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(54) Title: CONVERSION OF PLASTICS TO OLEFIN AND AROMATIC PRODUCTS

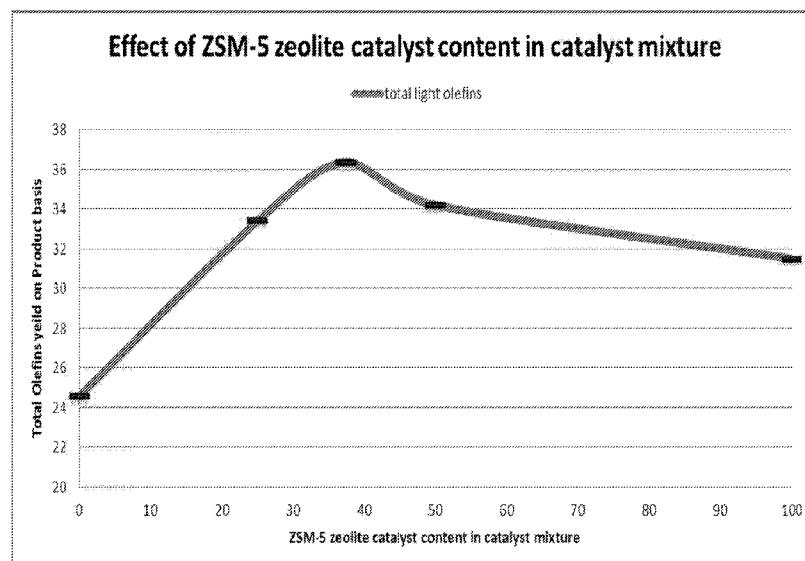


FIGURE 1

(57) **Abstract:** A catalyst composition useful for producing olefins and aromatic compounds from a feedstock is formed from a fluidized catalytic cracking (FCC) catalyst and a ZSM-5 zeolite catalyst, wherein the amount of ZSM-5 zeolite catalyst makes up from 10 wt.% or more by total weight of the FCC catalyst and the ZSM-5 zeolite catalyst. The catalyst composition may be used in a method of producing olefins and aromatic compounds from a feedstock by introducing a hydrocarbon feedstock and the catalyst composition within a reactor, at least a portion of the reactor being at a reactor temperature of 550°C or higher. The feedstock and catalyst composition are introduced into the reactor at a catalyst-to-feed (C/F) ratio of from 6 or greater.

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CONVERSION OF PLASTICS TO OLEFIN AND AROMATIC PRODUCTS

TECHNICAL FIELD

[0001] The invention relates to the conversion of plastics to olefin and aromatics through pyrolysis.

BACKGROUND

[0002] Waste plastics are mostly diverted to landfills or are incinerated, with a smaller fraction being diverted to recycling. Over the years, with increased regulations and levies on landfills, the percentage of the post-consumer waste being recycled or incinerated for energy recovery is gradually increasing. The 2009 statistics by Plastics Europe indicate that approximately 24.4 million tons of waste plastics were generated in Europe. Of this, 54% was treated either through recycling (22.6%) or energy recovery (31.3%). Plastics diverted to landfills were approximately 46.1%. Thus, waste plastics disposal into landfills is becoming increasingly difficult.

[0003] Pyrolysis of waste plastics to products like naphtha, ethylene, propylene, and aromatics can be classified under the category of feedstock recycling of waste plastics. With the naphtha prices increasing dramatically, steam crackers operating on naphtha feed are at a disadvantageous position compared to steam crackers operating on cheaper gaseous hydrocarbon feeds. If a portion of the naphtha feed to the steam crackers is replaced by an equivalent amount of products from plastics conversion processes, like pyrolysis, the economic situation for the steam crackers operating on naphtha feed will improve.

[0004] In order to make an impact on the economics of very large volumes in continuous steam cracker plant operations, it is necessary that the pyrolysis process is also continuous. No large scale plants exist today that directly convert waste plastics in a single step to petrochemicals. Previous attempts around the world have been focused on generation of liquid fuels from waste plastics. These plants were small in scale or modular in nature. Reactions carried out in such small scale plants are also carried out for longer residence times, making them less suitable for continuous operations on larger scales. Some earlier attempts have also focused at generating feedstocks for steam crackers from waste plastics. These rely on the availability of

steam cracker furnaces for being successful, however. Furthermore, conversion of these produced steam cracker feeds in cracker furnaces would typically result in production of high amounts of methane, which is undesirable.

[0005] What is therefore needed is a process for the conversion of plastics directly to petrochemical products, such as olefins and aromatics, that minimize formation of methane, and that maximizes the yield of olefins and aromatics.

SUMMARY

[0006] A method of producing olefins and aromatic compounds from a feedstock is carried out by introducing a hydrocarbon feedstock and a catalyst composition within a reactor, with at least a portion of the reactor being at a reactor temperature of 550°C or higher. The catalyst composition is a fluidized catalytic cracking (FCC) catalyst and a ZSM-5 zeolite catalyst, wherein the amount of ZSM-5 zeolite catalyst makes up from 10 wt.% or more of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst. The feedstock and catalyst composition are introduced into the reactor at a catalyst-to-feed ratio of from 6 or greater. At least a portion of the feedstock is allowed to be converted to at least one of olefins and aromatic compounds within the reactor. A product stream is removed containing said at least one of olefins and aromatic compounds from the reactor.

[0007] In certain specific embodiments the FCC catalyst comprises at least one of an X-type zeolite, a Y-type zeolite, a USY-zeolite, mordenite, faujasite, nano-crystalline zeolites, MCM mesoporous materials, SBA-15, a silico-alumino phosphate, a gallophosphate, and a titanophosphate.

[0008] The FCC catalyst may also comprise at least one of a Y-zeolite and a USY-zeolite embedded in a matrix, with the FCC catalyst having a total surface area of from 100 m²/g to 400 m²/g, coke deposition in an amount of from 0 to 0.5% by weight.

[0009] In some applications the FCC catalyst is a non-fresh FCC catalyst having from greater than 0 to 0.5% by weight of coke deposition. In certain embodiments, the FCC catalyst may have a total surface area of from 100 m²/g to 200 m²/g.

[0010] In some embodiments, the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 10 wt.% to 50 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst. In other embodiments, the amount of ZSM-5

zeolite catalyst of the catalyst composition makes up from 30 wt.% to 45 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst.

[0011] In certain instances, the reactor may be operated wherein said at least a portion of the reactor is at a reactor temperature of 570°C to 730°C. The reactor may be at least one of a fluidized bed reactor, bubbling bed reactor, slurry reactor, rotating kiln reactor, and packed bed reactor in some embodiments.

[0012] In some applications, the feedstock and catalyst composition may be introduced into the reactor at a catalyst-to-feed ratio of from 8 or greater. The feedstock may be at least one of polyolefins, polyethylene, polypropylene, polystyrene, polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamide, polycarbonate, polyurethane, polyester, natural and synthetic rubber, tires, filled polymers, composites, plastic alloys, plastics dissolved in a solvent, biomass, bio oils, and petroleum oils.

[0013] In another aspect of the invention, a catalyst composition useful for producing olefins and aromatic compounds from a hydrocarbon feedstock is provided. The catalyst composition comprises a mixture of fluidized catalytic cracking (FCC) catalyst and a ZSM-5 zeolite catalyst, wherein the amount of ZSM-5 zeolite catalyst makes up from 10 wt.% to 50 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst.

[0014] In certain more specific embodiments, the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 30 wt.% to 45 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst.

[0015] The FCC catalyst may comprise at least one of a Y-zeolite and a USY-zeolite embedded in a matrix in some applications, with the FCC catalyst having a total surface area of from 100 m²/g to 400 m²/g, coke deposition in an amount of from 0 to 0.5% by weight. In other applications, the FCC catalyst comprise at least one of an X-type zeolite, a Y-type zeolite, a USY-zeolite, mordenite, faujasite, nano-crystalline zeolites, MCM mesoporous materials, SBA-15, a silico-alumino phosphate, a gallophosphate, and a titanophosphate.

[0016] The FCC catalyst may be a non-fresh FCC catalyst having from greater than 0 to 0.5% by weight of coke deposition. In some instances, the non-fresh FCC catalyst may have a total surface area of from 100 to 200 m²/g.

[0017] In some embodiments, the FCC catalyst comprises at least one of a Y-zeolite and a USY-zeolite embedded in a matrix, with the FCC catalyst having a total surface area of from 100 m²/g to 400 m²/g. In certain instances, such FCC catalyst may be a non-fresh catalyst having from greater than 0 to 0.5% by weight of coke deposition. Such FCC catalyst may further have a total surface area of from 100 m²/g to 200 m²/g in some embodiments.

[0018] In certain applications, the FCC catalyst comprises at least one of a Y-zeolite and a USY-zeolite, with said at least one of a Y-zeolite and a USY-zeolite and the ZSM-5 zeolite catalyst each being embedded in the same matrix.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] For a more complete understanding of the present invention, reference is now made to the following descriptions taken in conjunction with the accompanying figures, in which:

[0020] FIGURE 1 is a plot of light gas olefin yields versus ZSM-5 zeolite catalyst content of catalyst compositions used in pyrolysis conversion of a plastic feedstock;

[0021] FIGURE 2 is a plot of light gas olefin yields versus reactor temperatures in pyrolysis conversion of a plastic feedstock using a catalyst composition of the invention;

[0022] FIGURE 3 is a plot of different light gas olefin yields versus ZSM-5 zeolite catalyst content of catalyst compositions used in pyrolysis conversion of a plastic feedstock;

[0023] FIGURE 4 is a plot of different light gas olefin yields versus reactor temperatures in pyrolysis conversion of a plastic feedstock using a catalyst composition of the invention;

[0024] FIGURE 5 is a plot of methane and ethylene yields versus ZSM-5 zeolite catalyst content of catalyst compositions used in pyrolysis conversion of a plastic feedstock;

[0025] FIGURE 6 is a plot of methane and ethylene yields versus reactor temperatures in pyrolysis conversion of a plastic feedstock using a catalyst composition of the invention;

[0026] FIGURE 7 is a plot of heavy liquid product yields versus ZSM-5 zeolite catalyst content of catalyst compositions used in pyrolysis conversion of a plastic feedstock;

[0027] FIGURE 8 is a plot of heavy liquid product yields versus reactor temperatures in pyrolysis conversion of a plastic feedstock using a catalyst composition of the invention;

[0028] FIGURE 9 is a plot of aromatic yields versus ZSM-5 zeolite catalyst content of catalyst compositions used in pyrolysis conversion of a plastic feedstock;

[0029] FIGURE 10 is a plot of aromatic yields versus reactor temperatures in pyrolysis conversion of a plastic feedstock using a catalyst composition of the invention;

[0030] FIGURE 11 is a plot of coke yield versus ZSM-5 zeolite catalyst content of catalyst compositions used in pyrolysis conversion of a plastic feedstock; and

[0031] FIGURE 12 is a plot of coke yield versus reactor temperatures in pyrolysis conversion of a plastic feedstock using a catalyst composition as disclosed herein.

DETAILED DESCRIPTION

[0032] As described herein, plastics and other hydrocarbons are converted through pyrolysis to monomers with high yields of light gas olefins (e.g., ethylene, propylene, and butenes) and aromatics, with low yields of methane. The conversion can be accomplished with a low residence time (on the order of seconds) making it ideally suited for large scale commercial operations.

[0033] The process utilizes fluid catalytic cracking (FCC) catalysts and a ZSM-5 zeolite catalyst additive that are used in combination with one another in a catalyst composition to facilitate the pyrolytic conversion of the plastic or hydrocarbon feed. The FCC catalysts are those useful in the cracking of petroleum feeds. Such petroleum feeds may include vacuum gas oil (350-550°C boiling range), atmospheric gas oil and diesel (220-370°C boiling range), naphtha (<35°C to 220°C boiling range) or residues (boiling at >550°C range) from a crude oil atmospheric and vacuum distillation units or the various such streams generated from all secondary processes in refineries including hydrotreating, hydrocracking, coking, visbreaking, solvent deasphalting, fluid catalytic cracking, naphtha reforming and such or their variants. The FCC catalysts are typically composed of large pore molecular sieves or zeolites.

Large pore zeolites are those having an average pore size of from 7 Å or more, more typically from 7 Å to about 10 Å. Suitable large pore zeolites for FCC catalysts may include X-type and Y-type zeolites, mordenite and faujasite, nano-crystalline Zeolites, MCM mesoporous materials (MCM-41, MCM-48, MCM-50 and other mesoporous materials), SBA-15 and silico-alumino phosphates, gallophosphates, and titanophosphates. Particularly useful are Y-type zeolites.

[0034] In Y-type zeolites used for FCC catalysts, the silica and alumina tetrahedral are connected by oxygen linkages. In order to impart thermal and hydrothermal stability, the Y-zeolite may be subjected to treatment to knock off some framework alumina (one of these routes is steaming at high temperature). Typically Y-zeolites have Si/Al ratio of about 2.5:1. The dealuminated Y-zeolite typically has a Si/Al ratio of 4:1 or more. The dealuminated Y-zeolite, with a higher framework Si/Al ratio, has stronger acid sites (isolated acid sites) and is thermally and hydrothermally more stable and is thus called ultrastable Y-zeolite (USY-zeolite). In units like fluid catalytic cracking where the catalysts see temperatures of 700°C and also moisture in a catalyst regenerator, the thermal and hydrothermal stability is important so that catalyst activity is maintained over a longer period of time. Hence, in such types of operation USY-zeolite may be the preferred FCC catalyst.

[0035] The ultrastable zeolites may also be rare-earth-exchanged. The rare-earth content may be higher than 0% and may be as high as 10% by weight of the zeolite, with from 0.1-3% by weight of zeolite being typical. The higher the rare earth content, however, the more olefinicity of the products is lost by favoring hydrogen transfer reactions to make paraffins. Some amount of rare earth in the zeolite Y may be useful because it imparts stability to the zeolite. The rare earth materials may include cerium, lanthanum, and other rare earth materials.

[0036] It should be understood that with respect to any concentration or amount range listed or described in the summary and detailed description as being useful, suitable, or the like, it is intended to include every concentration or amount within the range, including the end points, and is to be considered as having been specifically stated. For example, “a range of from 1 to 10” is to be read as indicating each and every possible number along the continuum from about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a specific few, it is to be understood that the

inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that the inventors are in possession of the entire range and all points within the range.

[0037] The FCC catalysts are typically the aforementioned zeolites embedded in an active matrix. The matrix may be formed from an active material, such as an active alumina material that could be amorphous or crystalline, a binder material, such as alumina or silica, and an inert filler, such as kaolin. The zeolite component embedded in the matrix of the FCC catalyst may make up from 10 to 90% by weight of the FCC catalyst. The FCC catalyst with the zeolite material embedded within the active matrix material may be formed by spray drying into microspheres. These catalysts are hard and have very good attrition resistance to withstand the particle-particle and particle-wall collisions that usually occur when the catalysts are fluidized. The particle size distribution for the FCC catalyst may range from greater than 0 to 150 microns. In certain embodiments, 90-95% of the particle size distribution may be within the range of from greater than 0 to 110 microns or 120 microns, with from 5-10% of the particles having particle sizes of greater than 110 microns. As a result of the distribution of particle sizes, the average or median particle size for the FCC catalyst is typically 70 to 75 microns. In certain instances, finer particles of the FCC catalyst may be used with larger particles to provide good fluidization. In certain embodiments, for example, 15% or less of the FCC catalyst may have a particle size of 40 microns or less. Good fluidization is imparted by presence of fines in a mix of fine and coarse particles. Loss of fine particles leads to de-fluidization.

[0038] The FCC catalysts may be further characterized based on certain physical, chemical, surface properties and catalytic activity. Fresh FCC catalysts have a very high surface area typically 300-400m²/g or higher and a high activity. As a result of the high activity of the fresh FCC catalyst, cracking of petroleum feeds with the fresh FCC catalyst usually results in high yields of coke, such as 8-10 wt.%, and light gas. The very high yields of coke can affect the heat balance of the reaction as all the heat generated by coke formation may not be needed for cracking. Heat removal from a reactor-regenerator system thus may be necessary. This means that the feed is not effectively utilized. It would be more economically valuable if just enough coke required for supporting the cracking process heat requirements was made, with the balance that otherwise goes into excess coke formation being used to form useful

products. Also, high yields of light gases (methane, ethane) from the fresh FCC catalyst are undesirable and may exceed the plant wet gas compressor equipment constraints or limits in an FCC complex. High yields of methane are undesirable because of its limited utility in forming chemicals (even though it is possible to form higher hydrocarbons from methane through syngas-methanol-olefins route). Ethane on the other hand may be used for making ethylene, a valuable chemical. In most cases, however, higher ethane yield is accompanied by a higher methane yield.

[0039] In order to overcome these problems, the FCC cracking unit is typically operated by maintaining a constant activity or conversion. This is done by having a circulating inventory of partially deactivated catalyst and then periodically purging a small portion of the used or non-fresh catalyst and making that up with fresh FCC catalyst. The use of used or non-fresh catalyst helps in maintaining the catalyst activity at a constant level without producing high levels of methane and coke. The circulating inventory of plant catalyst is partially deactivated or equilibrated under plant operating conditions. The portion of this catalyst that is purged out periodically is the spent catalyst. Thus in terms of catalyst activity it generally has the same activity of the circulating catalyst inventory in the FCC unit before make-up fresh catalyst is added. This catalyst make-up and purging is typically done on a regular basis in an operating FCC unit. The circulating catalyst inventory has roughly 50% or less of the surface area of the fresh catalyst and activity or conversion that is roughly 10 conversion units lower than that of fresh catalyst. In other words, if fresh catalyst were to provide a conversion of 80 wt.% of vacuum gas oil range material to dry gas (H₂-C₂), LPG (C₃-C₄), gasoline (35-220°C boiling hydrocarbons) and coke, then the circulating partially deactivated catalyst inventory could provide a conversion of 70 wt.%. The FCC fresh catalyst particles added through make-up to the circulating unit would on an average spend several days (age) in the unit before it is purged out. Thus, due to the fact that daily make-up is made to the catalyst inventory, the circulating catalyst inventory would typically have catalyst particles of different ages, i.e., there is an age distribution of catalyst particles in the inventory. The catalyst activity of a particle is proportional to its deactivation in the FCC unit which in turn is also proportional to the age of the catalyst. The following Table 1 below lists typical properties between fresh and spent FCC catalysts.

Table 1

Property	Fresh FCC Catalyst	Spent FCC Catalyst
Total surface area, m ² /g	320-360	130-170
Unit cell size, angstroms	24.4-24.7	24.2-24.4
Conversion of standard petroleum feed or activity, wt%	78-85	67-73
Ni+V, ppm	0	Typically 500-3000
Coke on the catalyst, wt%	0	0-0.5 typically
Sulfur oxide (Sox) reduction and/or Sulfur reduction additives present?	No	Yes*

* Sox and S reduction additives are usually from 10-15 wt.%. Sox and S reduction additives would not have catalyst activity for cracking and thus would dilute the catalyst activity. These additives are usually added to meet automotive fuel specification requirements for streams generated from the FCC unit and for mitigating Sox liberation to environment. Usually oxides of magnesium are used in such additives and they would be having lower or no conversion for breaking molecules and would thus reduce the ability of the FCC catalyst to convert heavier molecules to lighter molecules i.e. activity dilution.

[0040] The present invention can make use of either fresh FCC catalyst, non-fresh FCC catalyst, or a mixture of both. This may include spent FCC catalyst that is removed from the fluidized catalytic cracking process, as described previously. Because spent FCC catalyst is typically a waste product from the fluidized catalytic cracking process, its use in the conversion of plastics and other hydrocarbons to useful products is particularly advantageous. This is due to both its lower cost and availability and due to its favorable activity in not forming more coke and methane. The spent FCC catalyst is essentially “used” or “non-fresh” FCC catalyst that has been used in the fluidized catalytic cracking process and has been removed for replacement with fresh catalyst, as previously described. As used herein, the expression “non-fresh” with respect to the FCC catalyst is meant to encompass any FCC catalyst, as they have been described, that has some amount (i.e. greater than 0%) of coke deposition. Fresh FCC catalyst would have no coke deposits. In some embodiments, the coke deposition on the non-fresh FCC catalyst may be from 0.01%, 0.05%, 0.1%, 0.2%, 0.3%, 0.4% or more by weight of the catalyst. Typically, the coke deposition for the non-fresh FCC catalyst will range from greater than 0 to 0.5% by weight of the catalyst. The spent FCC catalyst may have non-fresh catalyst particles with differing degrees of catalyst coking due to differences in the catalyst ages of use in the cracking process. The non-fresh FCC catalyst also has a reduced surface area compared to fresh FCC catalyst due to catalyst hydrothermal deactivation in the FCC unit. Typical surface area for the non-fresh catalyst may range from 100 m²/g to 200

m^2/g . Additionally, in some embodiments the FCC catalyst may include a combination of non-fresh or spent FCC catalyst and fresh FCC catalyst and may be used in the pyrolysis conversion reaction.

[0041] The ZSM-5 zeolite catalyst additive used in combination with the FCC catalyst is a molecular sieve that is a porous material containing intersecting two-dimensional pore structure with 10-membered oxygen rings. Zeolite materials with such 10-membered oxygen ring pore structures are often classified as medium-pore zeolites. Such medium-pore zeolites typically have pore diameters ranging from 5.0 \AA to 7.0 \AA . The ZSM-5 zeolite is a medium pore-size zeolite with a pore diameter of from about 5.1 to about 5.6 \AA . The ZSM-5 zeolite and their preparation are described in U.S. Patent No. 3,702,886, which is herein incorporated by reference. The ZSM-5 zeolite may be free from any metal loading.

[0042] The ZSM-5 zeolite is also typically embedded in an active matrix, which may be the same or similar to those used for the zeolite of the FCC catalyst, as previously described. The matrix may be formed from an active material, such as an active alumina material, a binder material, such as alumina or silica, and an inert filler, such as kaolin.

[0043] The zeolite component embedded in the matrix of the ZSM-5 catalyst may make up from 5 to 90% by weight of the ZSM-5 zeolite catalyst and more typically 10 to 80% by weight of the ZSM-5 zeolite catalyst, and still more typically 10 to 50% by weight of the ZSM-5 zeolite catalyst. The ZSM-5 zeolite catalyst with the ZSM-5 zeolite material embedded within the active matrix material may also be formed by spray drying into microspheres. The particle size distribution for the ZSM-5 zeolite catalyst may range from greater than 0 to 150 microns. In certain embodiments, 90-95% of the particle size distribution may be within the range of from greater than 0 to 110 microns or 120 microns. The average or median particle size for the ZSM-5 zeolite catalyst is typically 70 to 75 microns. In certain instances, finer particles of the ZSM-5 zeolite catalyst may be used with larger particles to provide good fluidization. In certain embodiments, for example, 15% or less of the ZSM-5 zeolite catalyst may have a particle size of 40 microns or less.

[0044] In certain embodiments, the zeolite material (e.g. X-type zeolite or Y-type zeolite) of the FCC catalyst and the ZSM-5 zeolite may be embedded and formed within the same matrix material unit so that catalyst particles containing both the FCC

catalyst and ZSM-5 catalyst materials are formed. These particles may be of the same size and configuration as those previously described for the separate FCC catalyst and ZSM-5 zeolite catalyst. One of the advantages of combining the FCC and ZSM-5 zeolite component in a single matrix or particle is that it may result in a higher activity that can be obtained by minimizing the in-active diluents in the individual catalysts.

[0045] The catalysts selected for use in the plastic pyrolysis may have similar properties to FCC catalysts in terms of particle size distribution and attrition resistance, as these parameters may greatly influence the integrity of the catalyst recipe in an operating fluidized bed environment. Very fine particles can lead to their high losses due to their being entrained with product gases, while bigger catalyst particle sizes tend to not fluidize properly and result in non-uniform activity. In certain embodiments, however, pure forms of the FCC catalyst and the ZSM-5 zeolite without any matrix material or smaller particle sizes may be employed in systems where there is less probability of the catalyst being lost, such as in rotary kilns and slurry reactors.

[0046] In the present invention, plastic pyrolysis using the catalyst system produces valuable monomers of light gas olefins and aromatics, such as benzene, toluene, and xylenes. The process yields are tunable to the desired yields of olefins and aromatics by using a combination of the catalyst system and process operating conditions. It has been found that with a combination of FCC catalysts and ZSM-5 zeolite catalyst additive, as has been described, higher yields of olefins and aromatics can be obtained as compared to using only an FCC catalyst. Specifically, a catalyst system containing from 10 wt.% or more of ZSM-5 zeolite catalyst of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst provides increased yields of olefins and aromatics. As used herein, weight percentages of the ZSM-5 zeolite catalysts and FCC catalysts are based upon the total weight of the catalyst, including any matrix material, unless expressly stated otherwise. Where no matrix material is employed in the reactions the weight percentages of the ZSM-5 zeolite catalysts and FCC catalysts are the weight percentage of the zeolites only.

[0047] In certain embodiments, the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 10 wt.% to 50 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst. Thus, the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 10 wt.%, 15% wt.%, 20% wt.%, 25% wt.%,

30% wt.%, or 35% wt.% to 40% wt.%, 45% wt.%, or 50 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst. In still other embodiments, the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 30 wt.% to 45 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst. In further embodiments, the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 35 wt.% to 40 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst. In particular instances, it has been found that the highest yields of olefins and aromatics are produced when the ZSM-5 zeolite catalyst is used in an amount of approximately 37.5 wt.% by total weight of the FCC catalyst and the ZSM-5 zeolite catalyst.

[0048] The plastic feed used in the conversion reaction may include essentially all plastic materials, such as those formed from organic polymers. Non-limiting examples include polyolefins, such as polyethylene, polypropylene, etc., polystyrene, polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamide, polycarbonate, polyurethane, polyester, natural and synthetic rubber, tires, filled polymers, composites and plastic alloys, plastics dissolved in a solvent, etc. While plastic feeds may be used in the conversion reaction, other hydrocarbon materials may also be used as the feedstock. These hydrocarbons may include biomass, bio oils, petroleum oils, etc. Thus, while the present description is directed primarily to the conversion of plastic feeds, it should be understood that the invention has applicability to and encompasses the use of other hydrocarbons as well. When production of light gas olefins is desired, a plastic feed of polyolefins or that is primarily or contains a substantial portion of polyolefins may be preferred. Mixtures of various different plastic and hydrocarbon materials may be used without limitation.

[0049] The plastic feed may be provided in a variety of different forms. In smaller scale operations, the plastic feed may be in the form of a powder. In larger scale operations, the plastic feed may be in the form of pellets, such as those with a particle size of from 1 to 5 mm.

[0050] The catalyst and plastic feed may be mixed together prior to introduction into the reactor or may be fed separately. The amount or ratio of catalyst used to plastic feed may vary and may be dependent upon the particular system used and process conditions. Plastics can be converted using a very low or very high catalyst-to-feed (C/F) ratio. Longer contact times may be needed in the case of a low C/F ratio, while

shorter contact times may be need for a high C/F ratio. In testing, C/F ratios of from 4 to 12 were used, with C/F ratios of from 6 to 9 being most frequently used. In large scale industrial process wherein a circulating fluidized bed riser or downer may be used, the C/F ratio may be determined by the reactor heat balance or other parameters.

[0051] Various reactors may be used for the conversion process. For large scale operations, a circulating fluidized bed riser or downer reactor may be used. A bubbling bed reactor where the catalyst is bubbled in-situ, with the feed being added to the bubbling bed may also be used. Slurry-type reactors and rotating kiln-type reactors may also be used in some applications.

[0052] The catalyst composition composed of the FCC catalyst and ZSM-5 zeolite catalyst and the plastic feed are introduced (mixed or added separately) into a reactor, such as a fluidized bed reactor, as previously described. The reactor is operated at a reactor temperature wherein all or a portion of the reactor is at a temperature of 550°C or higher. In some embodiments, the reactor is operated at a reactor temperature wherein all or a portion of the reactor is at a temperature of 570°C or higher. In certain embodiments, the reactor is operated at a reactor temperature wherein all or a portion of the reactor is at a temperature of from 550°C to 730°C, more particularly from 570°C to 680°C, 690°C or 700°C. Reactor pressures may range from ambient to 50 bar(g) (5 MPa) and more typically from ambient to 3 bar(g) (0.3 MPa). Nitrogen, dry gas (H₂-C₂), steam or other inert gases or mixture of gases may be used as a carrier gas in which the catalyst and feed are entrained. A range of fluidization gas flow rates can be employed in different modes, such as bubbling fluidized bed mode, circulating fluidized bed mode, slurry tank reactor mode. Other reactor configurations and modes may also be used. In particular embodiments, a circulating fluidized mode may be used because it offers advantages on coke management, better heat transfer and contacting between feed and catalysts. The catalyst/feed ratio (C/F) can range from as low as 2 and as high as 30 and more typically in the range of 4-12.

[0053] The pyrolysis conversion of plastics to light gas olefins and aromatics may take place fairly rapidly, i.e. within a few seconds. The pyrolysis products produced include light gas olefins, such as ethylene, propylene, butenes, etc., and aromatics, such as benzene, toluene, xylenes, and ethyl benzene. These may be selectively produced in large quantities. Complete conversion of the feed plastics to various products occurs. Products produced include gases (H₂-C₄), gasoline or naphtha

(boiling point 35-220°C), diesel (boiling point 220-370°C), a small fraction of heavier stream (boiling point > 370°C) and coke. The yield of various products could be varied by using different catalyst recipe or any or all of the above mentioned parameters including contact time, fluidization flow rate and specific features of the reactor hardware, such as diameter, length or feed and/or gas distribution design or mixing/contacting related hardware modifications, recycles of products into the reactor for further conversion and such other parameters. Saturated products, such as methane, ethane, propane, and butanes, are also produced, as well as hydrogen gas (H₂). In testing, low yields of methane and butadiene were obtained (<2 wt.% and 0.5 wt.%, respectively). This indicates that even though the temperature severity employed is high (i.e. 550°C or higher), the observed activity is predominantly probably due to catalytic activity than thermal cracking. The catalyst composition can be used under conditions that successfully suppress methane formation and at the same time offer high conversions and minimize heavy products. The process also minimizes the formation of heavy liquid products, i.e., those product heavy ends boiling above 370°C.

[0054] The pyrolysis products produced can be used in a variety of processes. For example the light gas olefins formed (ethylene, propylene, and butenes) can be used in polymerization, the aromatics can be used as building blocks for derivatives or can be used as such in specific applications, the saturated gases can be cracked further to light gas olefins or can be directed to fuel gas (H₂-C₂) and LPG (C₃-C₄) pool or can be used as a fuel in the pyrolysis or any other process. The coke formed can be used as an energy source for supplying the necessary heat requirements for the pyrolysis process.

[0055] In summary, a method of producing olefins and aromatic compounds from a feedstock comprises: introducing a hydrocarbon feedstock and a catalyst composition within a reactor at least a portion of the reactor being at a reactor temperature of 550°C or higher, the catalyst composition comprising a fluidized catalytic cracking (FCC) catalyst and a ZSM-5 zeolite catalyst, wherein the amount of ZSM-5 zeolite catalyst makes up at least 10 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst, the feedstock and catalyst composition being introduced into the reactor at a catalyst-to-feed ratio of from 6 or greater; allowing at least a portion of the feedstock to be converted to at least one of olefins and aromatic compounds

within the reactor; and removing a product stream containing said at least one of olefins and aromatic compounds from the reactor. In the foregoing method, at least one of the following conditions applies: the FCC catalyst is comprised of at least one of an X-type zeolite, a Y-type zeolite, a USY-zeolite, mordenite, faujasite, nanocrystalline zeolites, MCM mesoporous materials, SBA-15, a silico-alumino phosphate, a gallophosphate, and a titanophosphate, more preferably wherein the FCC catalyst is comprised of at least one of a Y-zeolite and a USY-zeolite embedded in a matrix, the FCC catalyst having a total surface area of from 100 m²/g to 400 m²/g, coke deposition in an amount of from 0 to 0.5% by weight; the FCC catalyst is a non-fresh FCC catalyst having from greater than 0 to 0.5% by weight of coke deposition; the FCC catalyst has a total surface area of from 100 m²/g to 200 m²/g; the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 10 wt.% to 50 wt.% by total weight of the FCC catalyst and the ZSM-5 zeolite catalyst; the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 30 wt.% to 45 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst; said at least a portion of the reactor is at a reactor temperature of 570°C to 730°C; the feedstock and catalyst composition are introduced into the reactor at a catalyst-to-feed ratio of from 8 or greater; the feedstock comprises at least one of polyolefins, polyethylene, polypropylene, polystyrene, polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamide, polycarbonate, polyurethane, polyester, natural and synthetic rubber, tires, filled polymers, composites, plastic alloys, plastics dissolved in a solvent, biomass, bio oils, and petroleum oils; and the reactor is at least one of a fluidized bed reactor, bubbling bed reactor, slurry reactor, rotating kiln reactor, and packed bed reactor.

[0056] In any of the foregoing embodiment, a catalyst composition useful for producing olefins and aromatic compounds from a hydrocarbon feedstock comprises a mixture of fluidized catalytic cracking (FCC) catalyst and a ZSM-5 zeolite catalyst, wherein the amount of ZSM-5 zeolite catalyst makes up from 10 wt.% to 50 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst, preferably wherein the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 30 wt.% to 45 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst, more preferably wherein the FCC catalyst is comprised of at least one of a Y-zeolite and a USY-zeolite embedded in a matrix, the FCC catalyst having a

total surface area of from 100 m²/g to 400 m²/g, coke deposition in an amount of from 0 to 0.5% by weight; and wherein at least one of the following conditions is met: the FCC catalyst is comprised of at least one of an X-type zeolite, a Y-type zeolite, a USY-zeolite, mordenite, faujasite, nano-crystalline zeolites, MCM mesoporous materials, SBA-15, a silico-alumino phosphate, a gallophosphate, and a titanophosphate; the FCC catalyst is a non-fresh FCC catalyst having from greater than 0 to 0.5% by weight of coke deposition, the non-fresh FCC catalyst preferably having a total surface area of from 100 to 200 m²/g; the FCC catalyst is comprised of at least one of a Y-zeolite and a USY-zeolite embedded in a matrix, the FCC catalyst preferably having a total surface area of from 100 m²/g to 400 m²/g; the FCC catalyst is a non-fresh catalyst having from greater than 0 to 0.5% by weight of coke deposition, preferably wherein the FCC catalyst has a total surface area of from 100 m²/g to 200 m²/g; and the FCC catalyst is comprised of a of at least one of a Y-zeolite and a USY-zeolite, with said at least one of a Y-zeolite and a USY-zeolite and the ZSM-5 zeolite catalyst each being embedded in the same matrix.

[0057] The following examples serve to further illustrate the invention.

EXAMPLES

[0058] In each of the examples presented below, an in-situ fluidized bed lab tubular reactor having a length of 783 mm and an inner diameter of 15 mm was used. The reactor was housed in a split-zone 3-zone tubular furnace with independent temperature control for each zone. The size of each zone was 9.3 inches (236.2 mm). The overall heated length of the reactor placed inside the furnace was 591 mm. The reactor wall temperature was measured at the center of each zone and was used to control the heating of each furnace zone. The reactor had a conical bottom and the reactor bed temperature was measured using a thermocouple housed inside a thermowell and placed inside the reactor at the top of the conical bottom. Also, the reactor wall temperature was measured at the conical bottom to ensure that the bottom of the reactor was hot. The reactor bottom was placed at the middle of the furnace bottom zone for minimizing the effect of furnace end cap heat losses and maintaining the reactor bottom wall temperature within a difference of 20°C of the internal bed temperature measured.

[0059] The plastic feeds were in the form of a 200 micron plastic powder. The FCC catalyst was a spent FCC catalyst obtained from an operating refinery. The FCC spent catalyst used had a residual coke on it of 0.23 wt%. The ZSM-5 zeolite catalyst used was a commercially available ZSM-5 zeolite catalyst. The plastic feed was mixed with catalyst by swirling in a cup and then fed into the reactor.

[0060] The conversion products from the reactor were collected and condensed in a condenser. The uncondensed products were collected in a gas collection vessel and the gas composition was analyzed using a refinery gas analyzer (M/s AC Analyticals B.V., The Netherlands). Liquid products were characterized for their boiling point distribution using a simulated distillation GC (M/s AC Analyticals B.V., The Netherlands). In addition a detailed hydrocarbon analysis (up to C13 hydrocarbons) was carried out using a DHA analyzer (M/s AC Analyticals B.V., The Netherlands). The coke deposited on the catalyst was determined using an IR-based CO and CO₂ analyzer. The mass balances were determined by summing the yields of gas, liquid and coke. Individual product yields were determined and reported on a normalized product basis.

EXAMPLE 1

[0061] Tests were conducted using a pure HDPE plastic feed ground to 200 microns size and a catalyst composition of 75 wt.% FCC spent catalyst and 25 wt.% of ZSM5 zeolite catalyst. The plastic feed used was 0.75 g and the dry catalyst weight used was 4.5 g. This correlates to a C/F ratio of 5.98 (~6.0). The feed and the catalyst were fed to the reactor as described above. Before charging of the feed, the bed temperature as measured by the reactor internal thermocouple was 650°C. A flow of N₂ gas at 200 Ncc/min (normal cc/min) was used as a fluidizing and carrier gas. The results are presented in Table 2.

Table 2

C/F ratio	6.0
Reaction temperature at start	650.0
Methane	1.24
% H ₂ ,C ₁ ,C ₄ yield	54.1
% Liquid yield	44.2
% Coke yield	1.7
C ₄ =, wt%	16.3
C ₃ =, wt%	19.8
C ₂ =, wt%	6.3
Total olefins	42.4

This example shows that with pure polyolefinic feed, high gas yield is possible at high temperature severity without producing high yields of methane.

EXPERIMENTAL FOR EXAMPLES 2-13

[0062] For Examples 2-13, a mixed plastic feed formed from a mixture of polyolefins, polystyrene (PS) and PET was used having the following composition set forth in Table 3. The mixed plastic was used in the form of powder and was fed to the reactor along with catalyst as described earlier. Reactor temperatures at the start of reaction are those measured inside the reactor before feed and catalyst are charged. Fluidization N₂ gas flow was 175 Ncc/min.

Table 3

Material	Amount
HDPE	19 wt.%
LDPE	21 wt.%
PP	24 wt.%
C4-LLDPE	12 wt.%
C6-LLDPE	6 wt.%
PS	11 wt.%
PET	7 wt.%

EXAMPLE 2

[0063] Spent FCC catalyst was used with varying amounts of ZSM-5 zeolite catalyst from 0 to 100 percent. The testing was conducted at a reactor temperature of 670°C set before the start of reaction. A C/F ratio of 9 was used. The experiments were carried out with 6.8 g of dry catalyst and 0.75 g of plastic feed. The total light gas olefins (i.e., C₂ to C₄) were measured. The results are presented in Figure 1 and Table 4. As can be seen from Figure 1, the highest yields of light gas olefins was achieved when the amount of ZSM-5 zeolite catalyst additive in the catalyst mixture was at around 37.5 wt.%.

Table 4

ZSM-5 zeolite catalyst content in catalyst mixture	Wt. %	0	25	37.5	50	100
C/F ratio	g/g	9.1	9	9	9	8.9
Reaction temperature at start	°C	670	670	670	670	670
Dry catalyst fed	g	6.8	6.77	6.76	6.75	6.7
Feed weight transferred	g	0.75	0.75	0.75	0.75	0.75
Total light gas olefins (C ₂ +C ₃ +C ₄) yield	Wt. %	24.5	33.4	36.4	34.2	31.5

EXAMPLE 3

[0064] Tests to determine the effect of different reactor temperatures at the start of the reaction and different C/F ratios of 6 and 9 on the production of light gas olefin yields were conducted. These experiments were carried out by employing a catalyst mixture containing 62.5 wt.% of spent FCC catalyst and 37.5 wt.% of ZSM-5 zeolite catalyst at a C/F ratio of 9 and 75 wt.% of spent FCC catalyst and 25 wt.% of ZSM-5 zeolite catalyst at a C/F ratio of 6. When the feed and catalyst was charged, the reactor temperature fell rapidly and reached a minimum value and then climbed back to its original values before the start of reaction. Most of the temperature regain occurred within one minute after charging of reactor. The results are presented in Figure 2 and Tables 5 and 6. As can be seen from Figure 2, the light gas olefin yields increased with temperature and reached a maximum value at or around 670°C. With a higher C/F ratio of 9 (Table 5), the olefin yield increased compared to the lower C/F ratio (Table 6).

Table 5

Catalyst composition	Wt.%	Spent FCC(62.5%) + ZSM-5 zeolite catalyst (37.5%)	Spent FCC(62.5%) + ZSM-5 zeolite catalyst (37.5%)	Spent FCC(62.5%) + ZSM-5 zeolite catalyst (37.5%)	Spent FCC(62.5%) ZSM-5 zeolite catalyst (37.5%)
C/F ratio	g/g	9.0	7.0	9.0	9.95
Reaction temperature at start	°C	600	623	670	700
Dry catalyst fed	g	6.76	5.22	6.76	7.46
Feed weight transferred	g	0.75	0.75	0.75	0.75
Total light gas olefins yield (C ₂ +C ₃ +C ₄)	Wt.%	28.58	31.32	36.35	34.16

Table 6

Catalyst composition	Wt.%	Spent FCC(75%) + ZSM-5 zeolite catalyst (25%)	Spent FCC(77.3%) + ZSM-5 zeolite catalyst (22.7%)	Spent FCC(75%) + ZSM-5 zeolite catalyst (25%)	Spent FCC(75%) ZSM-5 zeolite catalyst (25%)
C/F ratio	g/g	6.0	6.0	6.0	6.0
Reaction temperature at start	°C	600	630	670	700
Dry catalyst fed	g	4.49	2.99	4.49	2.99
Feed weight transferred	g	0.75	0.5	0.75	0.5
Total light gas olefins yield (C ₂ +C ₃ +C ₄)	Wt.%	28.73	30.36	31.73	30.96

EXAMPLE 4

[0065] Tests to determine the yields of different olefins as a function of catalyst composition of spent FCC catalyst with varying amounts of ZSM-5 zeolite catalyst (i.e., 0 to 100%) were conducted. The reaction was carried out at a temperature of 670°C at the start of reaction and a C/F ratio of 9. The results are presented in Figure 3 and Table 7. As can be seen in Figure 3, propylene yields were highest at a ZSM-5 zeolite catalyst content of about 37.5 wt.%.

Table 7

ZSM-5 zeolite catalyst content in the catalyst mixture	Wt.%	0	25	37.5	50	100
C/F ratio	g/g	9.07	9.0	9.0	9.0	8.92
Reaction temperature at start	°C	670	670	670	670	670
Dry catalyst fed	g	6.80	6.77	6.76	6.75	6.70
Feed weight transferred	g	0.75	0.75	0.75	0.75	0.75
C ₄ Yield =	Wt.%	11.99	13.32	13.21	12.69	10.58
C ₃ Yield =	Wt.%	10.57	14.96	16.62	15.28	14.21
C ₂ Yield =	Wt.%	1.98	5.11	6.52	6.22	6.71
Total light gas olefins yield	Wt%	24.5	33.4	36.4	34.2	31.5

EXAMPLE 5

[0066] Tests to determine the effect of starting temperatures of the yields of different olefins were conducted. The amount of ZSM-5 zeolite catalyst was at 37.5

wt.% of the catalyst mixture. The C/F ratios used are provided in Table 8. The results are presented in Figure 4 and Table 8. As can be seen in Figure 4, the highest yields were obtained at a temperature of around 670°C.

Table 8

Catalyst composition	Wt.%	Spent FCC(62.5%) + ZSM-5 zeolite catalyst (37.5%)			
C/F ratio	g/g	9.0	7.0	9.0	9.95
Reaction temperature at start	°C	600	623	670	700
Dry catalyst fed	g	6.76	5.22	6.76	7.46
Feed weight transferred	g	0.75	0.75	0.75	0.75
C ₄ Yield =	Wt.%	11.77	12.54	13.21	11.89
C ₃ Yield =	Wt.%	12.59	13.90	16.62	15.61
C ₂ Yield =	Wt.%	4.22	4.89	6.52	6.66

EXAMPLE 6

[0067] Tests were conducted at an initial reaction temperature of 670°C with varying amounts of ZSM-5 zeolite catalyst from 0% to 100% in the catalyst composition. A C/F ratio of 9 was used. Ethylene and methane yields were then measured, with the results being presented in Figure 5 and Table 9. As can be seen in Figure 5 and from Table 9, methane yields did not vary significantly over the range of ZSM-5 zeolite catalyst content for the catalyst system. In comparison, the ethylene yields increased significantly from 2 wt.% to 7 wt.%, indicating that methane yields are being suppressed under the operating conditions and the catalyst composition employed.

Table 9

ZSM-5 zeolite catalyst content in the catalyst mixture	Wt.%	0	25	37.5	50	100
C/F ratio	g/g	9.07	9.0	9.0	9.0	8.92
Reaction temperature at start	°C	670	670	670	670	670
Dry catalyst fed	g	6.80	6.77	6.76	6.75	6.70
Feed weight transferred	g	0.75	0.75	0.75	0.75	0.75
Methane	Wt.%	1.00	0.81	0.90	0.79	1.13
Ethylene	Wt.%	1.98	5.11	6.52	6.22	6.71

EXAMPLE 7

[0068] Tests to determine the effect of starting temperatures on the yields of methane and ethylene were conducted. The catalyst composition was 62.5% wt.% FCC catalyst and 37.5 wt.% ZSM-5 zeolite catalyst, using a C/F feed ratio of 9. The

results are presented in Figure 6 and Table 10. As can be seen in Figure 6, over the range of temperatures, the methane yields varied from 0.4 wt.% to 1.3 wt.%, while ethylene yields varied from 4.2 wt.% to 6.7 wt.%. Again, the yields of methane were low, showing that the combination of catalyst composition and process conditions can suppress methane yields and increase ethylene production.

Table 10

Catalyst composition	Wt.%	Spent FCC(62.5%) + ZSM-5 zeolite catalyst (37.5%)			
C/F ratio	g/g	9.0	7.0	9.0	9.95
Reaction temperature at start	°C	600	623	670	700
Dry catalyst fed	g	6.76	5.22	6.76	7.46
Feed weight transferred	g	0.75	0.75	0.75	0.75
Methane	Wt.%	0.38	0.62	0.90	1.29
Ethylene	Wt.%	4.22	4.89	6.52	6.66

EXAMPLE 8

[0069] Tests to determine the yields of heavy liquid product (i.e., liquid product with a boiling point above 370°C) as a function of catalyst composition of spent FCC catalyst with varying amounts of ZSM-5 zeolite catalyst (i.e., 0 to 100%) were conducted. The reaction was carried out at a temperature of 670°C and a C/F ratio of 9. The results are presented in Figure 7 and Table 11. As can be seen in Figure 7, above a ZSM-5 zeolite catalyst content of 50 wt.% the catalyst activity for producing heavy liquid products is not optimal. The catalyst activity gets diluted with higher amounts of ZSM-5 zeolite catalyst above this range.

Table 11

ZSM-5 zeolite catalyst content in the catalyst mixture	Wt.%	0	25	37.5	50	100
C/F ratio	g/g	9.07	9.0	9.0	9.0	8.92
Reaction temperature at start	°C	670	670	670	670	670
Dry catalyst fed	g	6.80	6.77	6.76	6.75	6.70
Feed weight transferred	g	0.75	0.75	0.75	0.75	0.75
Heavies	Wt.%	0.64	0.50	0.39	1.54	1.48

EXAMPLE 9

[0070] Tests to determine the effect of starting temperatures on the yields of heavy liquid products (i.e., liquid product with a boiling point above 370°C) were conducted. The catalyst composition was approximately 75% wt.% FCC catalyst and 25 wt.% ZSM-5 zeolite catalyst, using a C/F feed ratio of 6. The results are presented

in Figure 8 and Table 12. As shown in Figure 8, at an initial reaction temperature of around 670°C the heavy liquid product is very low, with increasing heavy liquid products being produced as the temperature is increased.

Table 12

Catalyst composition	Wt.%	Spent FCC(75%) + ZSM-5 zeolite catalyst (25%)	Spent FCC(77.3%) + ZSM-5 zeolite catalyst (22.7%)	Spent FCC(75%) + ZSM-5 zeolite catalyst (25%)	Spent FCC(75%) + ZSM-5 zeolite catalyst (25%)
C/F ratio	g/g	6.0	6.0	6.0	6.0
Reaction temperature at start	°C	600	630	670	700
Dry catalyst fed	g	4.49	2.99	4.49	2.99
Feed weight transferred	g	0.75	0.5	0.75	0.5
Heavies	Wt.%	0.22	0.11	0.11	0.66

EXAMPLE 10

[0071] Tests to determine the yields of aromatics as a function of catalyst composition of spent FCC catalyst with varying amounts of ZSM-5 zeolite catalyst (i.e., 0% to 100%) were conducted. Aromatic product content was determined in the liquid product boiling at a temperature below 240°C. The reaction was carried out at a temperature of 670°C and a C/F ratio of 6. The results are presented in Figure 9 and Table 13. As shown in Figure 9, the liquid product is rich in aromatic content, with even higher aromatic content in liquid product being achieved with a ZSM-5 zeolite catalyst content of around 25 wt.% or higher.

Table 13

Catalyst composition	Temperature, °C	Dry catalyst fed	Feed weight transferred	Aromatic content in liquid, Wt.%
100 wt.% Spent FCC	670	9.00	1.50	64.62
Spent FCC(75 wt.%) + ZSM-5 zeolite catalyst (25 wt.%)	670	8.87	1.50	75.50
Spent FCC(62.5 wt.%) + ZSM-5 zeolite catalyst (37.5 wt.%)	670	8.95	1.50	74.71
100 wt.% ZSM-5 zeolite catalyst	670	8.97	1.50	77.89

EXAMPLE 11

[0072] Tests to determine the effect of starting temperatures on the aromatics content in liquid products boiling at a temperature below 240°C were conducted. The catalyst composition was 62.5 wt.% FCC catalyst and 37.5 wt.% ZSM-5 zeolite catalyst, using a C/F feed ratio of 6. The results are presented in Figure 10 and Table 14. As can be

seen in Figure 10, higher content of aromatics in liquid product is obtained at temperatures of 635°C or higher.

Table 14

Temperature, °C	Dry catalyst fed	Feed weight transferred	Aromatics content
700	8.95	1.50	75.37
670	8.95	1.50	74.71
635	8.95	1.50	75.03
600	8.95	1.50	69.23

EXAMPLE 12

[0073] Testing was conducted to determine the coke yields based on catalyst composition. The catalyst composition used was spent FCC catalyst with varying amounts of ZSM-5 zeolite catalyst of from 0 wt.% to 100 wt.%. A C/F ratio of 9 was used and the reactor temperature was 670°C. The results are presented in Figure 11 and Table 15.

Table 15

ZSM-5 zeolite catalyst content in the catalyst mixture	Wt.%	0	25	37.5	50	100
C/F ratio	g/g	9.07	9.0	9.0	9.0	8.92
Reaction temperature at start	°C	670	670	670	670	670
Dry catalyst fed	g	6.80	6.77	6.76	6.75	6.70
Feed weight transferred	g	0.75	0.75	0.75	0.75	0.75
Coke yield	Wt.%	5.72	4.86	4.93	4.59	4.58

EXAMPLE 13

[0074] Test to determine the effect of reactor temperature at the start of the reaction on coke yields were conducted. The catalyst used was 62.5 wt.% FCC catalyst and 37.5 wt.% ZSM-5 zeolite catalyst used at a C/F feed ratio of 9. The results are presented in Figure 12 and Table 16.

Table 16

Catalyst composition, Wt.%	Spent FCC(62.5%) + ZSM-5 zeolite catalyst (37.5%)			
Reaction set temperature	700	670	635	600
Dry catalyst fed	6.75	6.76	6.77	6.80
Feed weight transferred	0.75	0.75	0.75	0.75
Coke yield, Wt.%	4.40	5.00	4.60	6.00

From Figures 11 and 12 of Examples 12 and 13, respectively, it can be seen that the coke yield varies in the region of 4 wt.% to 6 wt.%. In a large scale conversion process like a FCC unit, the heat requirement for the conversion process is met by heat generated by the combustion of coke made by the process and the unit is heat balanced. The amount of coke formation in the pyrolysis conversion process according to the invention is adequate to support the required heat to balance a large scale continuous circulating fluidized bed riser – regenerator operations and hence the coke made in the process is gainfully utilized to support the heat balance. Any deficiency in heat balance can be overcome by injecting heavies (undesired product) or cracked product in the riser (additional olefins and coke make) or firing of heavy products in regenerator (fuel) without utilizing any other auxiliary fuel.

EXAMPLE 14

[0075] Tests were conducted to determine the effect of adding feed separately from the catalyst mixture into the reactor and compared with the case when well mixed feed and catalyst were added together. In the case of separate addition of feed and catalyst, 6 gm of catalyst mixture containing 75 wt.% spent FCC catalyst and 25 wt.% ZSM-5 zeolite catalyst was charged to the reactor and the reactor temperature was allowed to stabilize. At a reaction temperature of 620°C, 1 g of the plastic feed mixture with the composition of Table 3 was charged to the reactor and the products were collected. In the second experiment, the same quantities as above of a well mixed feed and catalyst were charged into a reactor where the start of reaction temperature was 620°C. The products were collected. In both the studies the fluidization N₂ gas flow at 150 Ncc/min was employed . The results of these two studies are presented in Table 17 below.

Table 17

Product yields	Catalyst and feed charged separately	Catalyst and feed charged together
% Gas yield	45.7	47.9
% Liquid yield	50.4	48.0
% Coke yield	4.0	4.1
C4=, wt%	13.2	12.8
C3=, wt%	14.5	16.0
C2=, wt%	5.0	5.6
Total olefins	32.7	34.4

[0076] Slightly higher conversions were achieved when the feed and catalyst were mixed well and charged, although the conversions are similar. From Table 17, it is clear that for effective utilization of catalyst, it is preferable that the feed and catalyst mixing is uniform. Deeper catalyst beds may therefore not offer sufficient mixing with feed. Hence, good mixing of feed and catalyst, preferably a co-current mixing of feed and catalyst may help in better conversion of feed.

[0077] While the invention has been shown in only some of its forms, it should be apparent to those skilled in the art that it is not so limited, but is susceptible to various changes and modifications without departing from the scope of the invention. Accordingly, it is appropriate that the appended claims be construed broadly and in a manner consistent with the scope of the invention.

CLAIMS

We claim:

1. A method of producing olefins and aromatic compounds from a feedstock, the method comprising:

introducing a hydrocarbon feedstock and a catalyst composition within a reactor at least a portion of the reactor being at a reactor temperature of 550°C or higher, the catalyst composition comprising a fluidized catalytic cracking (FCC) catalyst and a ZSM-5 zeolite catalyst, wherein the amount of ZSM-5 zeolite catalyst makes up at least 10 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst, the feedstock and catalyst composition being introduced into the reactor at a catalyst-to-feed ratio of from 6 or greater;

allowing at least a portion of the feedstock to be converted to at least one of olefins and aromatic compounds within the reactor; and

removing a product stream containing said at least one of olefins and aromatic compounds from the reactor.

2. The method of claim 1, wherein:

the FCC catalyst is comprised of at least one of an X-type zeolite, a Y-type zeolite, a USY-zeolite, mordenite, faujasite, nano-crystalline zeolites, MCM mesoporous materials, SBA-15, a silico-alumino phosphate, a gallophosphate, and a titanophosphate.

3. The method of claim 1 or claim 2, wherein:

the FCC catalyst is comprised of at least one of a Y-zeolite and a USY-zeolite embedded in a matrix, the FCC catalyst having a total surface area of from 100 m²/g to 400 m²/g, coke deposition in an amount of from 0 to 0.5% by weight.

4. The method of any one of claims 1 to 3, wherein:

the FCC catalyst is a non-fresh FCC catalyst having from greater than 0 to 0.5% by weight of coke deposition.

5. The method of any one of claims 1 to 4, wherein:

the FCC catalyst has a total surface area of from 100 m²/g to 200 m²/g.

6. The method of any one of claims 1 to 5, wherein:

the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 10 wt.% to 50 wt.% by total weight of the FCC catalyst and the ZSM-5 zeolite catalyst.

7. The method of any one of claims 1 to 6, wherein:

the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 30 wt.% to 45 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst.

8. The method of any one of claims 1 to 7, wherein:

said at least a portion of the reactor is at a reactor temperature of 570°C to 730°C.

9. The method of any one of claims 1 to 8, wherein:

the feedstock and catalyst composition are introduced into the reactor at a catalyst-to-feed ratio of from 8 or greater.

10. The method of any one of claims 1 to 9, wherein:

the feedstock comprises at least one of polyolefins, polyethylene, polypropylene, polystyrene, polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamide, polycarbonate, and polyurethane, polyester, natural and synthetic rubber, tires, filled polymers, composites, plastic alloys, plastics dissolved in a solvent, biomass, bio oils, and petroleum oils.

11. The method of any one of claims 1 to 10, wherein:

the reactor is at least one of a fluidized bed reactor, bubbling bed reactor, slurry reactor, rotating kiln reactor, and packed bed reactor.

12. A catalyst composition for producing olefins and aromatic compounds from a hydrocarbon feedstock, the catalyst composition comprising:

a mixture of fluidized catalytic cracking (FCC) catalyst and a ZSM-5 zeolite catalyst, wherein the amount of ZSM-5 zeolite catalyst makes up from 10 wt.% to 50 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst.

13. The catalyst of claim 12, wherein:

the amount of ZSM-5 zeolite catalyst of the catalyst composition makes up from 30 wt.% to 45 wt.% of the total weight of the FCC catalyst and the ZSM-5 zeolite catalyst.

14. The catalyst of claim 12 or claim 13, wherein:

the FCC catalyst is comprised of at least one of a Y-zeolite and a USY-zeolite embedded in a matrix, the FCC catalyst having a total surface area of from 100 m²/g to 400 m²/g, coke deposition in an amount of from 0 to 0.5% by weight.

15. The catalyst of any one of claims 1 to 14, wherein:

the FCC catalyst is comprised of at least one of an X-type zeolite, a Y-type zeolite, a USY-zeolite, mordenite, faujasite, nano-crystalline zeolites, MCM mesoporous materials, SBA-15, a silico-alumino phosphate, a gallophosphate, and a titanophosphate.

16. The catalyst of any one of claims 1 to 15, wherein:

the FCC catalyst is a non-fresh FCC catalyst having from greater than 0 to 0.5% by weight of coke deposition.

17. The catalyst of claim 16, wherein:

the non-fresh FCC catalyst has a total surface area of from 100 to 200 m²/g.

18. The catalyst of any one of claims 1 to 17, wherein:

the FCC catalyst is comprised of at least one of a Y-zeolite and a USY-zeolite embedded in a matrix, the FCC catalyst having a total surface area of from 100 m²/g to 400 m²/g.

19. The catalyst of claim 18, wherein:

the FCC catalyst is a non-fresh catalyst having from greater than 0 to 0.5% by weight of coke deposition.

20. The catalyst of claim 19, wherein:

the FCC catalyst has a total surface area of from 100 m²/g to 200 m²/g.

21. The catalyst of any one of claims 1 to 20, wherein:

the FCC catalyst is comprised of a of at least one of a Y-zeolite and a USY-zeolite, with said at least one of a Y-zeolite and a USY-zeolite and the ZSM-5 zeolite catalyst each being embedded in the same matrix.

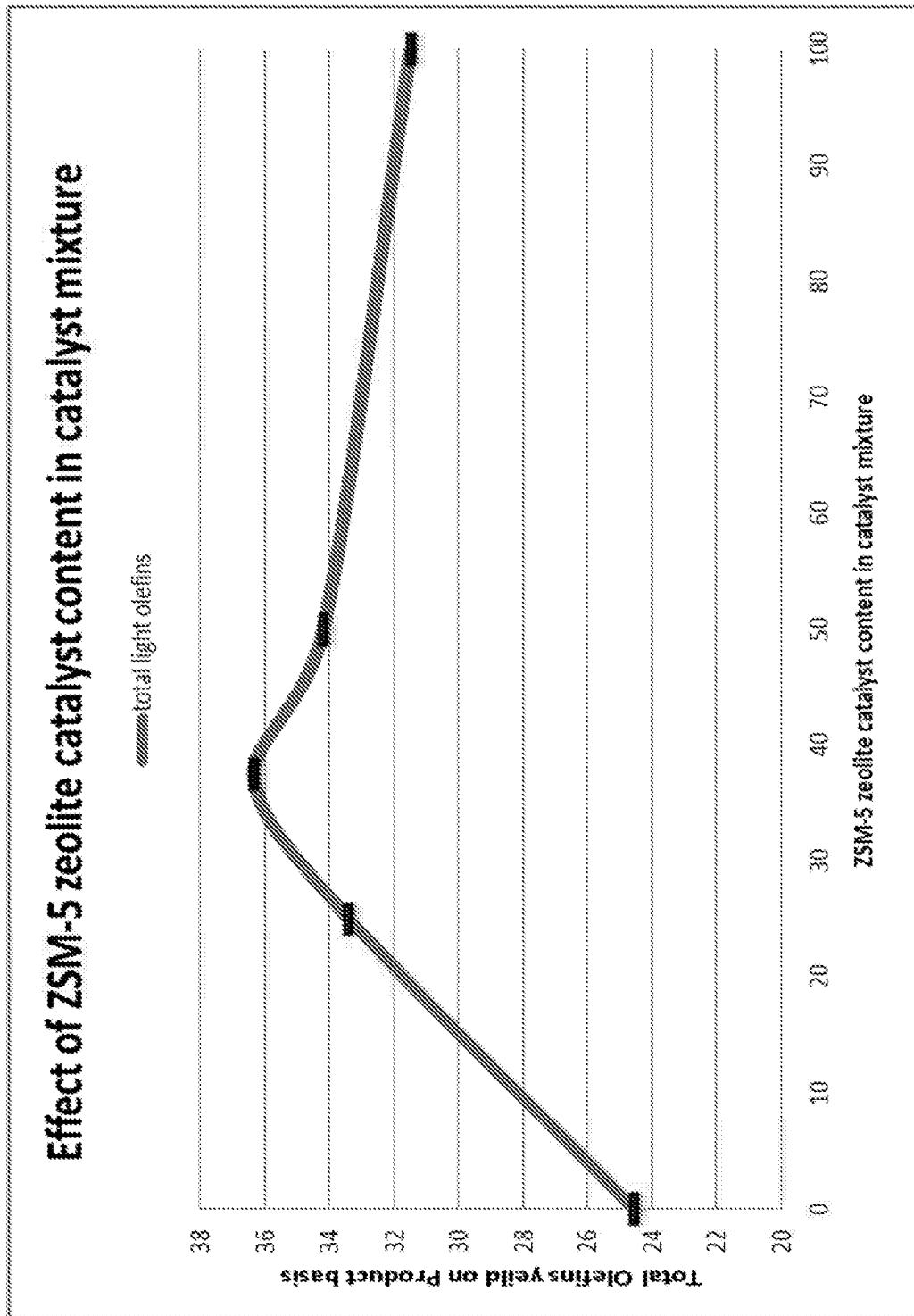


FIGURE 1

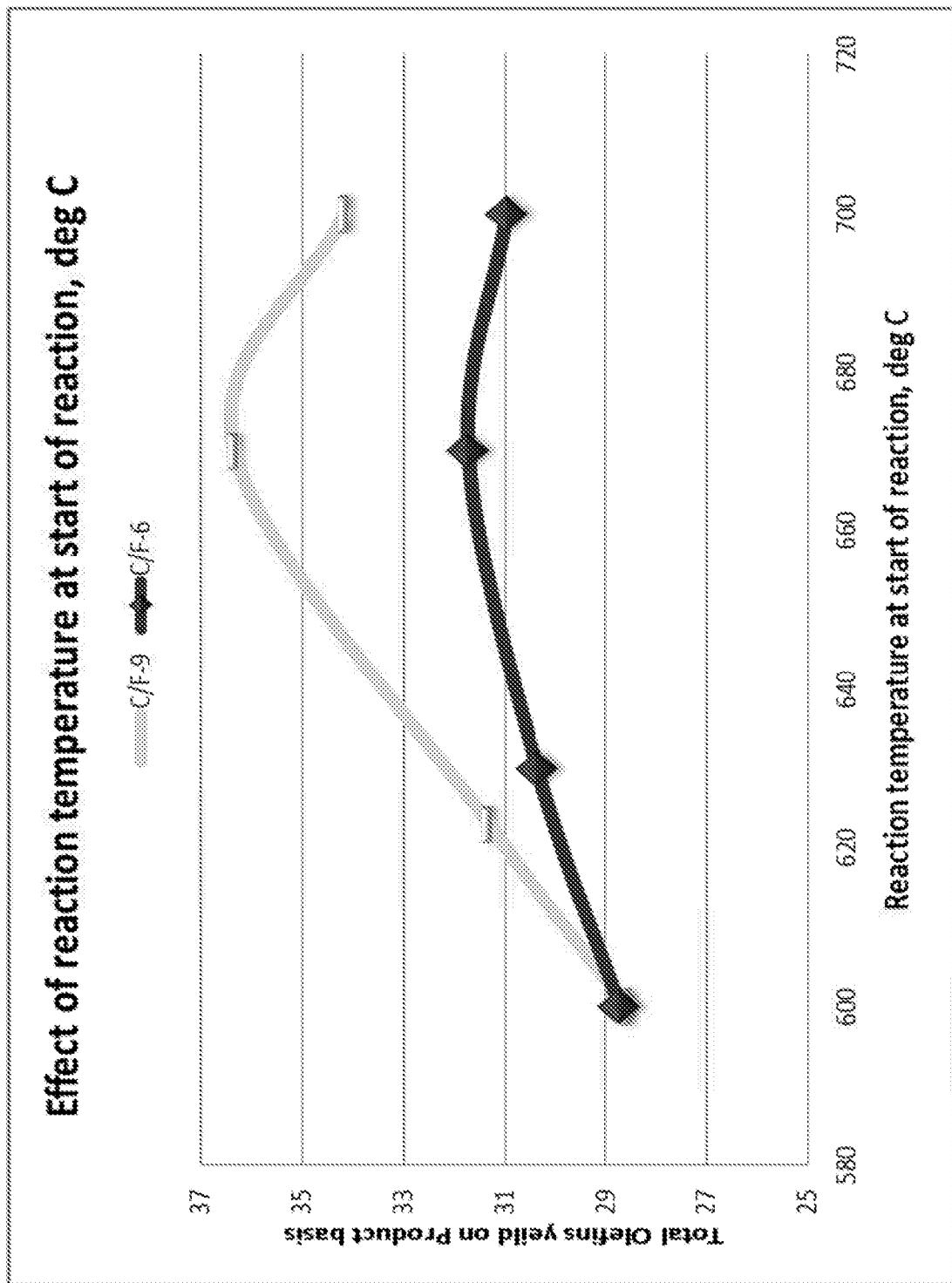


FIGURE 2

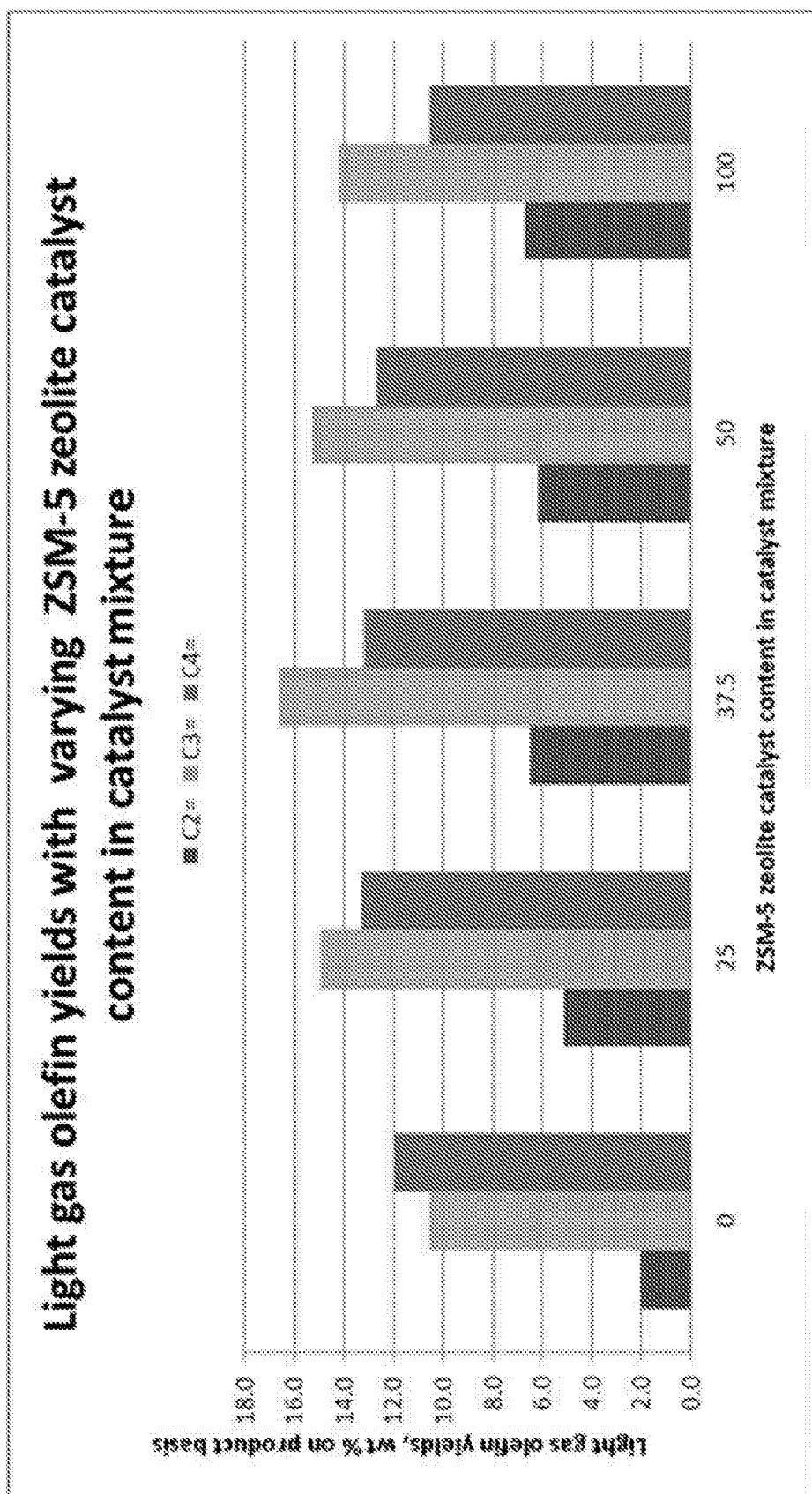


FIGURE 3

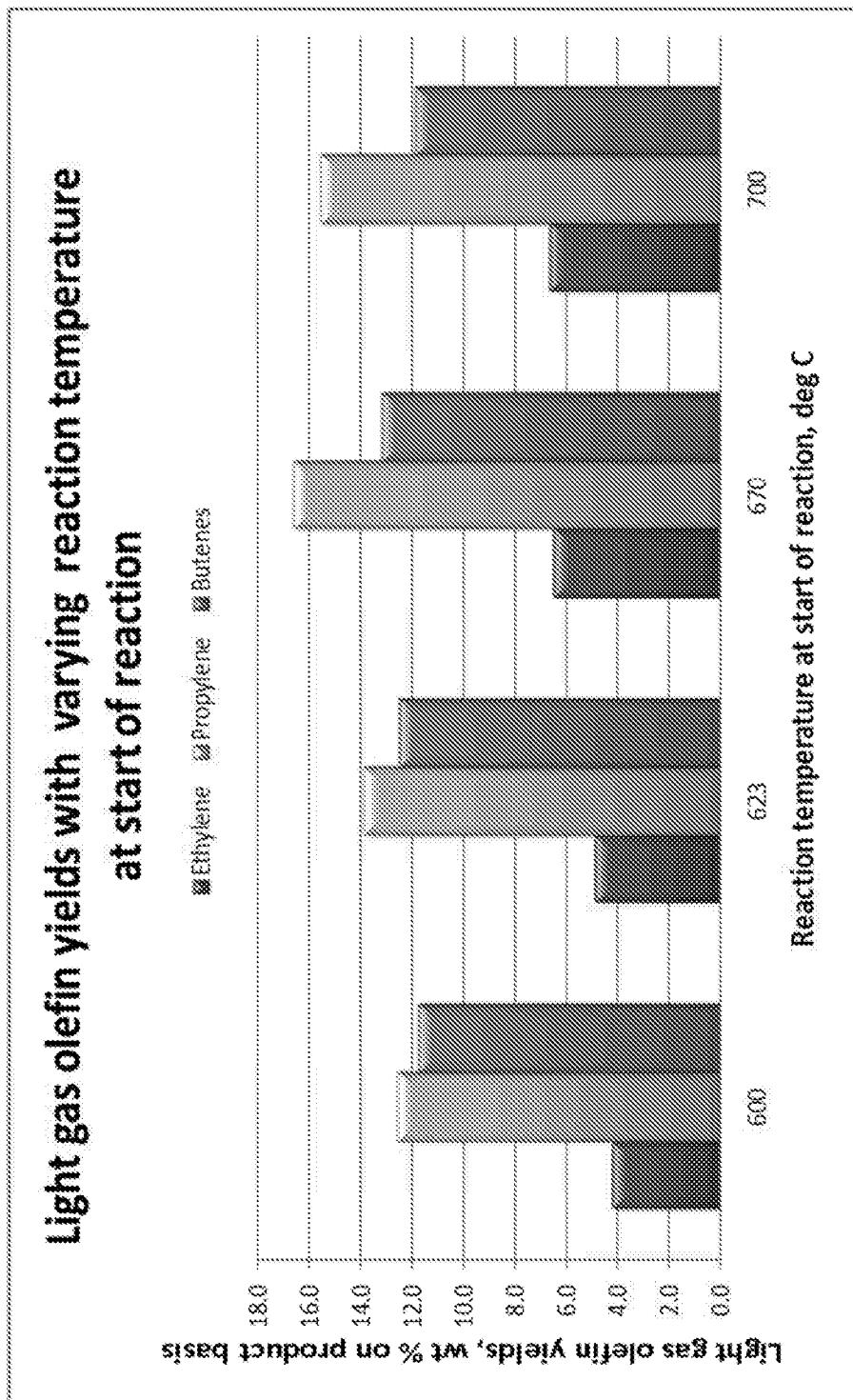


FIGURE 4

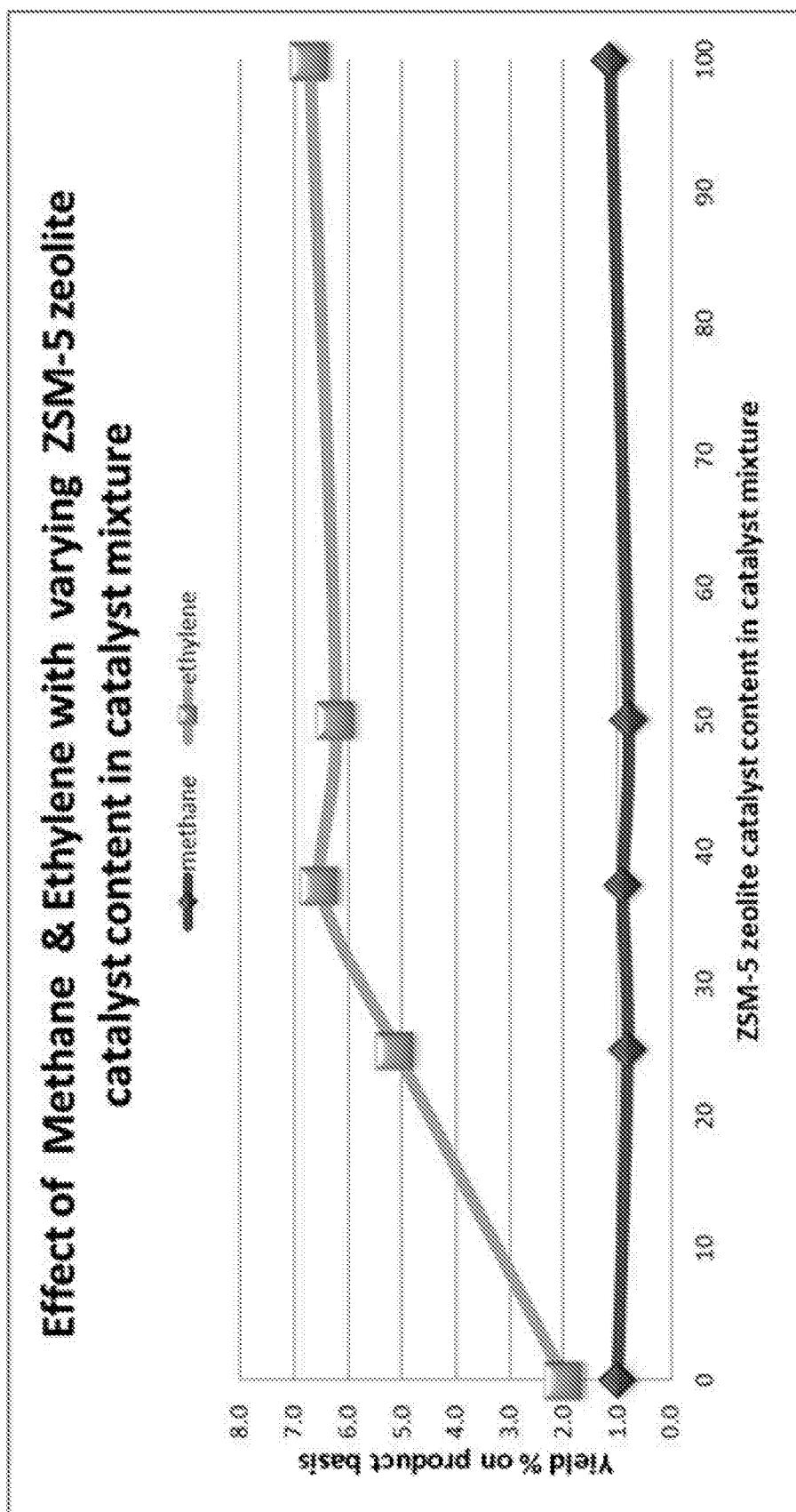
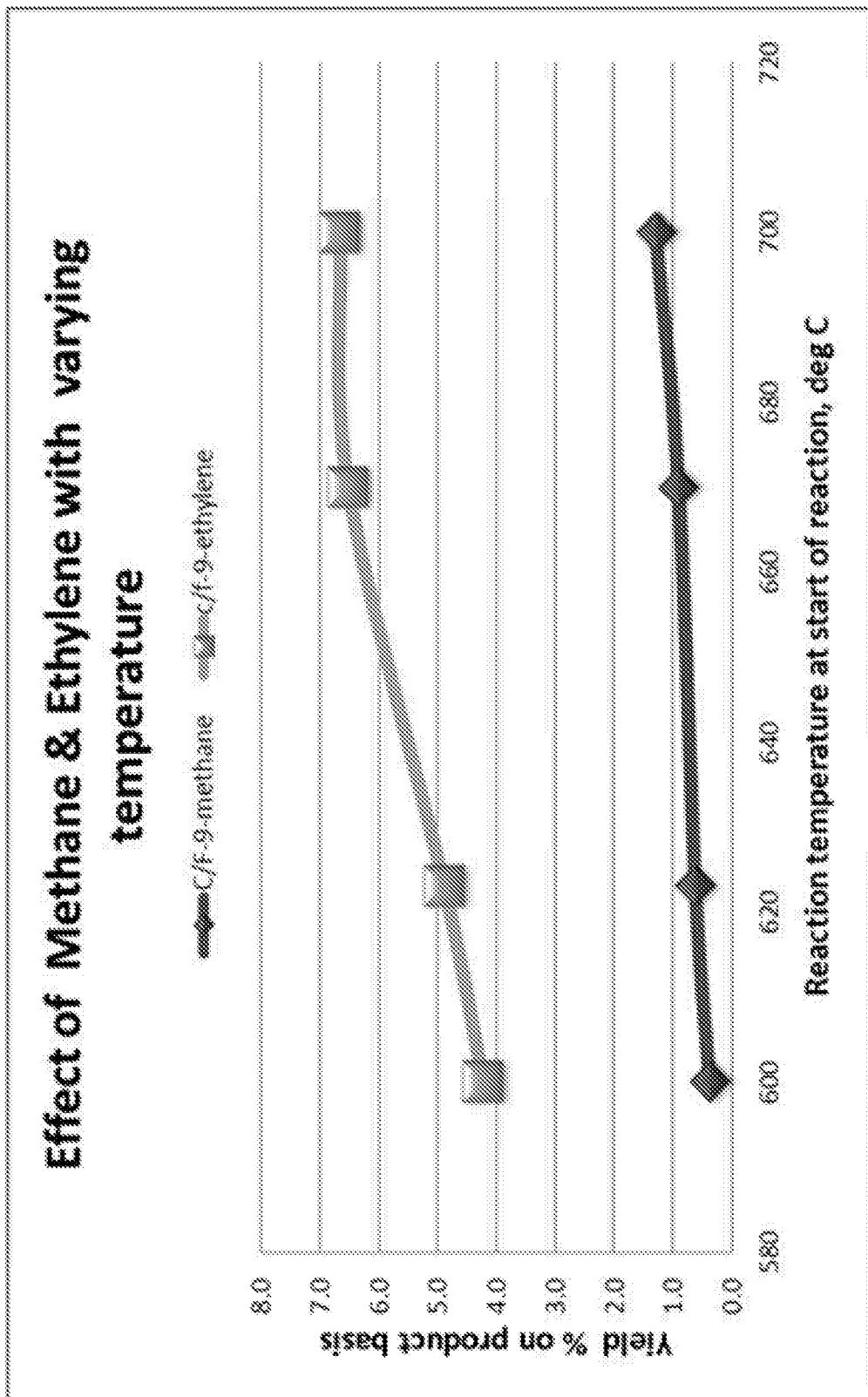


FIGURE 5



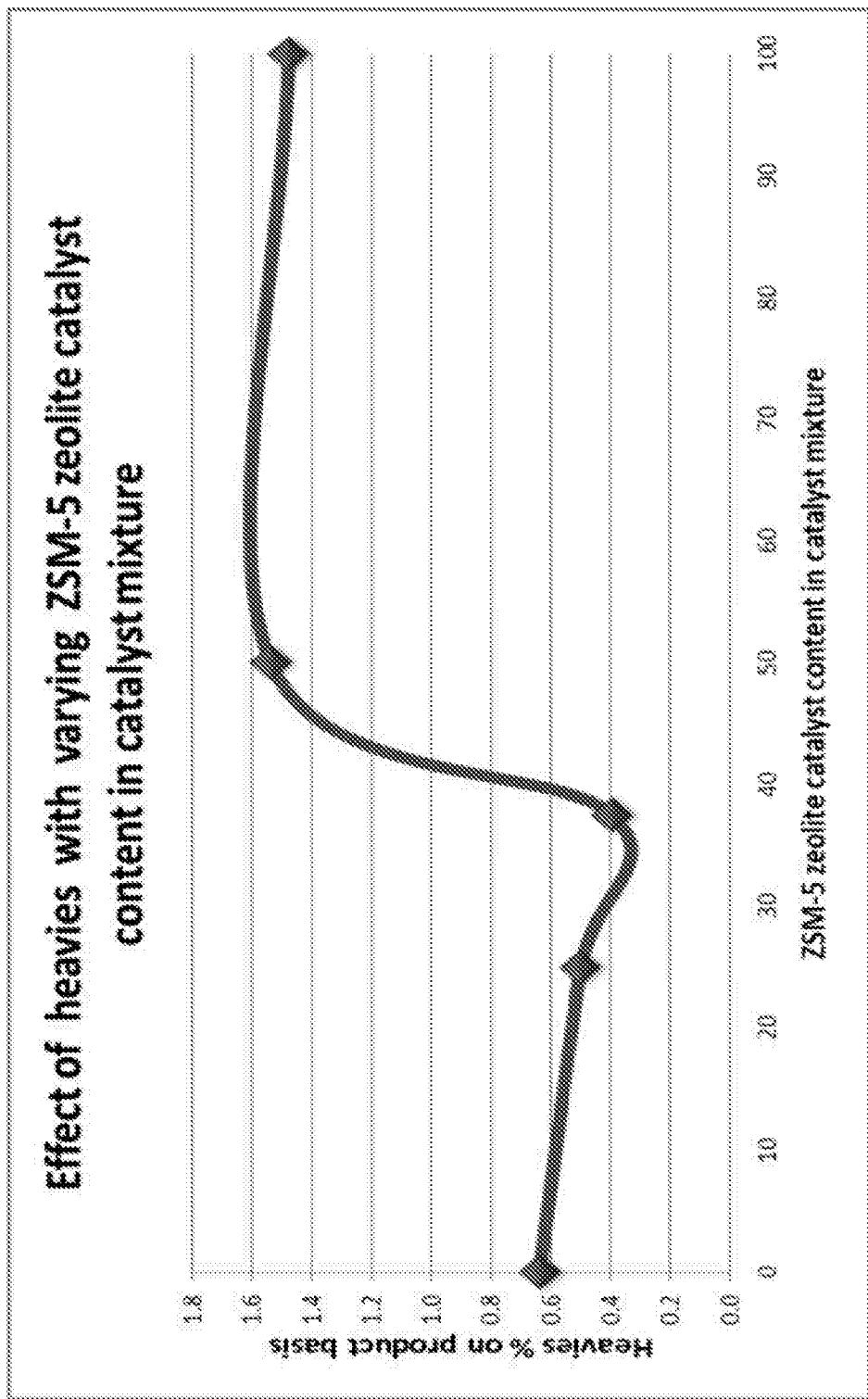


FIGURE 7

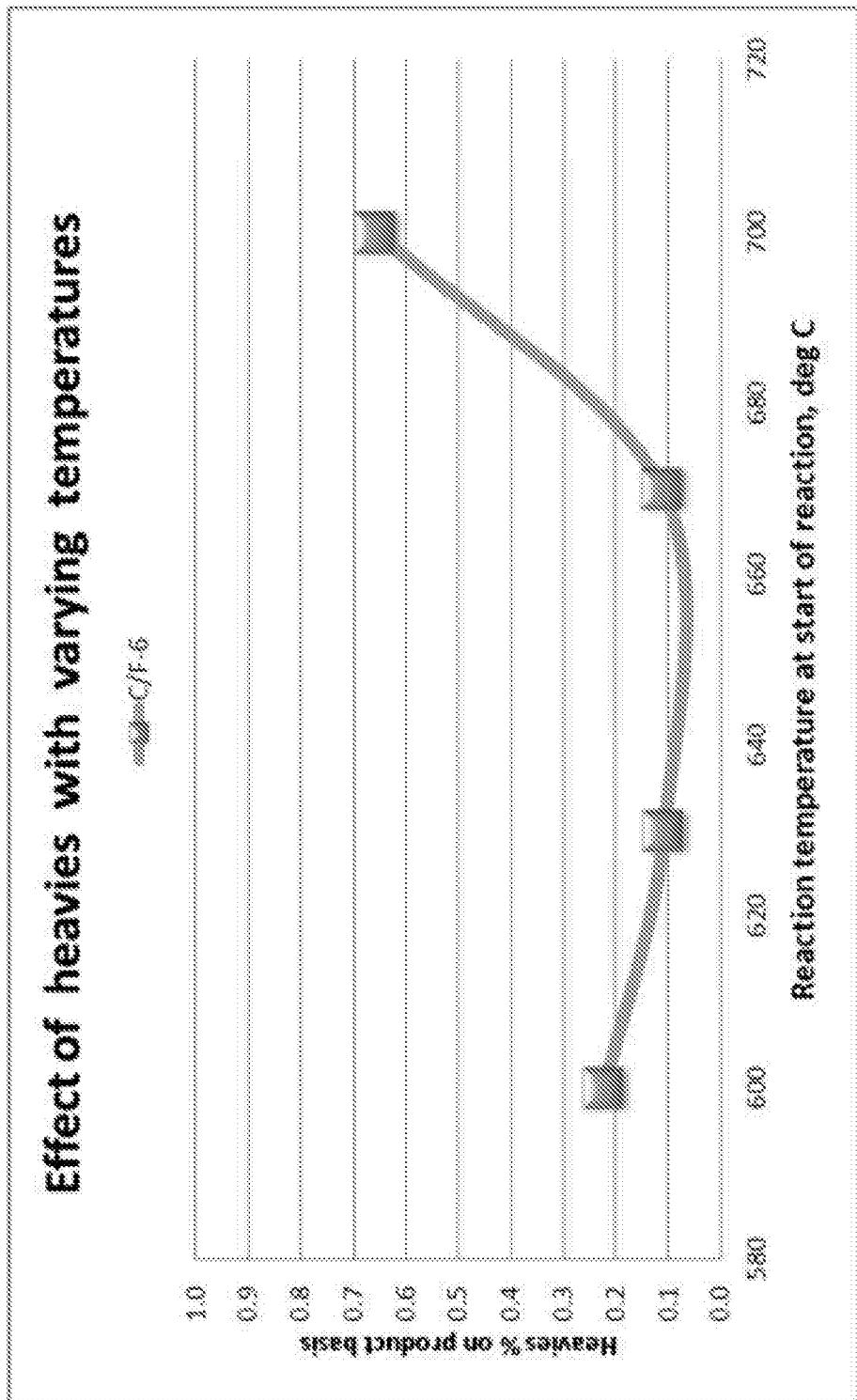


FIGURE 8

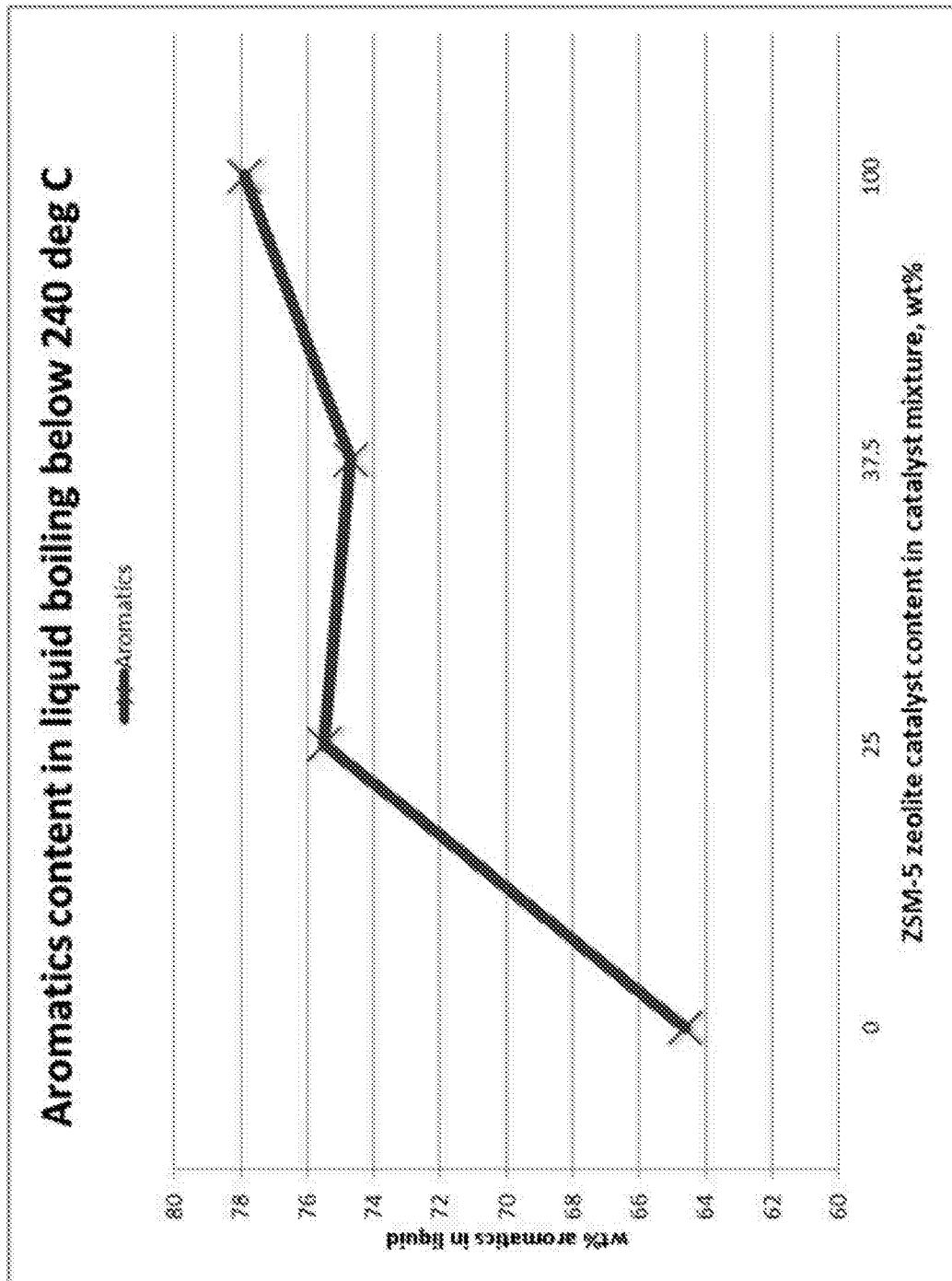


FIGURE 9

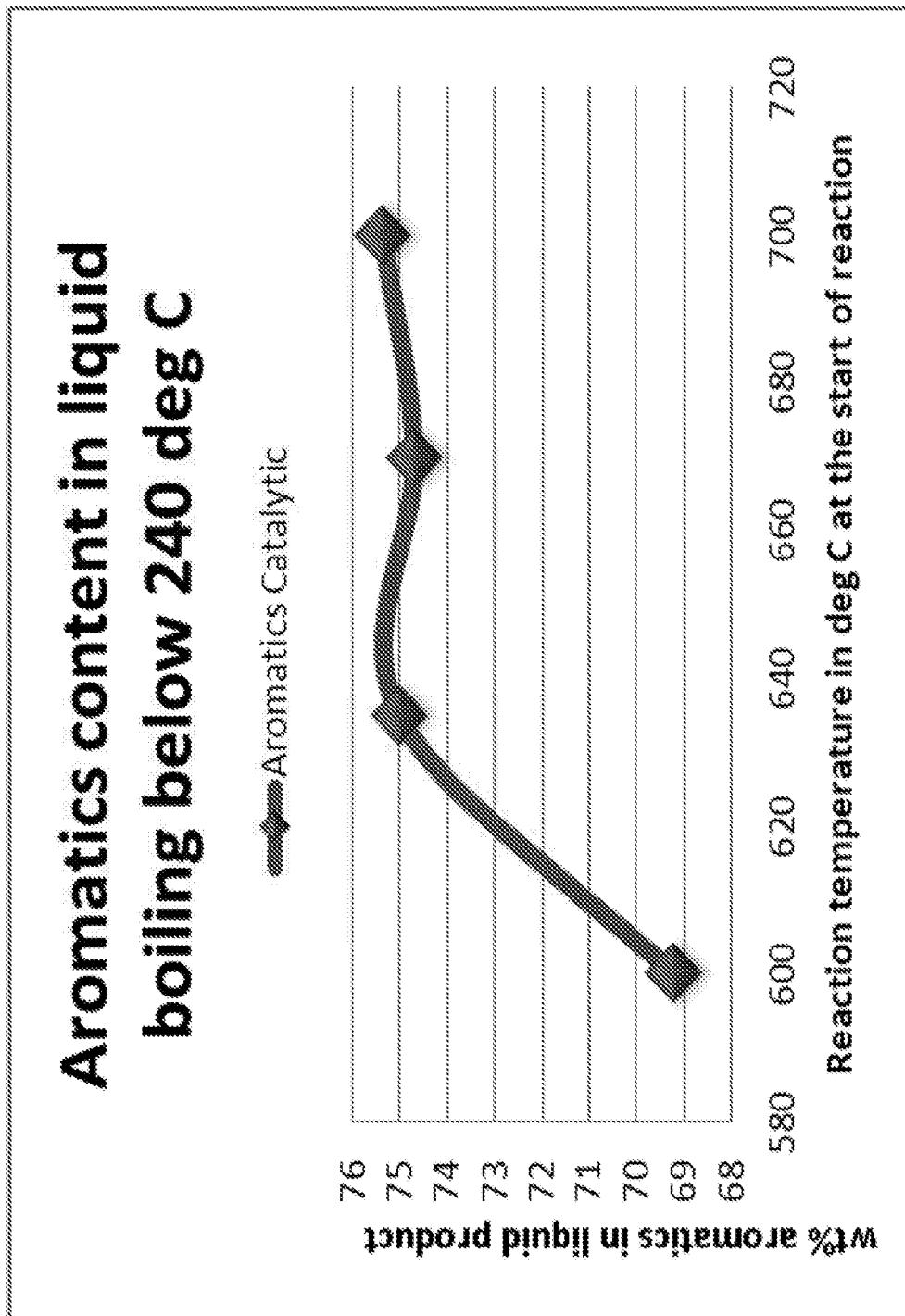


FIGURE 10

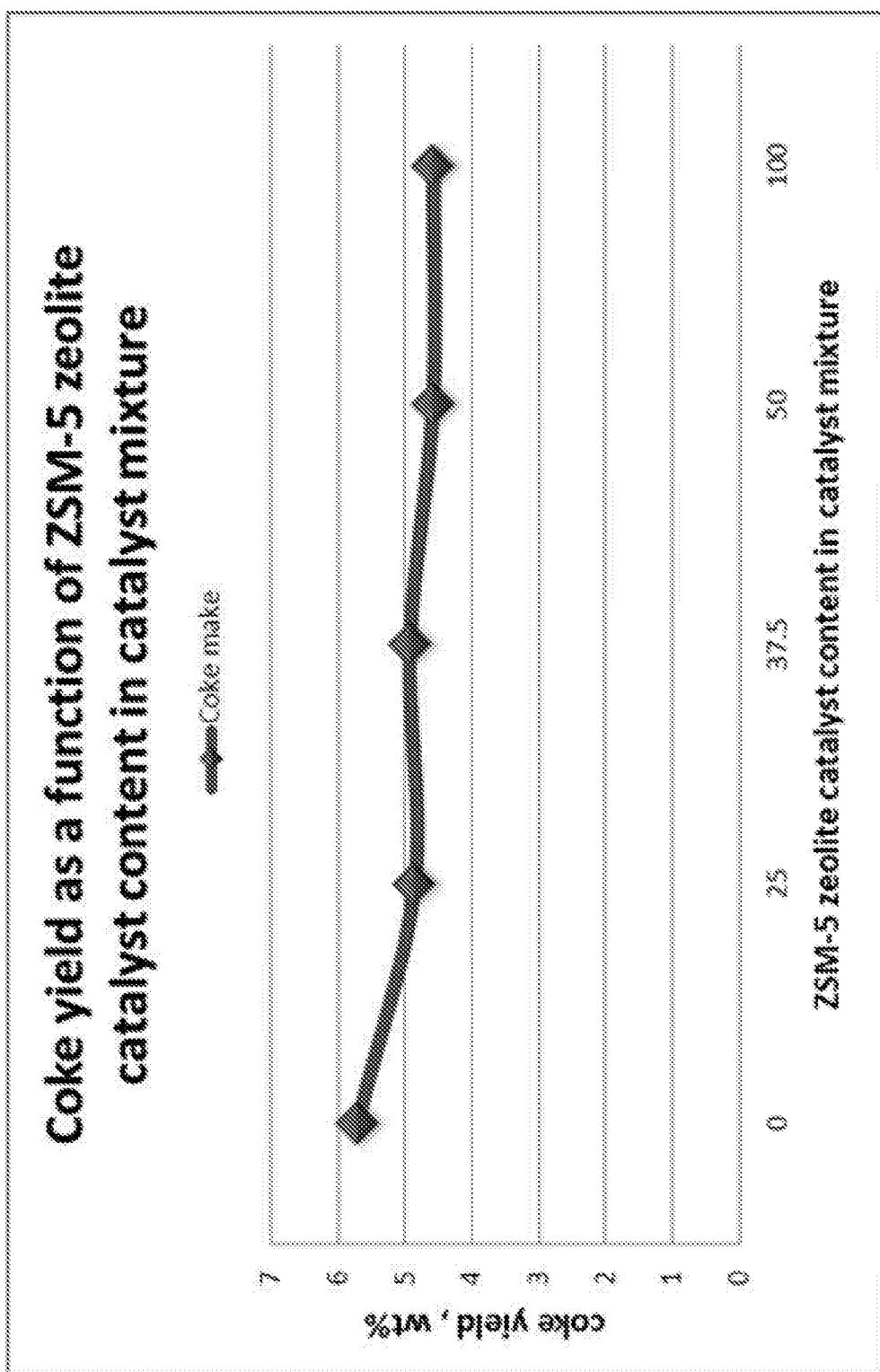


FIGURE 11

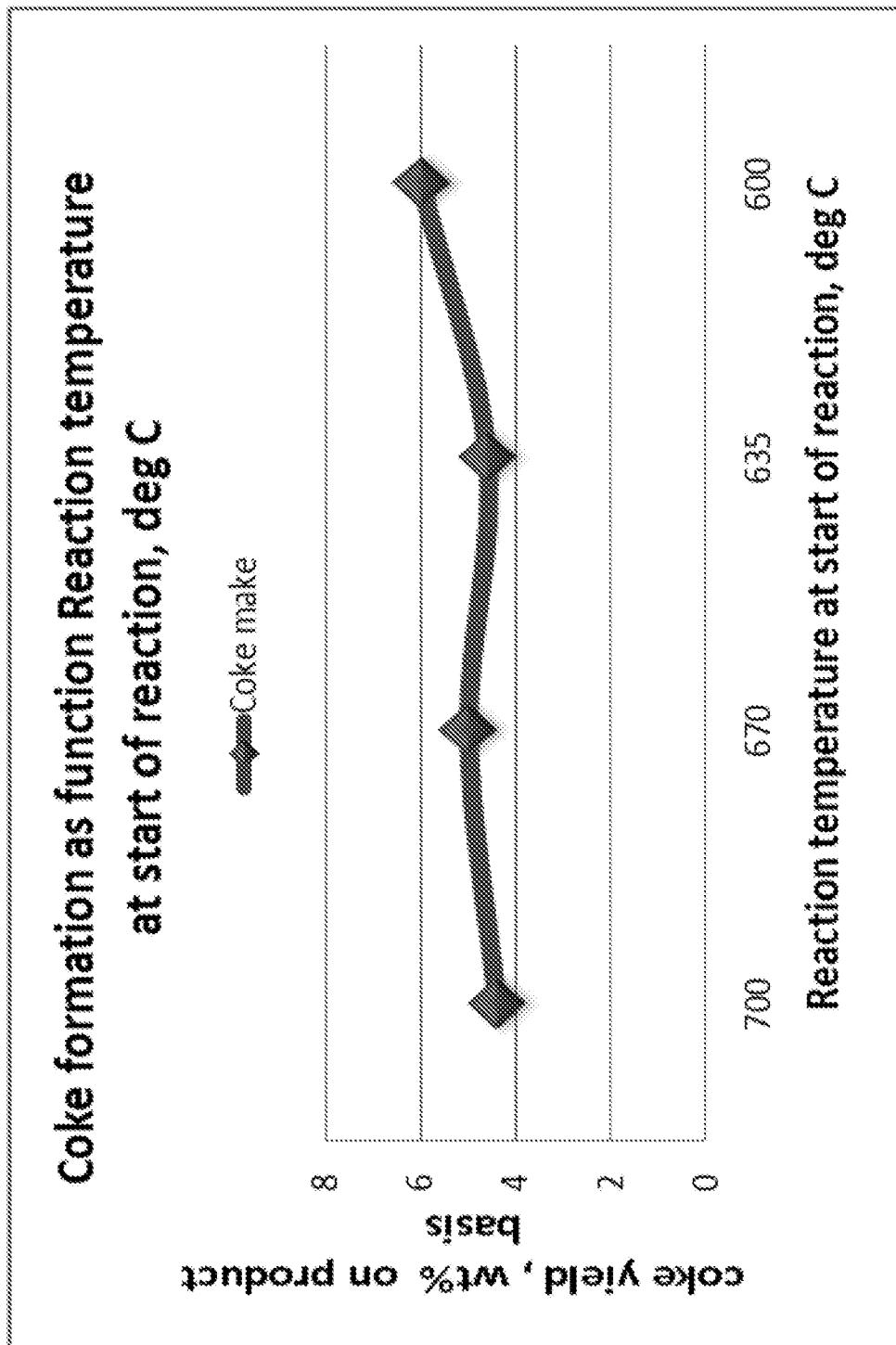


FIGURE 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2013/060826

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G1/10 B01J29/40 B01J35/10 C10G11/18
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G B01J

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/203042 A1 (HUBER GEORGE W [US] ET AL) 9 August 2012 (2012-08-09) claims 16, 22, 27, 32 ----- US 2011/163002 A1 (WHITE LLOYD S [US] ET AL) 7 July 2011 (2011-07-07) paragraphs [0030] - [0031] ----- US 2007/083071 A1 (CHOI SUN [KR] ET AL) 12 April 2007 (2007-04-12) claims 10-14 -----	1-21 1-21 1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "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

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"&" document member of the same patent family

Date of the actual completion of the international search

16 May 2014

Date of mailing of the international search report

27/05/2014

Name and mailing address of the ISA/

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Authorized officer

Bernet, Olivier

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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