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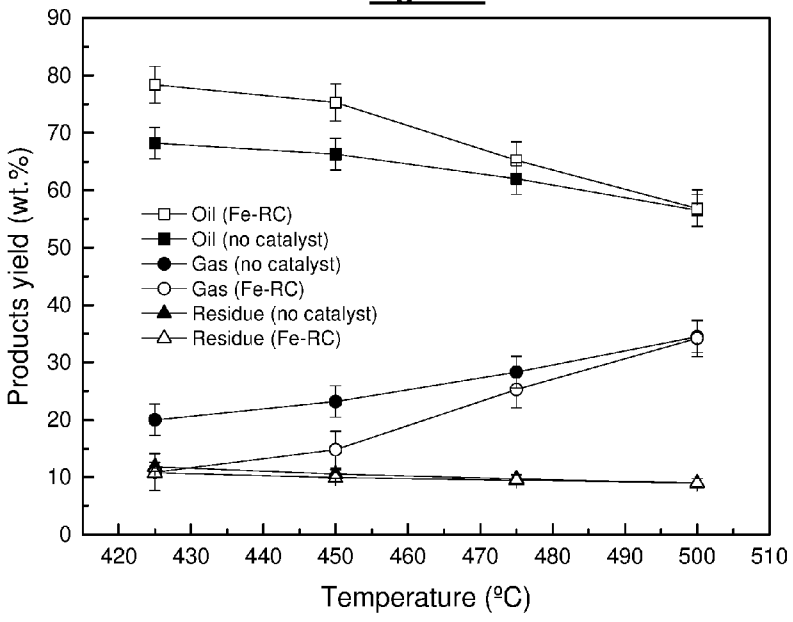
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[Continued on next page]

(54) Title: A PILLARED CLAY CATALYST

Figure 6



(57) Abstract: A pillared clay catalyst for catalytic pyrolysis is provided. The pillared clay catalyst comprises modified pillared clay, in which the pillared clay is modified by transition metal particles such as Ti, Zr, Fe, Co, Ni or Zn. A method of preparing the pillared clay catalyst and a catalytic pyrolysis method utilising the pillared clay catalyst are also provided.

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A pillared clay catalyst

Technical Field

The present invention relates to a pillared clay catalyst, particularly to a pillared clay catalyst for catalytic pyrolysis.

Background

Plastics are mainly made from non-renewable fossil fuels and their disposal poses a threat to the environment due to their non-biodegradable nature. Further, they occupy a large landfill space due to their low density. Therefore, recycling of plastic waste is important in alleviating the negative impacts associated with the disposal of plastics. While incineration is able to reduce the need for landfill space and recover energy from plastic waste, it operates at relatively high temperature and produces toxic gasses such as dioxin.

Pyrolysis is a promising plastic waste recycling method as it not only minimizes the need for landfill space, but also recovers great amount of energy in the form of liquid fuel and gaseous hydrocarbons with minimal negative impact to the environment. In pyrolysis without catalyst, plastic material is decomposed in random scissions, resulting in the formation of hydrocarbon products with wide range of carbon number, which cannot be readily used. The use of catalyst improves selectivity for desirable liquid fuel products in addition to reducing reaction time and temperature. A number of catalysts have been developed for pyrolysis of plastic materials. However, most of them are designed to treat a specific type of plastic material, which is mostly polyethylene (PE) or polypropylene (PP). Further, the catalysts fail to maintain high yield of valuable products especially when used for pyrolysis of mixed plastic feedstock that contain other plastic types such as polystyrene (PS) and polyethylene terephthalate (PET). Most catalysts developed to date are easily deactivated by polyethylene terephthalate (PET), which is a common constituent of mixed plastic waste. In order to achieve reliable activity, PET has to be removed from the mixed plastic waste stream prior to pyrolysis. This would incur additional steps as well as cost.

Diesel fuel is a type of liquid fuel used in compression-ignition engine, which is the type of engine ubiquitously employed in heavy duty vehicles, locomotives, ships and many other transport vehicles. Diesel has higher molecular weight as well as boiling point

than gasoline. Over the years, diesel fuel has gained popularity due to the high reliability and superior fuel efficiency of diesel engines as compared with that of gasoline engines. Driven by industrialization of fast-growing developing countries as well as increasing use of diesel in shipping (instead of heavy fuel oil), the demand for diesel is expected to grow in the future at a global level.

Most of the catalyst developments in catalytic pyrolysis are focused on the production of gasoline, instead of diesel, which has high demand in the market. There is therefore a need for an improved catalyst for use in pyrolysis of plastic.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved catalyst for catalytic pyrolysis, and a catalytic pyrolysis method using the improved catalyst.

In general terms, the invention relates to a pillared clay catalyst for catalytic pyrolysis, method to prepare the same and a catalytic method using the pillared clay catalyst. In particular, the pillared clay catalyst is for catalytic pyrolysis of plastic waste. The catalytic pyrolysis of the plastic waste using the pillared clay catalyst of the present invention converts the plastic waste into diesel fuel and enables an improved oil yield and higher selectivity for the diesel fraction. The catalyst comprises transition metal particles dispersed in its pillared clay structure, which results in improved catalytic performance in pyrolysis.

According to a first aspect, the present invention provides a pillared clay catalyst for catalytic pyrolysis comprising modified pillared clay, wherein the modified pillared clay comprises pillared clay modified by transition metal particles, the transition metal particles selected from the group consisting of: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Hs, Mt, Ds, Zn, Cd, Hg, Cn, Ti, Zr, Hf, Rf, and a combination thereof.

The pillared clay catalyst may have a liquid hydrocarbon yield of $\geq$60 weight % of a mass of plastic feedstock during pyrolysis of the plastic feedstock. In particular, the pillared clay catalyst may have a selectivity of C_{13}–C_{19} hydrocarbon of $\geq$30 weight % of the liquid hydrocarbon yield.

The pillared clay catalyst may be a macroporous catalyst. According to a particular aspect, the average pore diameter of the pillared clay catalyst may be ≥ 20 nm. According to another particular aspect, the average particle size of the pillared clay catalyst may be ≤600 µm. The pillared clay catalyst may have a Brunauer-Emmett-Teller (BET) surface area of about 100-400 m^2/g.

The pillared clay catalyst may comprise a suitable amount of transition metal particles. According to a particular aspect, the transition metal particles may constitute 10-35 weight % of the total weight of the pillared clay catalyst.

The transition metal particles may be present in any suitable form. According to a particular aspect, the transition metal particles are in the form of oxides or silicates.

The pillared clay catalyst may comprise a suitable type of clay for the purposes of the present invention. For example, the starting raw material for the modified pillared clay may comprise at least one clay selected from, but not limited to, the smectites or kaolin group of clay. In particular, the clay may be a smectite, such as but not limited to bentonite, saponite, montmorillonite, beidellite, nontronite, hectorite or sauconite. In particular, the clay may be a kaolin group of clay such as but not limited to kaolinite, halloysite, dickite, or nacrite.

The pillared clay catalyst may also comprise alumina and silica. According to a particular aspect, the molar ratio of silica to alumina may be from 4:1 to 50:1. In particular, the pillared clay catalyst may comprise about 2-26 weight % alumina of total weight of the pillared clay catalyst and about 45-87 weight % silica of total weight of the pillared clay catalyst.

According to a second aspect, there is provided a method of preparing the pillared clay catalyst of the first aspect. The method comprises:

- mixing clay material with deionized water to form a clay colloid;
- mixing transition metal particles selected from the group consisting of: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Hs, Mt, Ds, Zn, Cd, Hg, Cn, Ti, Zr, Hf, Rf, and a combination thereof, with an alkaline solution to obtain a transition metal solution with a pH of 1-4.5;
- adding the transition metal solution drop-wise to the clay colloid to obtain a modified clay colloid;

- ageing, washing and drying the modified clay colloid to obtain a pillared clay precursor;
- calcinating the pillared clay precursor to obtain the pillared clay catalyst; and
- optionally shaping the pillared clay catalyst to a particular shape or form.

Each of the steps of the method may be performed under suitable conditions. According to a particular aspect, the adding may be performed over a period of 1-20 hours. The adding may be performed at a temperature of about 15-95°C. Further, the calcinating may be at a temperature of about 300-600°C.

According to a third aspect, there is provided a catalytic pyrolysis method comprising: mixing clay material with deionized water to form a clay colloid;

- contacting the pillared clay catalyst according to the first aspect with a plastic feedstock; and
- catalytically pyrolysing the plastic feedstock into C_{13}–C_{19} hydrocarbon products.

The plastic feedstock may be any suitable feedstock. For example, the plastic feedstock may comprise a single type of plastic or a mixture of different types of plastic. In particular, the plastic feedstock comprises at least one of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC).

According to a particular aspect, the pillared clay catalyst and the plastic feedstock may be in a catalyst to feedstock (C/F) weight ratio of 0.01-0.5.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a general method of preparing a pillared clay catalyst according to the present invention;

Figure 2 shows the schematic representation of the experimental setup for catalytic pyrolysis of mixed plastics;

Figure 3 shows a schematic representation of a catalyst preparation system;

Figure 4 shows the XRD pattern of bentonite, Ti-pillared clay, Al-pillared clay, and Fe-pillared clay;

Figure 5 shows the carbon distribution of oil products derived from catalytic pyrolysis of mixed plastics using different catalysts;

Figure 6 shows a comparison of product yields derived from non-catalytic and catalytic pyrolysis at different temperatures (catalyst/feedstock ratio = 0.1 for catalytic pyrolysis); and

Figure 7 shows the oil yields derived from catalytic pyrolysis of mixed plastic waste with different amounts of Fe-pillared clay catalyst at different temperatures.

Detailed Description

The present invention provides an improved catalyst for catalytic pyrolysis. In particular, the improved catalyst is a pillared clay catalyst for use in the catalytic pyrolysis of plastic. In using the catalyst of the present invention, the pyrolysis of plastic material is improved in terms of oil yield and selectivity for diesel fraction in the product. Further, the catalyst of the present invention may be used on any suitable plastic material or a mix of plastic materials without requiring removal of any particular type of plastic before the pyrolysis process. Accordingly, the catalyst of the present invention is more versatile and enables operation costs to remain low.

According to a first aspect, there is provided a pillared clay catalyst for catalytic pyrolysis comprising modified pillared clay, wherein the modified pillared clay comprises pillared clay modified by transition metal particles. The transition metal particles may be of any suitable transition metals.

The pillared clay may be modified by the transition metal particles by any suitable method. In particular, the pillared clay may be modified by dispersing the transition metal particles in the pillared clay structure. For example, the pillared clay structure may be modified by way of intercalation. During intercalation, the transition metal particles may be included or inserted into the layered structure of the pillared clay.

The transition metal particles may comprise particles of a single transition metal or particles of different types of transition metals. The transition metal particles may be particles of an alloy of a transition metal and another metal. The another metal may be a transition metal or non-transition metal.

According to a particular aspect, the transition metal particles may be particles of transition metals from Group IIB, IVB or VIII of the Periodic Table. For example, the transition metal particles may be particles of transition metals selected from the group consisting of: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Hs, Mt, Ds, Zn, Cd, Hg, Cn, Ti, Zr, Hf, Rf, and a combination thereof. Even more in particular, the transition metal particles may be of Fe, Co, Ni, Zn, Ti or Zr. Even more in particular, the transition metal particles may be of Fe.

The transition metal particles comprised in the pillared clay may be in any suitable form. For example, the transition metal particles may be in the form of oxides or silicates of the transition metal. In particular, the transition metal particles may be in a form which would provide high thermal stability and strong Lewis acidity to the pillared clay catalyst.

The transition metal particles may be formed from any suitable form of the transition metal. For example, the transition metal particles may be formed from the chloride, nitrate or sulphate salts of the transition metal.

The pillared clay catalyst may comprise a suitable amount of the transition metal particles. According to a particular aspect, the transition metal particles may constitute 10-35 weight % of the total weight of the pillared clay catalyst. For example, the transition metal particles may constitute 11-33 weight %, 15-30 weight %, 17-28 weight %, 18-27 weight %, 20-25 weight %, 22-24 weight %. Even more in particular, the transition metal particles may constitute 11-33 weight % of the total weight of pillared clay catalyst.

The modified pillared clay may be formed from any suitable type of clay. According to a particular aspect, the starting raw material for the modified pillared clay may comprise at least one clay selected from, but not limited to, smectites or kaolin group of clay. In particular, the clay may be a smectite, such as but not limited to bentonite, saponite, montmorillonite, beidellite, nontronite, hectorite, sauconite or a combination thereof. In

particular, the clay may be a kaolin group of clay such as but not limited to kaolinite, halloysite, dickite, nacrite or a combination thereof. The clay may even be a combination of at least one smectite and at least one clay from the kaolin group. The clay may comprise commercial products containing the clays defined above. Even more in particular, the modified pillared clay may be formed from bentonite.

The pillared clay catalyst may comprise non-transition metal particles. The non-transition metal particles may be comprised in the form of oxides or silicates of the non-transition metals. For example, the pillared clay catalyst may comprise aluminium silicate. The non-transition metal particles may constitute 0-5 weight % of the total weight of the pillared clay catalyst.

The pillared clay catalyst may comprise silica and alumina. According to a particular aspect, the molar ratio of silica to alumina comprised in the pillared clay catalyst may be from 4:1 to 50:1. In particular, the molar ratio of silica to alumina may be 5:1-45:1, 10:1-40:1, 15:1-35:1, 20:1-30:1, 25:1-28:1.

The pillared clay catalyst may comprise about 2-26 weight % alumina of total weight of the pillared clay catalyst. In particular, the alumina may be 5-25 weight %, 7-23 weight %, 10-22 weight %, 12-20 weight %, 13-18 weight %, 15-17 weight % of the total weight of the pillared clay catalyst. Even more in particular, the alumina may be 7-20 weight % of the total weight of the pillared clay catalyst.

The pillared clay catalyst may comprise about 45-87 weight % silica of total weight of the pillared clay catalyst. In particular, the silica may be 47-85 weight %, 50-82 weight %, 55-80 weight %, 60-75 weight %, 65-70 weight % of the total weight of the pillared clay catalyst. Even more in particular, the silica may be 47-82 weight % of the total weight of the pillared clay catalyst.

The pillared clay catalyst of the present invention may be a macroporous catalyst. For the purposes of the present invention, a macroporous catalyst is defined as a catalyst comprising pores having an average pore diameter of ≥ 20 nm. In particular, the average pore diameter of the pores of the pillared clay catalyst is 20-200 nm, 30-180 nm, 40-170 nm, 50-150 nm, 60-120 nm, 70-110 nm, 80-100 nm, 85-95 nm. Even more in particular, the average pore diameter of the pores of the pillared clay catalyst is 20-60 nm. The pore size is an important property of the catalyst since the pyrolytic

performance is affected by the pore size of the catalyst. In particular, the pore size allows the selective compounds which have similar or smaller sizes with pore size of catalyst to react on an active site of the catalyst. For example, for plastic pyrolysis, the macroporous catalysts, which possess a larger pore size compared to microporous and mesoporous catalysts, increase accessibility of large molecules of hydrocarbon intermediates to provide selective compounds and therefore thermal decomposition, which would provide random cracking, is minimized.

The pillared clay catalyst of the present invention may have an average particle size of $\leq$600 µm. For the purposes of the present invention, the average particle size is defined as the sieve diameter of the catalyst which is the equivalent diameter corresponding to the diameter of a sphere passing through a sieve of defined mesh size with square or circular apertures. The preferred average particle size may be based on the process operation. In particular, the average particle size is 100-600 µm, 120-580 µm, 150-550 µm, 180-520 µm, 200-500 µm, 220-480 µm, 250-450 µm, 270-420 µm, 300-400 µm, 320-380 µm, 340-370 µm, 350-360 µm. Even more in particular, the average particle size is 200-300 µm. The average particle size of the catalyst affects the pyrolytic performance. In particular, a smaller particle size gives more surface area where reactants are able to contact active sites on the catalyst. However, a small particle size would restrict operations in the process such as in catalyst feeding to a reactor or lead to blockages in a reactor and thereby raise the pressure drop in a catalyst packed bed reactor.

The pillared clay catalyst may have a suitable surface area. According to a particular aspect, the pillared clay catalyst may have a Brunauer-Emmett-Teller (BET) surface area of about 100-400 m^2/g. In particular, the pillared clay catalyst may have a BET surface area of 120-380 m^2/g, 140-360 m^2/g, 160-340 m^2/g, 180-320 m^2/g, 200-300 m^2/g, 220-280 m^2/g, 240-260 m^2/g, 245-250 m^2/g. The BET surface area of the catalyst affects the pyrolytic performance. In particular, the BET surface area relates to the contacting area of reagents to active site of the catalyst. Therefore, a suitable area would allow the reactants to sufficiently contact the active site for production of the selective compounds during pyrolysis.

According to a second aspect, there is provided a method of preparing the pillared clay catalyst as described above. The method comprises:

- mixing clay material with deionized water to form a clay colloid;
- mixing transition metal particles selected from the group consisting of: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Hs, Mt, Ds, Zn, Cd, Hg, Cn, Ti, Zr, Hf, Rf, and a combination thereof, with an alkaline solution to obtain a transition metal solution with a pH of 1-4.5;
- adding the transition metal solution drop-wise to the clay colloid to obtain a modified clay colloid;
- ageing, washing and drying the modified clay colloid to obtain a pillared clay precursor;
- calcinating the pillared clay precursor to obtain the pillared clay catalyst; and
- optionally shaping the pillared clay catalyst to a particular shape or form.

The method 100 of preparing the pillared clay catalyst may be generally shown as steps 102 to 112 of Figure 1. Each of these steps will now be described in more detail.

Step 102 comprises preparing a clay colloid 114. In particular, the step 102 comprises mixing a clay material with deionized water to form the clay colloid 114. The mixing may be under suitable conditions. For example, the mixing of the step 102 may be under stirring.

The clay material used in the step 102 may be any suitable clay material. For example, the clay material may be as described above in relation to the starting raw material for the modified pillared clay. According to a particular embodiment, the step 102 may comprise mixing bentonite with deionized water to form colloid bentonite.

Depending on the clay material used in the step 102, a pre-treatment step to pre-treat the clay material may be required prior to the mixing of step 102. According to a particular aspect, if the clay material is calcium bentonite or potassium bentonite, the clay material may be subjected to an ion-exchange treatment. The ion-exchange treatment allows the calcium bentonite and potassium bentonite to undergo sodium beneficiation and/or sodium activation and thereby be converted to sodium bentonite to exhibit properties of sodium bentonite such as its viscosity and fluid loss of suspensions. The pre-treatment step to pre-treat the clay material may be required for other calcium and potassium clays as used in the step 102.

Depending on the particle size of the clay material used in step 102, the clay material may be required to be made into ground if the average particle size is ≥600 μm or lower than 30 mesh (American Society for Testing and Materials (ASTM) Standard). A lower particle size provides higher surface area of the catalyst contact area in the method.

Step 104 comprises preparing the transition metal solution 116. In particular, the step 104 comprises mixing an alkaline solution with at least one transition metal to form the transition metal solution 116. The mixing of the step 104 may comprise mixing the alkaline solution and the transition metal in a particular ratio such that the transition metal solution 116 has a final pH value of 1-4.5.

The alkaline solution may be an activating agent as it may provide a direct exchange of interlayer cations of clays by cationic precursors to form stable metal oxide pillars. In particular, the alkaline solution may comprise at least one of, but not limited to, sodium hydroxide, calcium hydroxide, and potassium hydroxide.

The at least one transition metal may be as described above in relation to the transition metal particles. According to a particular embodiment, the step 104 comprises mixing sodium hydroxide and iron chloride solution.

The step 104 may optionally comprise mixing additives with the alkaline solution and the transition metal to improve the inter-miscibility of the transition metal solution 116. Any suitable additive which improves inter-miscibility of the transition metal solution 116 may be used. For example, the additive may be, but not limited to, ethanol.

The transition metal solution 116 may be allowed to age for a period of time at a pre-determined temperature following the mixing of the step 104 so that the transition metal solution 116 attains equilibrium. For example, the period of time may be 1-24 hours, 2-20 hours, 3-18 hours, 4-15 hours, 5-12 hours, 6-10 hours, 7-8 hours. The period of time depends on the type of transition metal comprised in the transition metal solution 116. For example, the pre-determined temperature may be 10-100°C, 20-90°C, 30-80°C, 40-70°C, 45-60°C, 50-55°C. The pre-determined temperature depends on the type of transition metal comprised in the transition metal solution 116.

The transition metal solution 116 is then added to the clay colloid 114 according to step 106 to obtain a modified clay colloid 118. The In particular, the step 106 comprises adding the transition metal solution 116 to the clay colloid 114 drop-wise. The adding of the step 106 may be by any suitable technique. According to a particular embodiment, the adding of the step 106 may be by intercalation. During intercalation, the transition metal particles comprised in the transition metal solution 116 may be included or inserted into a layered structure of the clay colloid 114 to form the modified clay colloid 118.

The adding of the step 106 may be carried out under suitable conditions, depending on the transition metal solution 116. The adding of the step 106 may be carried out for a suitable period of time, depending on the process conditions such as the number of inlets in the reactor used, the amounts of the transition metal solution 116 and the clay colloid 114 involved in the step 106. For example, the adding of the step 106 may be carried out for 1-20 hours. In particular, the adding of the step 106 may be carried out for 1-19, 2-18, 3-17, 4-16, 5-15, 6-14, 7-13, 8-12, 9-10 hours. The adding of the step 106 may be carried out at a temperature of 15-95°C. For example, the adding of the step 106 may be carried out at a temperature of 20-90°C, 25-85°C, 30-80°C, 35-75°C, 40-70°C, 45-65°C, 50-60°C, 52-55°C. Even more in particular, the adding of the step 106 comprises adding at a temperature of 70°C.

Optionally, prior to the adding of the step 106, the clay colloid 114 may be subjected to acid treatment. Such acid treatment may improve the Brønsted acidity of the catalyst formed from the method 100.

The modified clay colloid 118 is then subjected to ageing, washing and drying according to step 108. The ageing, washing and drying of the step 108 may be carried out under suitable conditions. In particular, the ageing, washing and the drying of the step 108 may be carried out sequentially.

The ageing of the step 108 may be carried out for 2-24 hours. In particular, the ageing of the step 108 may be carried out for 2-23, 3-22, 4-20, 5-18, 6-15, 8-13, 9-12, 10-11hours. The ageing may be carried out with ultrasonication. The ageing of the step 108 may be carried out at a temperature of 15-75°C. The ageing of the step 108 may be carried out at a temperature of 15-75°C, 17-73°C, 20-70°C, 25-65°C, 30-65°C, 35-

60°C, 40-55°C, 50-53°C. Even more in particular, the ageing of the step 108 comprises ageing at 65°C for 22 hours.

The washing of the step 108 may comprise washing the modified clay colloid 118 with distilled or deionised water. The washing of the step 108 may be carried out repeatedly. In particular, the washing of the step 108 may be to remove the chloride, nitrate or sulphate ions which may be present in the modified clay colloid 118, depending on the transition metal used in preparing the transition metal solution 116. Any suitable washing technique may be used. For example, the washing may be by filtration or by centrifugation. Following the washing, the modified clay colloid 118 may be in the form of a slurry.

The drying of the step 108 may comprise drying the modified clay colloid 118 in the slurry form to obtain a pillared clay precursor 120. The drying of the step 108 may be by any suitable means under suitable conditions. For example, the drying may be with an air stream at a temperature of 40-80°C. In particular, the drying may be by using an air stream at a temperature of 45-75°C, 50-70°C, 55-65°C, 60-62°C. The drying of the step 108 may be carried out for a suitable period of time. The time for the drying may be dependent on the drying method and/or temperature involved in the drying method. For example, the drying of the step 108 may be carried out for 5-20 hours. In particular, the drying may be for 7-18 hours, 10-15 hours, 12-14 hours. Even more in particular, the drying of the step 108 comprises drying at 55°C.

Step 110 comprises calcinating the pillared clay precursor 120 to form a pillared clay catalyst 122. According to an optional embodiment, the pillared clay precursor 120 may be repeatedly subjected to the steps 104 to 108 prior to the calcinating of the step 110 in order to increase the content of the transition metal in the pillared clay catalyst 122.

The calcinating of the step 110 may comprise calcinating the pillared clay precursor 120 at a temperature of 300-600°C. In particular, the calcinating may be at a temperature of 320-580°C, 350-550°C, 370-520°C, 400-500°C, 420-480°C, 430-450°C. The calcinating may comprise a low heating rate. For example, the heating rate may be 1-50°C/minute. Even more in particular, the calcinating of the step 110 comprises calcinating at 5°C/minute to obtain Fe-pillar interlayered clay (Fe-PILC) catalyst.

The method 100 may further comprise an optional step 112 of shaping the pillared clay catalyst 122. In particular, the shaping may comprise physically modifying the pillared clay catalyst 122 to a suitable form. For example, the shaping of the step 112 may comprise, but is not limited to, grinding the pillared clay catalyst 122 into a powder form, modifying into granular form, pellet form, spherical form, or shaping into various shapes and sizes. In particular, the pillared clay catalyst 122 may be shaped into a suitable form and shape to suit its use in a particular type of pyrolytic reactor.

According to a third aspect, there is provided a catalytic pyrolysis method comprising:

- contacting the pillared clay catalyst described above with a plastic feedstock; and
- catalytically pyrolysing the plastic feedstock into C_{13}–C_{19} hydrocarbon products.

The plastic feedstock may be any suitable feedstock. For example, the plastic feedstock may comprise a single type of plastic or a mixture of different types of plastic. In particular, the plastic feedstock may comprise at least one of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC).

The catalytic pyrolysis method of the present invention may also be used in the pyrolysis of other hydrocarbon materials other than plastic, such as halogenated polymers, wax, tar, petroleum residue and heavy oil.

According to a particular aspect, the pillared clay catalyst and the plastic feedstock may be in a catalyst to feedstock (C/F) weight ratio of 0.01-0.5. The C/F weight ratio may vary depending on the design of the pyrolytic reactor used in the pyrolysis method. In particular, the C/F weight ratio may be 0.03-0.4, 0.05-0.3, 0.08-0.2, 0.09-0.1.

The pyrolysing may be carried out under suitable conditions. For example, the temperature at which the pyrolysing is carried out may be 350-600°C. In particular, the pyrolysing may be at a temperature of 350-580°C, 360-550°C, 370-520°C, 400-500°C, 420-480°C, 430-450°C.

The pyrolysing may be carried out in the presence of a carrier gas. Any suitable carrier gas may be used for the purposes of the present invention. For example, the carrier

gas may be an inert gas. In particular, the carrier gas may be, but not limited to, nitrogen, helium, argon, or mixtures thereof.

The catalytic pyrolysis method may be carried out in any suitable pyrolytic reactor. For example, the pyrolytic reactor may be a fluidized bed reactor, a tube reactor, a rotary kiln reactor, a stirred tank reactor, a screw conveyor, and the like.

An example of a setup of the apparatus in which the catalytic pyrolysis method of the present invention may be carried out is provided in Figure 2.

The catalytic pyrolysis method of the present invention enables a high yield of liquid hydrocarbon to be obtained as a result of the pillared clay catalyst used in the method. According to a particular aspect, the pillared clay catalyst enables a liquid hydrocarbon yield of ≥ 60 weight % of a mass of plastic feedstock during the pyrolysis of the plastic feedstock. Further, the pillared clay catalyst may enable a selectivity of C_{13}–C_{19} hydrocarbon of ≥ 30 weight % of the liquid hydrocarbon yield in the catalytic pyrolysis method. In particular, the C_{13}–C_{19} hydrocarbon is the diesel fraction.

The pillared clay catalyst of the present invention provides advantages over conventional pyrolytic catalysts. In particular, the diesel oil yield achieved by the pillared clay catalyst of the present invention in pyrolysis of mixed plastics is much higher compared to commonly-used catalysts such as zeolite-based catalysts. This is as a result of the transition metal particles dispersed in the clay structure, resulting in improved catalytic performance in pyrolysis. In particular, the pillared clay catalyst of the present invention have a less acidic clay structure, thereby reducing the tendency of over-cracking and favouring the production of hydrocarbons in the diesel range leading to a higher yield of the liquid oil product and a lower yield of the less valuable gaseous products. In particular, as exemplified below, the pillared clay catalyst of the present invention may achieve higher selectivity for the diesel fraction (such as >55 weight % of liquid oil products) as compared with other commonly used catalysts which obtain <43 weight % of liquid oil products. Since the resultant carbon number distribution of pyrolytic oil is concentrated in the diesel range of C_{13}–C_{19} hydrocarbon, there is minimal effort required in further processing the pyrolytic oil into high-quality diesel fuel, thereby saving costs.

Further, the use of the pillared clay catalyst of the present invention in catalytic pyrolysis also results in the reduction of energy consumption since a lower reaction temperature and less reaction time is required for the pyrolysis method. There is also no need for the removal of specific types of plastic such as PET from a plastic feedstock since the pillared clay catalyst may be used for pyrolysis of various types of plastic, unlike other commonly used catalysts. The absence of the need for pre-sorting the feedstock significantly reduces operating cost in terms of manpower as well as associated equipment. This also makes it easier to scale up the pyrolysis method of the present invention as an effective and efficient plastic waste recycling method. The pillared clay catalyst of the present invention also possess high thermal stability with minimal loss of transition metal loaded on the clay over a long period of operation.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Having now generally described the invention, the same will be more readily understood through reference to the following examples which are provided by way of illustration, and are not intended to be limiting.

EXAMPLE

Example 1

Feedstock

The feedstock used in the pyrolysis experiments was a mixture of polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) with an approximate weight ratio (PE:PP:PS:PET) of 42:35:18:5. This ratio resembles the composition of municipal plastic waste generated in Singapore as obtained from the National Environment Agency (NEA) of Singapore.

The samples PE (density: 0.95 g/cm^3), PP (density: 0.9 g/cm^3) and PET (density: 1.3-1.4 g/cm^3) were in granular form with a nominal granule size of 3 mm, while PS (density: 1.05 g/cm^3) was in powder form with a mean particle size of 250 μm. The granular PE was purchased from Alfa Aesar (USA), whereas PP, PET and PS were obtained from Goodfellow Cambridge Ltd (UK).

Catalysts development

Seven representative examples of pillared clay catalysts were prepared as shown in Table 1.

The drying method used was by centrifuging the modified clay colloid and discarding the supernatant. The clay was then dried in a laboratory oven at 55°C for 8 hours.

All the catalysts synthesized consisted of about 11-33 weight % of transition metal, about 7-20 weight % of alumina, and about 47-82 weight % of silica. Bentonite obtained from Sigma-Aldrich (USA) was selected as the starting raw material for the clay material. The types of transition metal salt used for each type of clay catalyst were as follows: titanium(IV) chloride, iron(III) chloride hexahydrate and cobalt(II) nitrate hexahydrate (from Sigma-Aldrich, USA), zinc nitrate hexahydrate (from Merck, Germany), zirconium(IV) chloride and nickel(II) nitrate hexahydrate (from Strem Chemicals, Inc, USA). Sodium hydroxide pellets purchased from Merck (Germany) were used to prepare the transition metal solutions.

The efficiency of these catalysts in pyrolysis was compared with several commonly-used catalysts in the pyrolysis of mixed plastics such as Al-pillared clay (Sigma Aldrich (Singapore)), zeolite-based catalyst (ZSM-5) (Alfa Aesar (USA)) and mesoporous catalysts (Zr-MCM-41, Al-SBA-15 and Fe-SBA-15).

TYPES OF CATALYSTS							
	Ti-pillared clay	**Zr-pillared clay**	**Fe-pillared clay**	**Fe/Al-pillared clay**	**Co-pillared clay**	**Ni-pillared clay**	**Zn-pillared clay**
Group to which transition metal belongs	IVB	IVB	VIII	VIII	VIII	VIII	IIB
Materials	Titanium tetrachloride, bentonite, hydrogen chloride	Zirconium (IV) chloride, bentonite, sodium hydroxide	Iron (III) chloride, bentonite, sodium hydroxide	Iron (III) chloride, aluminium chloride, bentonite, sodium hydroxide	Cobalt (II) nitrate, bentonite, sodium hydroxide	Nickel (II) nitrate, bentonite, sodium hydroxide	Zinc nitrate, bentonite, sodium hydroxide
Amount of metal	8 mmol Ti^{4+}/g bentonite	8 mmol Zr^{4+}/g bentonite	4 mmol Fe^{3+}/g bentonite	2 mmol Fe^{3+}, 2 mmol Al^{3+}/g bentonite	8.6 mmol Co^{2+}/g bentonite	8.6 mmol Ni^{2+}/g bentonite	8.6 mmol Zn^{2+}/g bentonite
Ageing temperature/time for the transition metal solution	24°C / 3hr	24°C / 24 hr	65-70°C / 24 hr	40-45°C / 24 hr	24°C / n.a. with ultrasonication	24°C / n.a. with ultrasonication	24°C / n.a. with ultrasonication
Temperature for the adding of the step 106	24°C	24°C	65°C	70°C	24°C	24°C	24°C
Temperature/time for the ageing of the step 108	24°C/16 hr	24°C/24 hr	60-75°C/22 hr	60-75°C/22 hr	24°C/24 hr	24°C/24 hr	24°C/24 hr
Temperature, heating rate of the calcinating of the step 110	400°C, 5°C/min	400°C, 1°C/min	300°C, 5°C/min	300°C, 5°C/min	300°C, 5°C/min	300°C, 5°C/min	300°C, 5°C/min

Table 1: Details of the seven catalysts prepared

Catalyst dosage

The C/F ratio commonly used for clay-based catalysts falls in the range from 0.1 to 1, whereas the commonly used C/F ratio for zeolite-based catalysts and mesoporous catalysts ranges from 0.01 to 0.5. Due to the lower acidity and weaker cracking activity of the pillared clay catalysts, the C/F ratios used for the pillared clay catalysts were higher than those for zeolite-based catalysts and mesoporous catalysts in order to provide adequate catalytic activity for pyrolysis.

After conducting several preliminary pyrolysis experiments with different dosage of pillared clay catalysts, a reduction of oil yield was observed as the C/F ratio exceeded 0.3, due to excessive cracking. Hence, C/F ratio of 0.3 was selected for all pillared clay catalysts experiments to ensure sufficient catalytic activity while avoiding over-cracking. On the other hand, the optimal C/F ratios for Fe-SBA-15 and other mesoporous catalysts (Zr-MCM-41 and Al-SBA-15) were found to be 0.05 and 0.03, respectively.

Experimental apparatus and setup

All catalytic pyrolysis experiments, except that with ZSM-5, were conducted using an unstirred, horizontal tube reactor. The schematic diagram of the experimental setup is shown in Figure 2.

In each experiment, 10 g of mixed plastic feedstock (PE:PP:PS:PET = 42:35:18:5) was mixed with catalyst (powder form) in the reaction vessel and heated up in the horizontal tube reactor at 10°C/min to a final temperature of 500°C. N_2 gas was supplied to the reactor at a flow rate of 200 ml/min to create an inert environment as well as to purge the gaseous and liquid products out of the reactor. The liquid product was then condensed and collected in the oil collector.

Experiment with ZSM-5 was conducted using similar conditions, which included the use of an unstirred tube reactor, 100 g feedstock, N_2 flow of 1000 ml/min (sufficient to purge the gaseous and liquid products out of the reactor) and a reaction temperature of 500°C (heating rate: 20°C/min).

Analysis of pyrolysis products

In each experiment, the liquid product collected was weighed and the yield of liquid product was calculated in weight percentage with respect to feedstock. The liquid product was then subjected to gas chromatography-mass spectrometry (GC-MS) analysis to examine its composition. The GC-MS system used consisted of an Agilent 7890B GC system (USA) equipped with an Agilent HP-5 MS column (length: 30 m, internal diameter: 0.25 mm), coupling with Agilent 5977A MSD (USA). The injection volume was 1 µL and the split ratio was set to 100:1. The temperature of the injection port, quadrupole and ion source were set to 250°C, 150°C and 230°C, respectively. Oven temperature was programmed at an initial temperature of 40°C and subsequently raised in a stepwise manner (increased at 1°C/min to 45°C and held for 2 min, followed by temperature increase at 5°C/min to 150°C and holding time of 2 min, 10°C/min to 210°C without temperature holding, and finally an temperature increase at 20°C/min to 280°C and holding time of 10 min).

The carbon numbers of liquid products were identified by matching their mass spectrum profile against the mass spectrum profile of an alkane standard solution that contains C_8-C_{20} (purchased from Sigma-Aldrich, USA). Subsequently, the total mass percentage of the fraction of interest was calculated.

Results of catalytic pyrolysis of mixed plastics

Table 2 summarizes the efficiency of seven representative examples of the said pillared clay catalysts in catalytic pyrolysis of mixed plastics. The transition metals incorporated into the seven catalysts were from the IIB, IVB and VIIIB group of the Periodic Table.

As shown in Table 2, all representative examples of the pillared clay catalyst, in particular the Fe-, Co- and Zn-pillared clay, exhibited high oil yield (as high as 71.96 weight %) and excellent selectivity for the diesel fraction in the pyrolysis of mixed plastic materials.

Catalyst name	Group to which the transition metal belongs	Yield of liquid hydrocarbon (wt% of the mass of feedstock)	Selectivity for diesel product[a] (wt% of the liquid product fraction)
Ti-pillared clay	IVB	62.43 wt%	> 30 wt%
Zr-pillared clay	IVB	60.55 wt%	> 35 wt%
Fe-pillared clay	VIII	71.00 wt%	> 55 wt%
Fe/Al-pillared clay	VIII	68.20 wt%	>30 wt%
Co-pillared clay	VIII	70.90 wt%	> 40 wt%
Ni-pillared clay	VIII	60.60 wt%	> 35 wt%
Zn-pillared clay	IIB	71.96 wt%	> 50 wt%

[a] *Diesel fraction was defined by a carbon number range of C13-C19*

Table 2: Catalytic pyrolysis of mixed plastics using pillared clay catalysts

Comparison between pillared clay catalysts and other commonly-used catalysts

The efficiency of several commonly-used catalysts in pyrolysis of mixed plastic feedstock was examined and compared with an exemplary embodiment (Fe-pillared clay) of the pillared clay catalyst (as shown in Table 3).

As compared with all the commonly-used catalysts, the Fe-pillared clay catalyst exhibited considerably high oil yield and superior selectivity for the diesel fraction in pyrolysis of mixed plastics. The capability to obtain high oil yield from pyrolysis of mixed plastics (especially PET-containing plastic wastes) is highly beneficial to large-scale application of the catalytic pyrolysis in the industry as it eliminates the need for pre-sorting of feedstock which can lead to an additional cost in terms of manpower and associated equipment. In addition, the high ratio of diesel fraction achieved is highly favourable as it reduces the effort needed for the subsequent fuel-upgrading process (which further upgrades the pyrolytic oil to high-quality diesel fuel that can be readily used).

As compared with all clay-based catalysts (including the Fe-pillared clay catalyst and common Al-pillared clay), the zeolite-based catalyst and mesoporous catalysts tended to result in low oil yield and/or poor selectivity for the diesel fraction. This can be attributed to the highly acidic nature as well as small pore size of the catalyst which increases the tendency of over-cracking.

Catalyst name	Catalyst type	C/F ratio	Yield of liquid hydrocarbon (wt% of the mass of feedstock)	Selectivity for diesel product[a] (wt% of the liquid product fraction)
Fe-pillared clay[b] (an exemplary embodiment of the said catalyst)	Clay-based, macroporous	0.3	>70 wt%	>55 wt%
Al-pillared clay	Clay-based, macroporous	0.3	63.16 wt%	42.14 wt%
ZSM-5	Zeolite-based, microporous	0.1	39.8 wt%	<15 wt%
Zr-MCM-41	mesoporous	0.03	55.49 wt%	26.48 wt%
Al-SBA-15	mesoporous	0.03	63.24 wt%	34.92 wt%
Fe-SBA-15	mesoporous	0.05	54.69 wt%	30.06 wt%

[a] *Diesel fraction was defined by a carbon number range of C13-C19*

[b] *Composition of the catalyst (wt% of total catalyst weight) was: i) Transition metal: 17-27 wt%; ii) Alumina: 13-23 wt%; iii) Silica: 50-70 wt%*

Table 3: Comparisons of pillared clay catalyst and other commonly used catalysts in pyrolysis of mixed plastics

While the clay structure of both Al-pillared clay and the Fe-pillared clay catalysts are of much lower acidity, the overall acidity of Al-pillared clay is still higher than the Fe-pillared clay catalyst owing to its strong Brønsted acidity. As a result, a relatively severe cracking is associated with pyrolysis using Al-pillared clay, as implied by its low oil yield. Besides, aluminium particles present in Al-pillared clay were shown to result in a lower selectivity for the diesel fraction as compared with the transition metals loaded in the Fe-pillared clay catalysts.

Despite a relatively high catalyst dosage generally required for catalytic pyrolysis with clay-based catalyst, the overall cost of pyrolysis using the said catalyst are estimated to be at least 40% lower than that of pyrolysis using zeolite-based catalysts or mesoporous catalysts since the raw materials for clay-based catalyst are of much lower cost as compared with zeolite-based catalysts or mesoporous catalysts.

Example 2

An example of a catalyst preparation system is provided. The system is capable of producing up to 2 kg of pillared clay catalysts per batch. The system is composed of two polyvinylidene fluoride (PVDF) reactors, a peristaltic pump and a filtering apparatus. Each reactor contains a stirrer, an immersion heater, a thermocouple and several inlets on the top of the reactors, as well as outlets at the wall and bottom of the reactors. During the preparation, the transition metal solution and clay colloid are prepared in the two separate PVDF reactors. During the adding step, the clay colloid is slowly pumped into the PVDF reactor which contains the transition metal solution using a peristaltic pump. The filtering apparatus is used for the washing of modified clay colloid. During the washing process, the water suspension of clay is pumped into the filtering apparatus where water will pass through the ceramic cartridges located inside apparatus while clay will be retained on the surface of the cartridges. After washing, the clay is scraped off the cartridges and proceeds to the subsequent drying step. The schematic diagram of the catalyst preparation system are shown in Figure 3.

Example 3

Characterization of catalysts

The Fe-pillared clay catalyst (Fe-PILC) and the Ti-pillared clay catalyst (Ti-PILC) were characterized together with other conventional catalysts (unmodified bentonite (Sigma Aldrich (Singapore)), Al-pillared clay catalyst (Sigma Aldrich (Singapore)), AL-ZSM-5 (Alfa Aesar (USA))). In particular, the textural properties and acidity were characterized as follows.

Textural properties

Textural properties of the catalysts were determined by a Micrometrics ASAP 2010 nitrogen gas adsorption analyser at 77 K. The samples were degassed under vacuum at 150°C for 6 hours before the measurements. Surface areas of the catalysts were estimated using the BET and BJH equations. Total pore volumes were measured at P/P_o = 0.99 and the micropore volumes were determined using the t-plot method. The results are shown in Table 4.

	S_{BET}[a] (m^2g^{-1})	S_{ESA}[b] (m^2g^{-1})	S_{MA}[b] (m^2g^{-1})	V_{MPV}[b] (cm^3g^{-1})	V_{TPV}[c] (cm^3g^{-1})	d001 Å
Fe-pillared clay	133.2	94.6	9.582	0.0036	0.190	14.8
Ti-pillared clay	282.1	260.9	28.92	0.0076	0.235	14.5
Unmodified Bentonite	34.64	22.3	12.6	0.0057	0.0908	11.9
Al-pillared clay	218.1	69.1	26.0	0.069	0.229	20.5
Al-ZSM-5	393.9				0.258	n.a.

a Multi-point BET method.

b External surface area, micropore surface area and micropore volume from t-plot analysis

c Total pore volume at P/Po equal to 0.99

Table 4: Textual properties (via BET characterization) of the various catalysts

Acidity (via NH_3-TPD characterization)

The acidity of the catalysts was measured by temperature programmed desorption (TPD) of ammonia using a MicromeriticsAutoChem 2920 chemisorption analyser. Prior to the adsorption experiments, each sample (86-300 mg) was pre-treated with nitrogen stream in a quartz U-tube at 500°C, followed by a temperature reduction to 100°C. The adsorption experiments were performed by supplying the samples with small pulses of ammonia in argon gas at 100°C until saturation. Subsequently, the samples were exposed to a flow of pure argon gas (50 mL/min) for 2 hours at 100°C to remove the reversibly and physically bound ammonia from the surface of the samples. Finally, the samples were subjected to desorption with temperature increased from 100 to 500°C (heating rate: 10°C/min) in argon stream (50 mL/min), followed by temperature holding for 15 minutes to ensure complete desorption of the adsorbates. The amount of ammonia desorbed within a given temperature range reflected the acid site concentration, whereas the temperature range in which most of the ammonia was desorbed indicates the acid strength of the acid sites. The results are shown in Table 5.

	Weak acid site (Lewis acid site)	Strong acid site (Bronsted acid site)	Total acidity
Fe- pillared clay	0.0176 (204)	0.120 (721)	0.138
Ti- pillared clay	0.0393 (222)	0.101 (672)	0.140
Unmodified bentonite	–	0.170 (661)	0.170
Al- pillared clay	0.0363 (239)	0.108 (638)	0.144
Al-ZSM-5	0.238	0.269	0.507

( ) = Peak-temperature of desorption peaks associated with the acid site, °C

Table 5: Acidity ($mmolNH_3.g^{-1}$) of the various catalysts

X-ray diffraction (XRD)

XRD patterns of the catalysts were collected in a RigakuUltima IV diffractometer using Cu Kα radiation source (λ=1.54056 Å) at 40 kV and 20 mA with a scan rate of 0.5 degree/minute.

It was found that the textural properties and acidity of catalyst are important properties for chemical reactions. A suitable BET surface area, type and amount of acid of catalyst are required to produce the selective products. The prepared Ti-pillared clay catalyst and Al-pillared clay catalyst provided surface areas in range of 218-282 m^2/g, while the Fe-pillared clay catalyst showed a lower surface area (133 m^2/g). Metal-pillared clay catalysts possess significantly lower total acidity compared with that of Al-ZSM-5, and this would cause lower cracking to provide higher yield of liquid oil product and lower yield of less valuable gaseous products. Moreover, it should be noted that different metal types in pillared clay catalysts exert different strength of weak acid sites. The pillared clay catalysts provide much lower total acidity compared with the commercial catalyst (Al-ZSM-5) (0.14 vs 0.51). For XRD pattern of clay catalysts, all the pillared clay catalysts presented the 001 reflection (the 2θ angle at 7°) with basal spacing larger than 11.9 Å (see BET characterization), indicating that pillaring procedures for the pillared clay catalysts was successful with resultant expansion of the interlayer distances. Metal-PILC showed improved surface areas and d001 spacing (expansion of the interlayer distances by metal replacement) compared with unmodified clay (bentonite) which presents no-pillared material. The results are shown in Figure 4.

Example 4

Catalytic pyrolysis of mixed plastics (batch process)

A batch pyrolysis experiment was carried out in a laboratory scale installation which included an unstirred 3 dm^3 reactor and a condensation-separation apparatus. In a typical run, the catalyst was mixed with a mixed plastic sample in a proportion of 10 wt% (i.e. the ratio of catalyst to plastic was constant for all the experiment). The weight of each plastic sample was about 10 g per run. The mixture was placed into the reactor, which was first heated at a rate of 40°C/minute to 300°C, followed by a temperature holding of 5 minutes. The temperature was subsequently increased to a

final temperature of 450°C at 10°C/min, followed by a temperature holding of 30 minutes. The gas and oil vapour generated were purged out of the reactor by nitrogen flow (flow rate: 200 mL/min) to an oil condenser cooled by running water. The incondensable gaseous product was collected in a Tedlar® gas sampling bag to be analysed by GC-TCD-FID analysis (gas chromatography, thermal conductivity detectors, flame-ionisation detectors) afterwards. After pyrolysis, the solid residues remained in the reaction vessel, while the oil products collected in the oil tank, as well as the wax products collected from the condenser and the connecting pipelines were weighed. The yield of the residues (exclusive of catalyst), oil and wax were calculated as weight percentage with respect to the plastic feedstock. Gas yield was calculated by subtracting the weight percentage of residues, oil and wax products from 100%.The results of the pyrolysis yields as shown in Table 6 are the mean value of at least three pyrolysis runs carried out in the same conditions and which did not differ more than three points in the percentage.

The composition of the oil and wax products collected was examined using a gas chromatograph (Agilent 7890B GC system, USA) equipped with Agilent HP-5 MS column (length: 30 m, I.D: 0.25 mm), coupling with a mass spectrometer (Agilent 5977A MSD, USA). The injection volume was 1 µL and the split ratio was set to 100:1. The temperature of the injection port, quadrupole and ion source were set at 250, 150 and 230°C, respectively. Oven temperature was programmed at an initial temperature of 40°C and subsequently raised in a stepwise manner (increased at 1°C/min to 45°C and held for 2 minutes, followed by temperature increase at 5°C/min to 150°C and held for 2 minutes, 10°C/min to 210°C without temperature holding, and finally an temperature increased at 20°C/min to 280°C and held for 10 minutes). The flow rate of helium carrier gas was set to 20 mL/min. Identification of different constituents of the oil and wax products was done by computer matching against the NIST11 mass spectral library (WileyRegistryTM), the peaks representing the major constituents were further verified by comparing their mass spectrum profile of the oil and wax products with that of a calibration standard.

From this study, the oil yields from plastic pyrolysis using different pillared interlayered clay (PILC) catalysts were derived, as shown in Table 6. The oil, gas and residues were in the range of 60-72 wt%, 25-38 wt% and 0.1-8 wt%, respectively. Ti-

PILC, Zr-PILC and Ni-PILC showed lower yields of oil (60-62 wt%) and higher gas yields (33-38 wt%) compared with the other metal PILC catalysts.

Catalyst [b]	Oil product	Gas product	Residue
Commercial bentonite	64.71	35.19	0.10
Ti-PILC	62.43	34.17	3.40
Zr-PILC	60.55	38.43	7.91
Fe-PILC	70.96	25.30	3.70
Fe/Al-PILC	68.20	30.00	1.80
Co-PILC	70.90	28.70	0.40
Ni-PILC	60.60	33.30	6.10
Zn-PILC	71.96	27.44	0.60

Table 6: Influence of catalyst on the yield of pyrolytic products (in weight %)

a Reaction conditions: 10 g of plastic mixture, Nitrogen (200 mL/min), heating from room temperature to a final temperature of 500°C with heating rate of 10°C/min.

b The mass ratio of catalyst to feedstock (C/F) was 0.3.

Transition metal-pillared clays improve hydrocarbon cracking compared with unmodified clay (bentonite) which provides high amounts of heavy hydrocarbon compounds (about 69 wt% of C_{20}-C_{30}). Ti-PILC is the most cracking catalyst to give lower carbon range of oil product among other transition metal-PILCs. Fe-PILC contributes the highest amount of C_{13}-C_{19} (diesel range) and has a lower cost of catalyst preparation compared to other transition metals such as Ti and Zn, as shown in Figure 5.

Example 5

Catalytic pyrolysis of mixed plastics using Fe-PILC (continuous process)

The Fe-PILC used in this example was that as prepared in Example 1. The Fe-clay catalyst was selected as the potential metal-pillared clay to use for demo prototype studies. The demo-prototype of the process had been developed to treat mixed plastic waste by converting them into valuable products as liquid fuels. The demo-prototype included three main units (dechlorination unit/catalytic pyrolysis reactor/reforming reactor). It should be noted that the results from this study were derived from a continuous process of dechlorination unit (pre-treatment of PVC) and catalytic pyrolysis reactor. The Fe-clay was applied for catalytic pyrolysis reaction to convert pre-treated melt plastic into selective hydrocarbon vapours. Then, the selective vapours may be

condensed to derive oil products or further upgraded into higher grade of oil product via a reforming reactor.

The details of experimental operation for continuous dechlorination and catalytic pyrolysis of mixed plastic wastes are as follows.

A vented screw conveyor, which consists of a horizontal segment and a vertical segment, was specially designed for melting and thermal dechlorination of plastic feedstock. Gaseous hydrogen chloride generated from dechlorination of PVC was exhausted from the vent-holes located along the wall of the conveyor, and neutralized in a HCl trap by 2 mol/L sodium hydroxide (NaOH) solution. The temperature of the vented screw conveyor was set at 300°C. The feeding rate of plastic feedstock into the conveyor was 1.65 kg/hr (2 rpm of screw speed). After dechlorination, molten dechlorinated plastic was conveyed into the stirred tank reactor where catalytic pyrolysis took place. The temperature inside the tank reactor was set at 425-500°C and the speed of the stirrer was fixed at 20 rpm. In each catalytic pyrolysis run, the catalyst (powder form) was added into the reactor through the catalyst hopper when dechlorinated plastic first entered the reactor. Nitrogen flow was constantly supplied to the tank reactor at a flow rate of 1 L/min to purge out the gas and oil vapour generated from the pyrolysis. After pyrolysis, pyrolytic oil vapour was condensed and collected in oil tanks. Incondensable pyrolytic gas was collected in a Tedlar® gas sampling bag for further analysis. Pyrolytic oil and gas samples were taken for analysis every 10 min after the continuous operation had reached steady state. Each result presented is the mean value of at least three runs. Unlike oil and gas samples, solid residue sample was collected at once after completion of each run. The yield of the residues (excluding catalyst) and oil products were calculated as weight percentage (wt %) with respect to the plastic feedstock. The analysis methods for composition of the oil and wax was examined using a gas chromatograph as mentioned in Example D.

From this experiment, catalytic pyrolysis using Fe-PILC gives higher oil yield and lower gas yields compared with non-catalytic pyrolysis, as shown in Table 7. However, higher temperature of catalytic pyrolysis shows less differences of the yields (See Figure 6). Catalytic pyrolysis at 425°C showed the highest oil yield and the largest difference of oil yield (~10 wt%).

The presence of the catalyst contributed to the selective products of C_9-C_{12} (>40 wt%), while non-catalytic pyrolysis provides almost equivalent amount at different carbon fractions. This can be seen from the results shown in Table 7. It may be noted that lower yield of C_{13}-C_{19} was attained compared with the results from horizontal tube reactor, this could be due to better heat transfer derived from using stirred tank reactor at catalytic pyrolysis which would provide better cracking into lower carbon range. Nevertheless, this catalyst still provided a high selectivity of oil product in range of C_9-C_{19} (>70 wt%) which would produce valuable products of kerosene and diesel.

Conditions	Carbon distribution in oil product (wt%)			
	C_6-C_8	C_9-C_{12}	C_{13}-C_{19}	C_{20}-C_{30}
Non catalytic pyrolysis	24.61	29.37	26.68	19.22
Catalytic pyrolysis	17.39	42.39	30.13	10.09

Table 7: Carbon distribution of oil products derived from non-catalytic and catalytic pyrolysis at 425°C

The effect of ratio of catalyst to feedstock on yield was further studied and it was found that 0.2 of C/F ratio gives maximum oil yields at catalytic pyrolysis temperature of 425-500°C. This is shown in Figure 7. The lesser effect of C/F ratio on oil yield was obtained with increase in reaction temperature and at 510°C presents no effect of C/F ratio on oil yield.

Claims

1. A pillared clay catalyst for catalytic pyrolysis comprising modified pillared clay, wherein the modified pillared clay comprises pillared clay modified by transition metal particles, the transition metal particles selected from the group consisting of: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Hs, Mt, Ds, Zn, Cd, Hg, Cn, Ti, Zr, Hf, Rf, and a combination thereof.

2. The pillared clay catalyst according to claim 1, wherein the transition metal particles constitute 10-35 weight % of total weight of the pillared clay catalyst.

3. The pillared clay catalyst according to claim 1 or 2, wherein the transition metal particles are in the form of oxides or silicates.

4. The pillared clay catalyst according to any preceding claim, wherein a starting raw material for the modified pillared clay comprises at least one selected from the group consisting of smectites and kaolin.

5. The pillared clay catalyst according to claim 4, wherein the smectites comprise at least one of bentonite, saponite, montmorillonite, beidellite, nontronite, hectorite or sauconite.

6. The pillared clay catalyst according to claim 4, wherein the kaolin comprises at least one of kaolinite, halloysite, dickite, or nacrite.

7. The pillared clay catalyst according to any preceding claim, wherein the pillared clay catalyst comprises a molar ratio of silica to alumina is from about 4:1 to 50:1.

8. The pillared clay catalyst according to any preceding claim, wherein the pillared clay catalyst comprises 2-26 weight % alumina of total weight of the pillared clay catalyst and 45-87 weight % silica of total weight of the pillared clay catalyst.

9. The pillared clay catalyst according to any preceding claim, wherein the pillared clay catalyst is a macroporous catalyst.

10. The pillared clay catalyst according to claim 9, wherein the pillared clay catalyst comprises an average pore diameter of ≥20 nm.

11. The pillared clay catalyst according to any preceding claim, wherein the pillared clay catalyst has an average particle size of ≤600 μm.

12. The pillared clay catalyst according to any preceding claim, wherein the pillared clay catalyst has a Brunauer-Emmett-Teller (BET) surface area of about 100-400 m^2/g.

13. The pillared clay catalyst according to any preceding claim, wherein the pillared clay catalyst has a liquid hydrocarbon yield of ≥60 weight % of a mass of plastic feedstock during pyrolysis.

14. The pillared clay catalyst according to claim 13, wherein the pillared clay catalyst has a selectivity of C_{13}–C_{19} hydrocarbon of ≥ 30 weight % of the liquid hydrocarbon yield.

15. A method of preparing the pillared clay catalyst according to any preceding claim, the method comprising:

- mixing clay material with deionized water to form a clay colloid;
- mixing transition metal particles selected from the group consisting of: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Hs, Mt, Ds, Zn, Cd, Hg, Cn, Ti, Zr, Hf, Rf, and a combination thereof, with an alkaline solution to obtain a transition metal solution with a pH of 1-4.5;
- adding the transition metal solution drop-wise to the clay colloid to obtain a modified clay colloid;
- ageing, washing and drying the modified clay colloid to obtain a pillared clay precursor;
- calcinating the pillared clay precursor to obtain the pillared clay catalyst; and
- optionally shaping the pillared clay catalyst to a particular shape or form.

16. The method according to claim 15, wherein the adding is performed over a period of 1-20 hours at a temperature of 15-95°C.

17. The method according to claim 15 or 16, wherein the calcinating is at a temperature of 300-600°C.

18. A catalytic pyrolysis method comprising:

- contacting the pillared clay catalyst according to any of claims 1 to 14 with a plastic feedstock; and
- catalytically pyrolysing the plastic feedstock into C_{13}–C_{19} hydrocarbon products.

19. The method according to claim 18, wherein the plastic feedstock comprises at least one of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC).

20. The method according to any of claims 18 to 19, wherein the pillared clay catalyst and the plastic feedstock are in a catalyst to feedstock (C/F) weight ratio of 0.01-0.5.

Figure 1

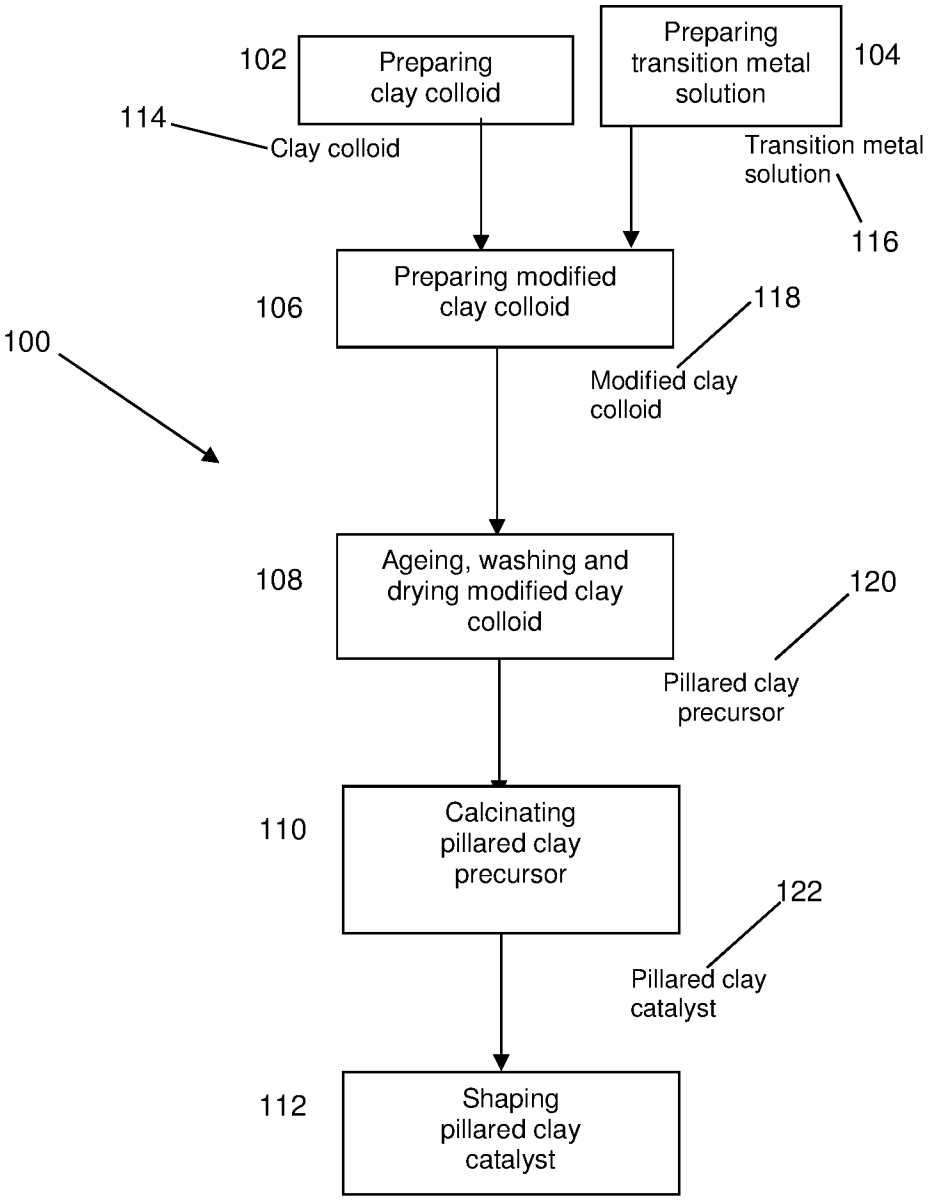

102
Preparing clay colloid
104
Preparing transition metal solution
114
Clay colloid
Transition metal solution
116
106
Preparing modified clay colloid
118
Modified clay colloid
100
108
Ageing, washing and drying modified clay colloid
120
Pillared clay precursor
110
Calcinating pillared clay precursor
122
Pillared clay catalyst
112
Shaping pillared clay catalyst

Figure 2

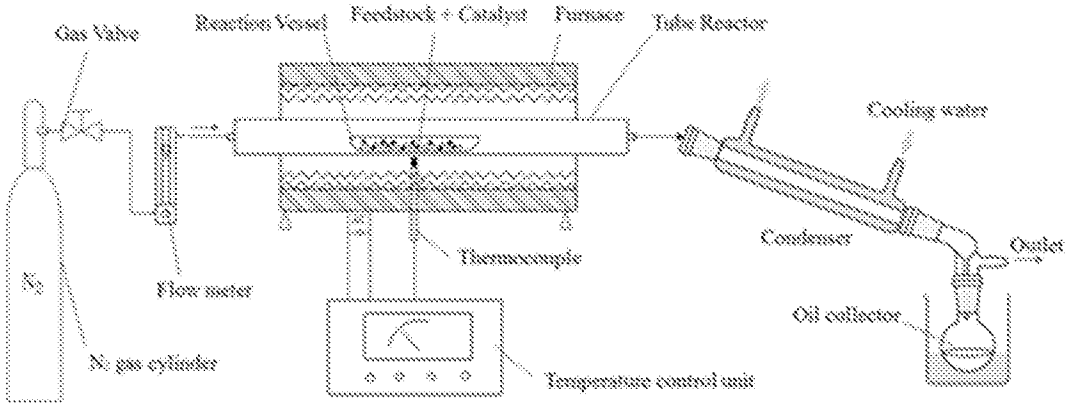


Figure 3

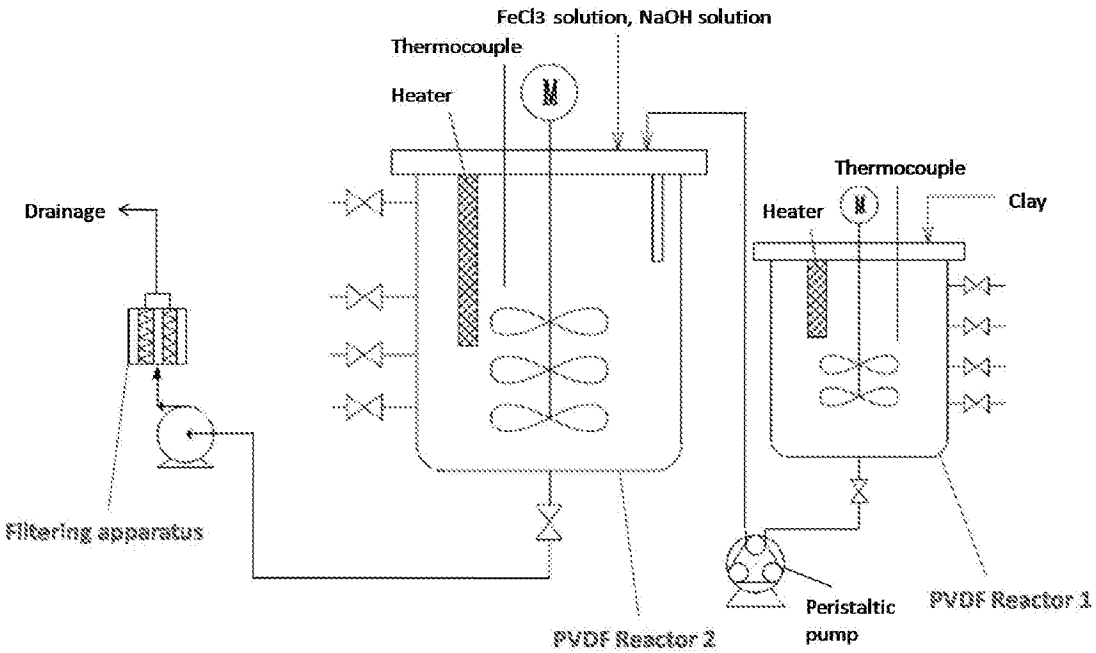


Figure 4

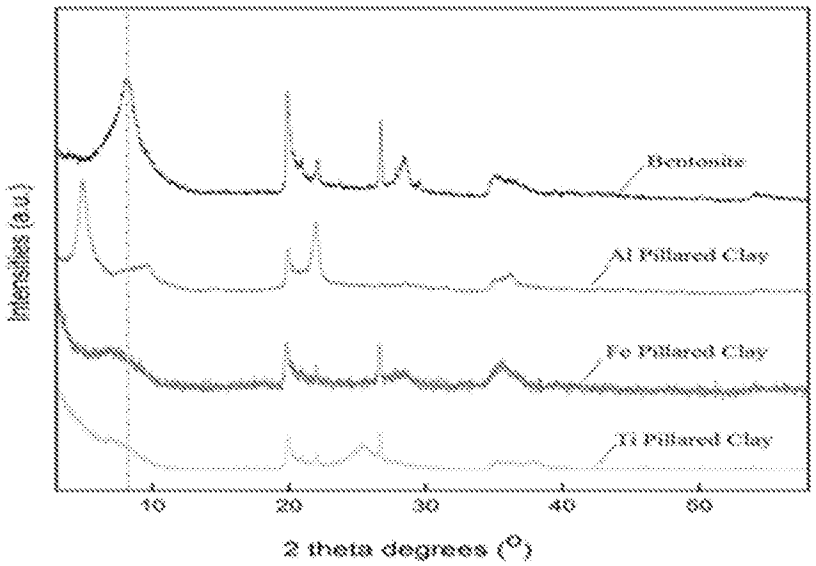


Figure 5

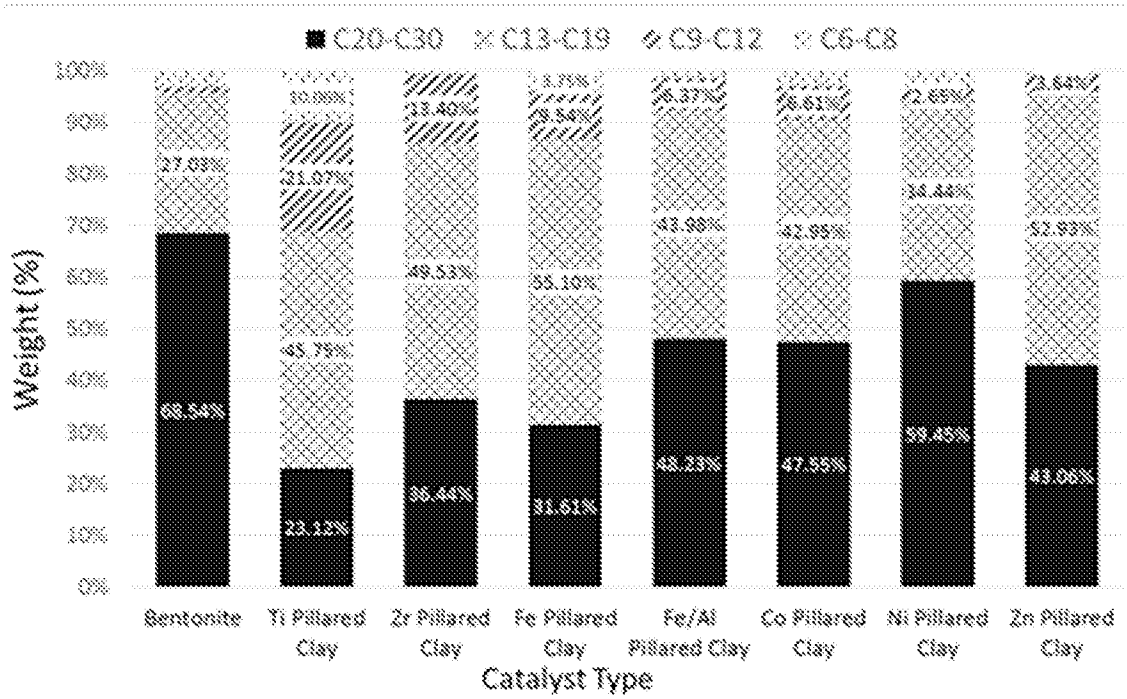


Figure 6

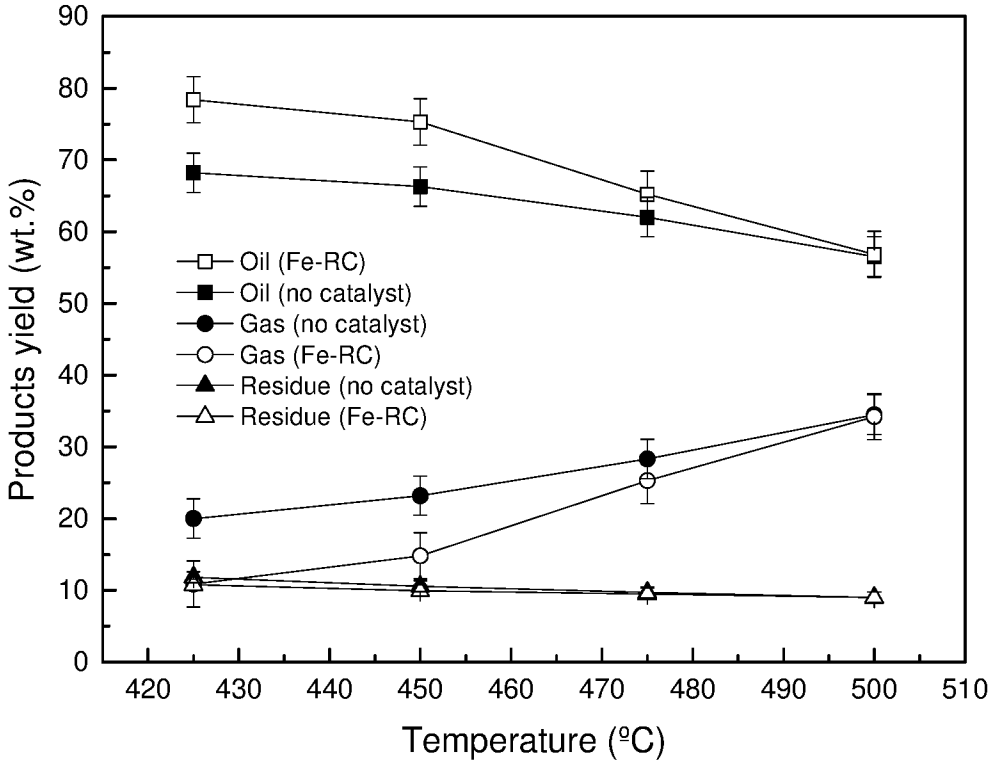
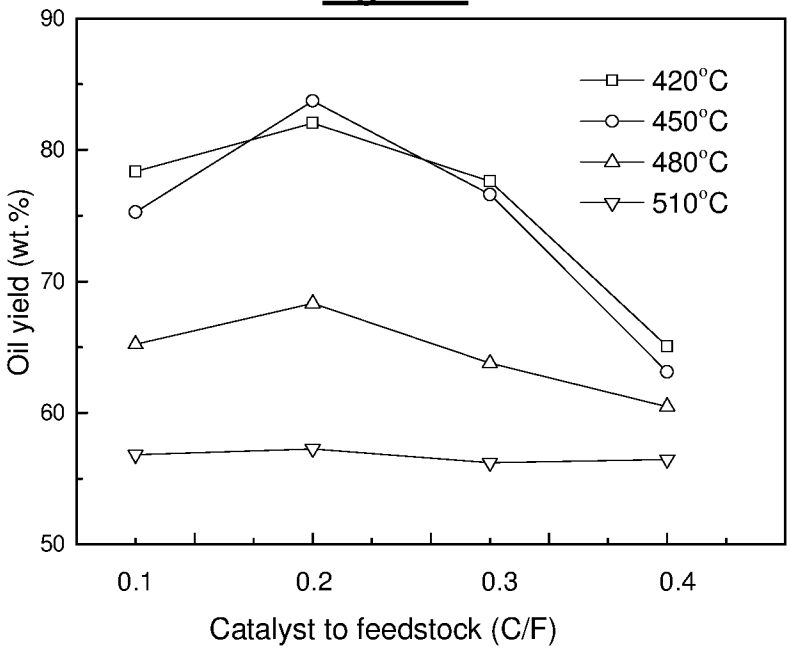


Figure 7



INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050200

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J, B09B, C08J, C10B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: EPODOC, WPIAP, FAMPAT
Keywords: Pillared clay, bridged clay, intercalated, smectites, bentonite, iron, titanium, zirconium, cobalt, nickel, zinc, pyrolysis, plastics, polyethylene, polypropylene, polystyrene and related terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE STEFANIS, A. ET AL., Catalytic pyrolysis of polyethylene: A comparison between pillared and restructured clays. *Journal of Analytical and Applied Pyrolysis*, 7 June 2013, Vol. 104, pages 479-484 [Retrieved on 2016-06-07] <DOI:10.1016/J.JAAP.2013.05.023> see abstract, page 481 left column paragraph 7, Table 1, Figure 2 (bottom)	1-14, 18-20
X	JP 2000-219884 A (WATANABE SEISAKUSHO KK ET AL.) 8 August 2000 see [0001], [0008], [0013], [0014], [0017]-[0019], [0034]-[0038] in the machine translation	1-14, 18-20
X	US 2006/0076299 A1 (FENG, J. ET AL.) 13 April 2006 see [0016], [0035], [0054]-[0058]	1-17

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07/06/2016 *(day/month/year)*	14/06/2016 *(day/month/year)*

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050200

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4665044 A (PINNAVAIA, T. J. ET AL.) 12 May 1987 see column 2 line 55-66, column 4 line 33 - column 5 line 50, Table 1 & 2	1-17
X	US 5415850 A (YANG, R. T. ET AL.) 16 May 1995 see abstract, column 7 line 53 - column 8 line 60, column 9 line 23-39 & line 52-68, Table 1	1-17
X	US 6521559 B1 (LONG, R. ET AL.) 18 February 2003 see column 3 line 29-44, column 4 line 15-65	1-17
X	US 6475944 B1 (YANG, H.-S. ET AL.) 5 November 2002 see column 5 line 10-45, Table 1	1-17
X	US 5037787 A (LANDAU, S. D. ET AL.) 6 August 1991 see column 1 line 6-10, column 4 line 16-41, column 7 line 28-43	1-5
X	US 4666877 A (VAUGHAN, D. E. W.) 19 May 1987 see column 1 line 8-12, claims 1, 6 and 11	1, 3-5
X	US 5364980 A (KERBY, M. C. ET AL.) 15 November 1994 see column 6 line 35 - column 7 line 25	1, 3-5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2016/050200

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2000-219884 A	08/08/2000	NONE	
US 2006/0076299 A1	13/04/2006	NONE	
US 4665044 A	12/05/1987	US 4629712 A US 4665045 A	16/12/1986 12/05/1987
US 5415850 A	16/05/1995	NONE	
US 6521559 B1	18/02/2003	NONE	
US 6475944 B1	05/11/2002	DE 10015696 A1	25/10/2001
US 5037787 A	06/08/1991	NONE	
US 4666877 A	19/05/1987	AT 80326 T DE 3686719 T2 EP 0256185 A1	15/09/1992 01/07/1993 24/02/1988
US 5364980 A	15/11/1994	NONE	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2016/050200

Supplemental Box
(Classification of Subject Matter)

Int. Cl.
B01J 29/04 (2006.01)
B01J 21/16 (2006.01)
B01J 23/06 (2006.01)
B01J 23/40 (2006.01)
B01J 23/74 (2006.01)