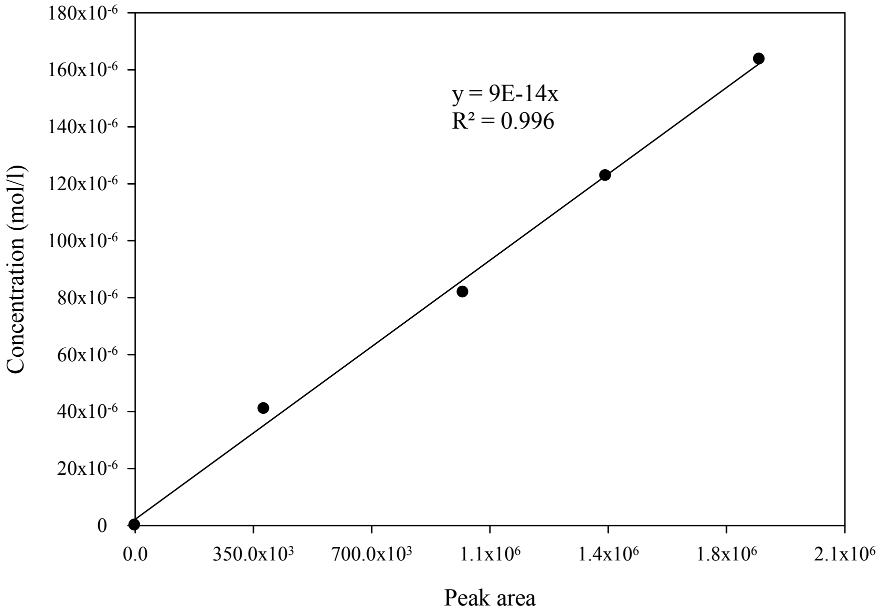
Appendix Figure B1 Standard curve of methane



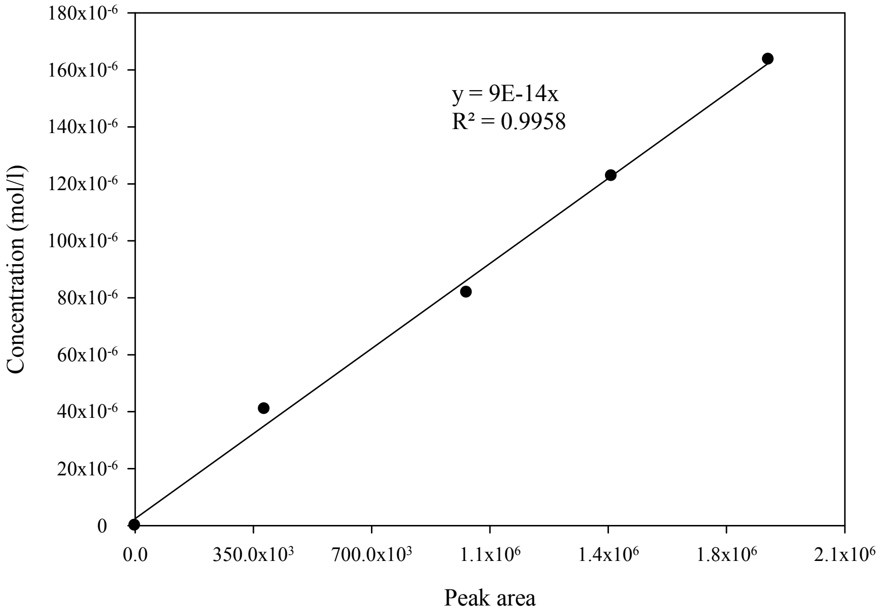
Appendix Figure B2 Standard curve of ethylene



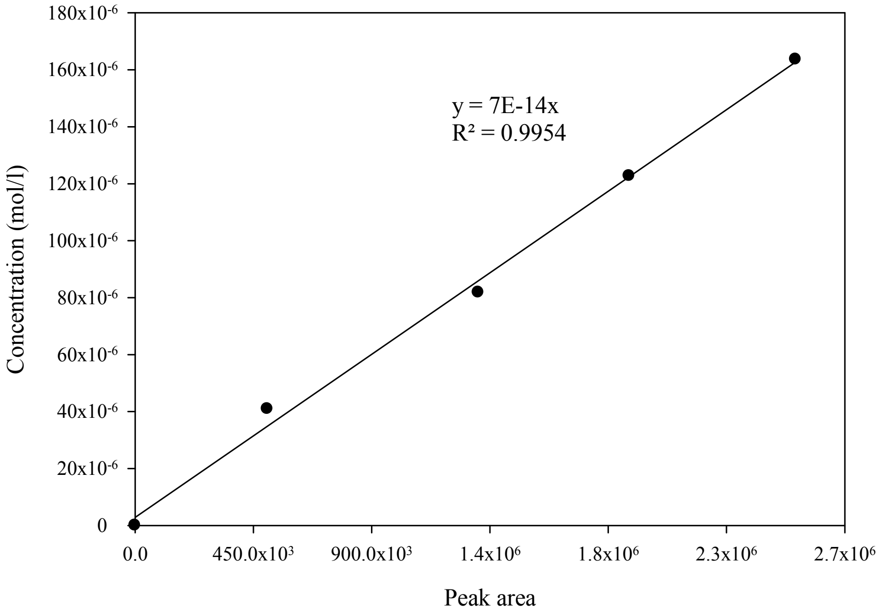
Appendix Figure B3 Standard curve of ethane



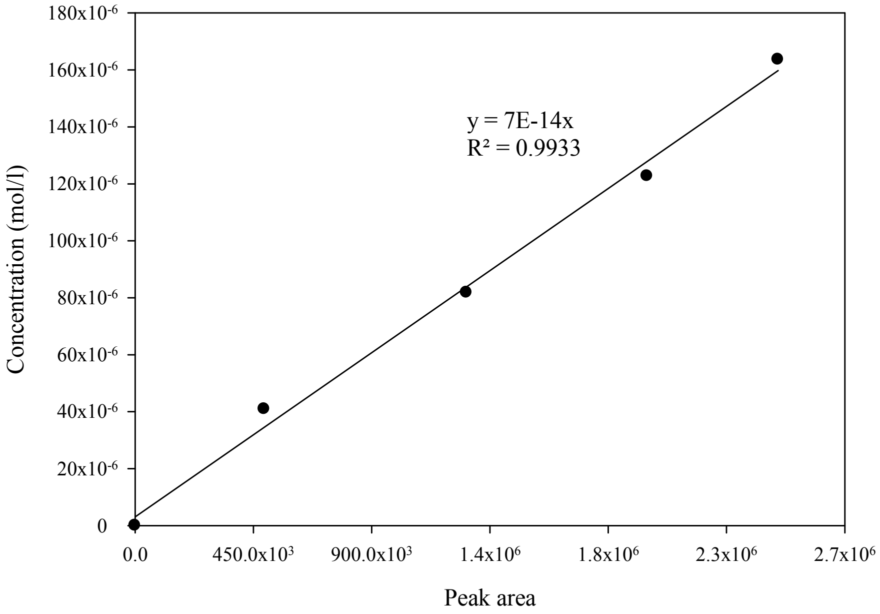
Appendix Figure B4 Standard curve of propylene



Appendix Figure B5 Standard curve of propane



Appendix Figure B6 Standard curve of n-butene



Appendix Figure B7 Standard curve of n-butane

Appendix Table B1 Peak area and concentration of methane, ethylene, ethane, propylene, propane, n-butene and n-butane in pyrolysis gas of waste plastics mixture, rice husk and their blends.

		Sample (rice husk/WPL ratio)				
		WPL	**30/70**	**50/50**	**70/30**	**rice husk**
Methane	Area	155942	631899	384603	146126	109072
	Concentration (mole/l)	4.68×10^{-5}	1.90×10^{-4}	1.15×10^{-4}	4.38×10^{-5}	3.27×10^{-5}
Ethylene	Area	281535	297957	205578	120918	28088
	Concentration (mole/l)	2.82×10^{-5}	2.98×10^{-5}	2.06×10^{-5}	1.21×10^{-5}	2.81×10^{-6}
Ethane	Area	447873	592130	330533	184550	32159
	Concentration (mole/l)	4.48×10^{-5}	5.92×10^{-5}	3.31×10^{-5}	1.85×10^{-5}	3.22×10^{-6}
Propylene	Area	1569125	898903	398930	297867	28721
	Concentration (mole/l)	1.41×10^{-4}	8.09×10^{-5}	3.59×10^{-5}	2.68×10^{-5}	2.58×10^{-6}
Propane	Area	780983	541927	250579	225937	17196
	Concentration (mole/l)	7.03×10^{-5}	4.88×10^{-5}	2.26×10^{-5}	2.03×10^{-5}	1.55×10^{-6}
n-Butene	Area	18304	26800	12779	7793	2260
	Concentration (mole/l)	1.28×10^{-6}	1.88×10^{-6}	8.95×10^{-7}	5.46×10^{-7}	1.58×10^{-7}
n-Butane	Area	756346	459571	230932	211437	9234
	Concentration (mole/l)	5.29×10^{-5}	3.22×10^{-5}	1.62×10^{-5}	1.48×10^{-5}	6.46×10^{-7}

Appendix C

Heating values of wax and liquid products

Appendix Table C1 Heating values of wax and liquid products obtained from co-pyrolysis process by bomb calorimeter

Sample	Heating value (cal/g)	Heating value (MJ/kg)
WPL	11152.9	(11152.9x4.184)/1000 = 46.66
30/70	10693.3	(10693.3x4.184)/1000 = 44.74
50/50	10312.6	43.15
70/30	9626.19	40.28
Rice husk	4211.64	17.62
Bio-oil from rice husk	1018.15	4.26
30/70 with H-ZSM-5 catalyst	11068.3	46.31

Appendix D

Example of kinetic parameters calculation

Example of kinetic parameters calculation of RH/HDPE mixture co-pyrolysis

Conversion (x) or weight loss fraction can be calculated by

$$x = \frac{W_0 - W_t}{W_0 - W_f} \tag{3}$$

Where x is conversion, W_0 is the original mass of the test sample, W_t is the mass at time t or T and W_f is final mass at the end of pyrolysis.

Conversion (x) was substituted in equation 4 to determine kinetic parameter (activation energy, E, and pre-exponential factor, A).

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HE}(1-\frac{2RT}{E})\right] - \frac{E}{RT} \tag{4}$$

Where x is conversion, T is temperature (K), A is pre-exponential factor (min^{-1}), E is activation energy (J/mol), H is heating rate (K/min) and R is gas constant (8.314 J/mol·K).

One-step integral method

W_o = 99.99 % (at room temperature)
W_f = 17.18 % (at 700°C)

Conversion (x) at any temperature was calculated by

$$x = \frac{W_o - W_t}{W_o - W_f} = \frac{99.99 - W_t}{99.99 - 17.18}$$

Conversion (x) at T = 400°C (673 K), W_t = 73.53 %, was

$$x = \frac{99.99 - 73.53}{99.99 - 17.18} = 0.3195$$

$$\ln[\frac{-\ln(1-x)}{T^2}] = \ln\left[\frac{-\ln(1-0.3195)}{(673)^2}\right] = -13.9781$$

Multi-step integral method

For example, the reaction temperature range was 415-520°C.

W_o = 72.41 % (at 415°C)
W_f = 19.56 % (at 520°C)

Re-calculated conversion (x) at any temperature (T) was

$$x = \frac{72.41 - W_t}{72.41 - 19.56}$$

Conversion (x) at T = 450°C (723 K), W_t = 66.87 %, was

$$x = \frac{72.41 - 66.87}{72.41 - 19.56} = 0.1048$$

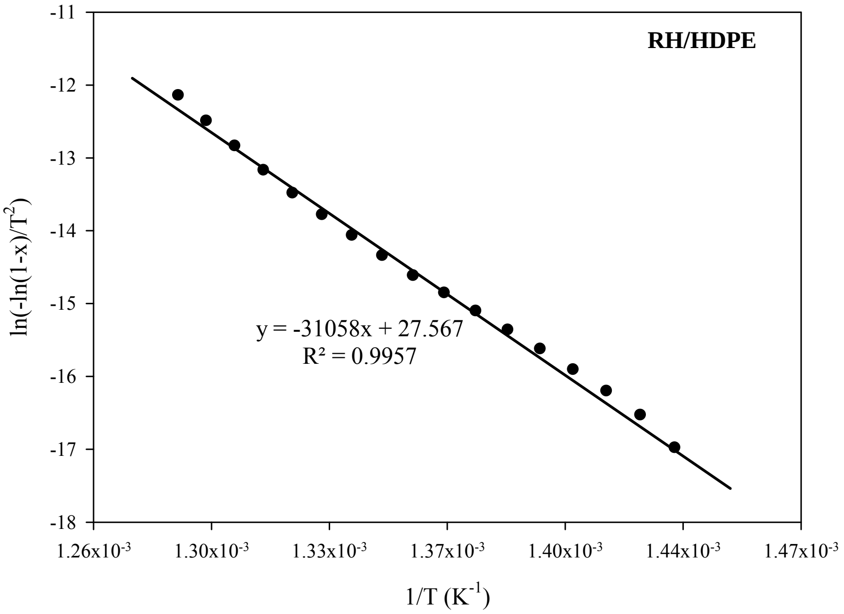
$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{-\ln(1-0.1048)}{(723)^2}\right] = -15.3674$$

Calculation data of conversion (x) and $\ln[-\ln(1-x)]/T^2$ and 1/T at each temperature are shown in Appendix Table D1. Conversions (x) were plot versus 1/T to determine kinetic parameters as shown in Appendix Figure D1.

Appendix Table D1 Calculation data of multi-step integral method in the temperature range 415-520°C.

T (°C)	T (K)	W_t (%)	1/T (K^{-1})	W_o (%)	W_f (%)	x	ln[-ln(1-x)/T^2]
415	688	72.41	0.001453	72.41	19.56	0	-*
420	693	71.94	0.001443	72.41	19.56	0.008893	-17.8001
425	698	71.34	0.001433	72.41	19.56	0.020246	-16.9860
430	703	70.72	0.001422	72.41	19.56	0.031977	-16.5372
435	708	70.04	0.001412	72.41	19.56	0.044844	-16.2066
440	713	69.21	0.001403	72.41	19.56	0.060549	-15.9122
445	718	68.15	0.001393	72.41	19.56	0.080605	-15.6294
450	723	66.87	0.001383	72.41	19.56	0.104825	-15.3674
455	728	65.26	0.001374	72.41	19.56	0.135289	-15.1091
460	733	63.3	0.001364	72.41	19.56	0.172375	-14.8593
465	738	61.01	0.001355	72.41	19.56	0.215705	-14.6227
470	743	57.77	0.001346	72.41	19.56	0.277010	-14.3473
475	748	53.83	0.001337	72.41	19.56	0.351561	-14.0714
480	753	49.06	0.001328	72.41	19.56	0.441816	-13.7876
485	758	43.42	0.001319	72.41	19.56	0.548534	-13.4905
490	763	37.08	0.001311	72.41	19.56	0.668496	-13.1755
495	768	30.67	0.001302	72.41	19.56	0.789782	-12.8431
500	773	25.24	0.001294	72.41	19.56	0.892526	-12.4983
505	778	21.71	0.001285	72.41	19.56	0.959319	-12.1497
510	783	20.15	0.001277	72.41	19.56	0.988836	-11.8233
515	788	19.71	0.001269	72.41	19.56	0.997162	-11.5701
520	793	19.56	0.001261	72.41	19.56	1	-*

* Undefined



Appendix Figure D1 Plot of ln(-ln(1-x)/T^2) vs 1/T of rice husk and HDPE at the ratio of 1:1 (by weight) pyrolysis calculated by multi-step integral method in the temperature range 415-520°C.

Activation energy was calculated from slope as following;

$$\text{slope} = -\frac{E}{R} = -31058$$

$$E = 31058 \times 8.314 = 258{,}216 \text{ J/mol} = 258.2 \text{ kJ/mol}$$

Pre-exponential factor was calculated from y intercept as following;

$$\text{y intercept} = \ln\left[\frac{AR}{HE}(1-\frac{2RT}{E})\right] = 27.567$$

T in above equation was substituted by T at $W_t = (W_o+W_f)/2$

$$A = \frac{HE\exp(27.567)}{R\left(1-\frac{2RT}{E}\right)} = \frac{(20)(258{,}216)\exp(27.567)}{8.314\left(1-\frac{2(8.314)(755.5)}{258{,}216}\right)} = 6.12 \times 10^{17} \text{ min}^{-1}$$

CIRRICULUM VITAE

NAME : Mr. Piriya Pinthong

BIRTH DATE : February 20, 1985

BIRTH PLACE : Bangkok, Thailand

EDUCATION :

YEAR	INSTITUTE	DEGREE/DIPLOMA
2006	Kasetsart Univ.	B.S. (Industrial Chemistry)

POSITION/TITLE : -

WORK PLACE : -

SCHOLARSHIP/AWARD : Assistantship from National Center of Excellence for Petroleum, Petrochemical and Advanced Materials (PPAM)