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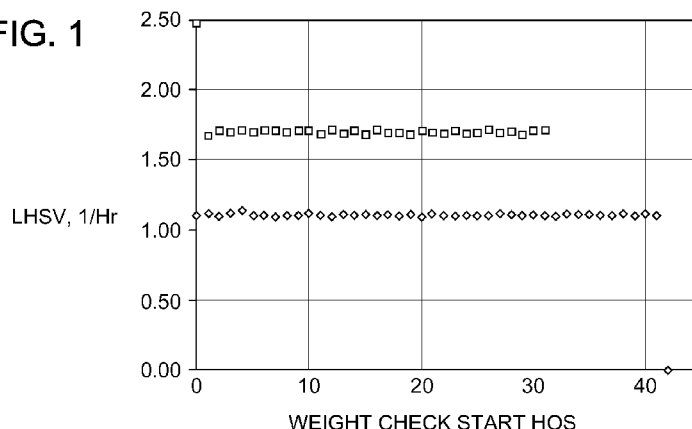
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(54) Title: HIGH TEMPERATURE PLATFORMING PROCESS

FIG. 1



(57) Abstract: A process for reforming a hydrocarbon stream is presented. The process involves increasing the processing temperatures in the reformers. The reformers are operated under different conditions to utilize advantages in the equilibriums, but require modifications to prevent increasing thermal cracking and to prevent increases in coking. The process utilizes a common catalyst, and common downstream processes for recovering the desired aromatic compounds generated.

HIGH TEMPERATURE PLATFORMING PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Application No. 13/440,487 which was filed on April 5, 2012, which claimed priority to U.S. Provisional Application No. 61/480,695, filed April 29, 2011.

FIELD OF THE INVENTION

[0002] The present invention relates to the process of enhancing the production of aromatic compounds. In particular the improvement and enhancement of aromatic compounds such as benzene, toluene and xylenes from a naphtha feedstream through changing process conditions.

BACKGROUND OF THE INVENTION

[0003] The reforming of petroleum raw materials is an important process for producing useful products. One important process is the separation and upgrading of hydrocarbons for a motor fuel, such as producing a naphtha feedstream and upgrading the octane value of the naphtha in the production of gasoline. However, hydrocarbon feedstreams from a raw petroleum source include the production of useful chemical precursors for use in the production of plastics, detergents and other products.

[0004] The upgrading of gasoline is an important process, and improvements for the conversion of naphtha feedstreams to increase the octane number have been presented in US Patents 3,729,409, 3,753,891, 3,767,568, 4,839,024, 4,882,040 and 5,242,576. These processes involve a variety of means to enhance octane number, and particularly for enhancing the aromatic content of gasoline.

[0005] Processes include splitting feeds and operating several reformers using different catalysts, such as a monometallic catalyst or a non-acidic catalyst for lower boiling point hydrocarbons and bi-metallic catalysts for higher boiling point hydrocarbons. Other improvements include new catalysts, as presented in US Patents 4,677,094, 6,809,061 and 7,799,729. However, there are limits to the methods and catalysts presented in these patents, and which can entail significant increases in costs.

SUMMARY OF THE INVENTION

[0006] The present invention is a process for improving the yields of aromatics from a hydrocarbon feedstream. In particular, the process converts non-aromatic hydrocarbons in a naphtha feedstream to aromatics in the C6 to C8 range. The non-aromatics include paraffins, olefins and naphthenes. The process improves the yields of aromatics over the currently used methods of processing a naphtha feedstream. The process includes passing a regenerated catalyst to a reformer. A hydrocarbon feedstream is passed to the reformer, and contacts the catalyst at an elevated temperature to create an effluent stream and a catalyst effluent stream. The elevated temperature is a temperature greater than 540 °C. The effluent stream is passed to a first fractionation unit to create an overhead stream comprising light gases and a bottoms stream comprising reformate. The reformate is passed to an aromatics extraction unit to generate a purified aromatics product stream.

[0007] The process can include splitting the hydrocarbon feedstream to generate a light hydrocarbon feedstream and a heavy hydrocarbon feedstream. The light hydrocarbon feedstream is then passed to a reformer that is operated at the elevated temperature conditions, with the heavy hydrocarbon feedstream passed to a reformer operated at normal operating conditions that includes a temperature between 500°C and 540°C.

[0008] Other objects, advantages and applications of the present invention will become apparent to those skilled in the art from the following drawings and detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Figure 1 shows the LHSV vs. weight check with added sulfur;

[0010] Figure 2 shows the C8 aromatics increase vs. weight check with sulfur;

[0011] Figure 3 shows the C5+ increase vs. weight check start HOS;

[0012] Figure 4 shows the total aromatics increase;

[0013] Figure 5 shows the hydrogen increase;

[0014] Figure 6 shows the increase in the average reaction block temperature vs. weight check start HOS;

[0015] Figure 7 shows the increase in the average reaction block temperature vs. catalyst life;

- [0016] Figure 8 shows the total aromatics increase vs. catalyst life;
[0017] Figure 9 shows the increase in hydrogen vs. catalyst life;
[0018] Figure 10 shows the C5+ increase vs. catalyst life;
[0019] Figure 11 shows the C8 aromatics increase vs. catalyst life; and
5 [0020] Figure 12 shows a reformer with a tail heater and a tail reformer reactor.

DETAILED DESCRIPTION OF THE INVENTION

- [0021] Reforming of a hydrocarbon stream for the production of aromatics is an important process. In general, high operating temperatures are preferred for operating a reformer, as the equilibriums at the higher temperatures favors the formation of aromatic compounds. However, the reforming process is operated at a lower temperature due to the thermal cracking and the metal catalyzed coking that occurs as the temperature is increased. It has been found that using reactor vessels with non-metallic coatings allow for higher temperature operations, without the accompanying increase in coking or thermal cracking.
- 10 [0022] The present invention provides for increased aromatics yields by changing the normal operating parameters for the hydrocarbon reformation process. The reformation process is a process of converting paraffinic hydrocarbons to aromatic hydrocarbons through cyclization and dehydrogenation. The cyclization and dehydrogenation goes through many steps, and can generate olefins as well as naphthenes. In turn the olefins can be cyclized and dehydrogenated, and the naphthenes can be dehydrogenated.
- 20 [0023] Increasing the temperature would normally be a preferred condition, since the higher temperatures shift the equilibriums of the reforming reactions to favor the production of aromatics. However, increasing the temperatures increases the formation of coke on the catalyst, and more rapidly deactivates the catalyst. Increasing temperatures also increases thermal cracking for the heavier hydrocarbons, and can start or increase metal catalyzed coking on the surfaces of the reactor vessel or piping used to transport the hydrocarbons to the reformer. This in turn requires more energy to regenerate the catalyst on a more frequent basis. Currently, the reformation process has been optimized to run at lower temperatures to balance the production of aromatics against the costs in time and energy of regenerating the catalyst, as well as minimizing thermal cracking and metal catalyzed coking.
- 30

[0024] The present invention is for the generation of aromatic compounds from a hydrocarbon feedstream. The process includes passing a regenerated catalyst to a reformer, and passing the hydrocarbon feedstream to the reformer operated at an elevated temperature to create a first effluent stream, and a catalyst effluent stream. The process further includes
5 passing the first effluent stream to a first fractionation unit, thereby creating an overhead stream comprising light gases, and a bottoms stream comprising reformat. The reformat is passed to an aromatics extraction unit to generate a purified aromatics product stream.

[0025] The elevated temperature of operation is the inlet temperature of the feedstream, and is a temperature of at least 540°C, with a preferred temperature between 540°C and
10 580°C. The process further includes operating the reactor such that contact times between the feedstream and catalyst are shortened. The space velocity is increased over normal commercial operating conditions. The reaction conditions include a liquid hour space velocity (LHSV) of the present invention in the range from 0.6 hr⁻¹ to 10 hr⁻¹. Preferably, the LHSV is between 0.6 hr⁻¹ and 5 hr⁻¹, with a more preferred value between 1 hr⁻¹ and 5
15 hr⁻¹, and with a most preferred value between 2 hr⁻¹ and 5 hr⁻¹. The catalyst also has a residence time in the reformer between 0.5 hours and 36 hours.

[0026] Due to the elevated temperature, the problems of potential increased thermal cracking are addressed by having a shorter residence time of the hydrocarbon process stream in the equipment at the elevated temperature. The increased temperature can also increase
20 coking on metallic surfaces of the transfer equipment and the reactor internals.

[0027] An aspect of the process can use a reformer with an internal coating made of a non-coking material. The non-coking material can comprise an inorganic refractory oxide. The non-coking coating can be a material selected from ceramics, metal oxides, metal sulfides, glasses, silicas, and other high temperature resistant non-metallic materials.

[0028] The process can also utilize piping, heater internals, and reactor internals using a stainless steel having a high chromium content. Stainless steels having a chromium content of 17% or more have a reduced coking ability.

[0029] The process can also include adding compounds to change the ability to reduce the amount of coking. One example is the injection of a sulfur compound, such as H₂S, into
30 the feedstream. The presence of a small amount of sulfur reduces the coking in the high temperature reforming.

[0030] In one embodiment of the present invention, the process involves separating the hydrocarbon feedstream to process the lighter components of the feedstream at a higher temperature and at a higher LHSV. The process includes passing the hydrocarbon feedstream to a fractionation column to generate an overhead stream having C7 and lighter hydrocarbons, and a bottoms stream having C8 and heavier hydrocarbons. The overhead stream is passed to a first heating unit to raise the temperature of the overhead stream to a first temperature. The heated overhead stream is passed to a first reformer that is operated at a first set of reaction conditions, which includes a first temperature, and creates a first process stream. The bottoms stream is passed to a second reformer operated at a second set of reaction conditions, which includes a second temperature, and creates a second process stream.

[0031] The first temperature is greater than the second temperature, and the first temperature is at least 540°C. The operation of the different reformers is such that the space velocity in the first reformer is greater than the space velocity in the second reformer.

[0032] The first and second process streams are passed to a reformat splitter to generate a reformat overhead stream, and a reformat bottoms stream. The reformat overhead stream is passed to an aromatics extraction unit to generate a purified aromatics stream and a raffinate stream. The purified aromatics stream comprises C6 to C8 aromatic compounds. For limiting the purified aromatics compounds to C6 and C7 aromatic compounds, the reformat splitter can be operated such that the reformat overhead comprises C6 and C7 aromatics, with the reformat bottoms stream comprising C8 and heavier aromatic compounds.

[0033] The present invention is a process for generating aromatics from a hydrocarbon feedstream. The process includes passing the hydrocarbon feedstream to a reformer, wherein the reformer is operated at a temperature greater than 540°C, and the internal surfaces of the reactor are coated with a non-coking material to generate a process stream comprising aromatic compounds. The process stream is passed to a fractionation unit to separate light gas components comprising C4 and lighter hydrocarbons, as well hydrogen and other light gases from the process stream. The fractionation unit generates an overhead stream having the light gas components and a bottoms stream having C5 and heavier hydrocarbons. The

bottoms stream is passed to an aromatics extraction unit to create a purified aromatics stream and a raffinate stream having a reduced aromatics content.

[0034] The reforming process contacts the hydrocarbon feedstream with a catalyst and performs dehydrogenation and cyclization of hydrocarbons. The process conditions include a
5 temperature greater than 540°C, and a space velocity between 0.6 hr⁻¹ and 10 hr⁻¹.

Preferably the space velocity is between 0.6 hr⁻¹ and 8 hr⁻¹, and more preferably, the space velocity is between 0.6 hr⁻¹ and 5 hr⁻¹.

[0035] The process of the present invention allows for greater heating through altering the reactor surfaces, and the equipment that delivers the heated hydrocarbon feedstream to
10 the reactors. This includes the transfer equipment, such as piping between the fired heaters and the reactor, as well as the internal walls to the surfaces in the fired heaters exposed to the feedstream. The internal surfaces can be sulfide, or coated with non-coking materials, or using a non-coking metallurgy.

[0036] In one embodiment, the process for the generation of aromatics from a
15 hydrocarbon feedstream includes heating the hydrocarbon feedstream to a first temperature. The heated hydrocarbon feedstream is passed to a first reformer, which is operated at a first set of reaction conditions, to generate a first reformer effluent stream. The first reformer effluent stream is heated to a second temperature, and the heated first reformer effluent stream is passed to a second reformer. The second reformer is operated at a second set of
20 reaction conditions and generate a second reformer effluent stream. The second reformer effluent stream is passed through a heat exchanger to preheat the feedstream.

[0037] The first temperature is a temperature between 500°C and 540°C, and the second temperature is greater than 540°C. Each reformer can include a plurality of reactors with inter-reactor heaters, wherein each inter-reactor heater heats the stream to a desired
25 temperature, and wherein . For the first reformer, each inter-reactor heater will heat the process streams to the second temperature before passing to the second reformer. With more than two reformers, all reformers except the last one will have the entering process stream heated to the first temperature and the inlet process stream to the last reformer will be heated to the second temperature.

[0038] The process can include a tail heater. The tail heater is used to heat the second reformer effluent to a third temperature. The heated second reformer effluent is then passed
30

to a tail reactor. The third temperature is also greater than the first temperature, and preferably is greater than 540°C.

[0039] The reforming process is a common process in the refining of petroleum, and is usually used for increasing the amount of gasoline. The reforming process comprises mixing
5 a stream of hydrogen and a hydrocarbon mixture and contacting the resulting stream with a reforming catalyst. The usual feedstock is a naphtha feedstock and generally has an initial boiling point of 80°C and an end boiling point of 205°C. The reforming reactors are operated with a feed inlet temperature between 450°C and 540°C. The reforming reaction converts
10 paraffins and naphthenes through dehydrogenation and cyclization to aromatics. The dehydrogenation of paraffins can yield olefins, and the dehydrocyclization of paraffins and olefins can yield aromatics.

[0040] The reforming process is an endothermic process, and to maintain the reaction, the reformer is a catalytic reactor that can comprise a plurality of reactor beds with interbed
15 heaters. The reactor beds are sized with the interbed heaters to maintain the temperature of the reaction in the reactors. A relatively large reactor bed will experience a significant temperature drop, and can have adverse consequences on the reactions. The catalyst can also pass through inter-reformer heaters to bring the catalyst up to the desired reformer inlet
temperatures. The interbed heaters reheat the catalyst and the process stream as the catalyst and process stream flow from one reactor bed to a sequential reactor bed within the reformer.
20 The most common type of interbed heater is a fired heater that heats the fluid and catalyst flowing in tubes. Other heat exchangers can be used.

[0041] Reforming catalysts generally comprise a metal on a support. The support can include a porous material, such as an inorganic oxide or a molecular sieve, and a binder with
a weight ratio from 1:99 to 99:1. The weight ratio is preferably from 1:9 to 9:1. Inorganic
25 oxides used for support include, but are not limited to, alumina, magnesia, titania, zirconia, chromia, zinc oxide, thorium, boria, ceramic, porcelain, bauxite, silica, silica-alumina, silicon carbide, clays, crystalline zeolitic aluminosilicates, and mixtures thereof. Porous materials and binders are known in the art and are not presented in detail here. The metals preferably are one or more Group VIII noble metals, and include platinum, iridium, rhodium, and
30 palladium. Typically, the catalyst contains an amount of the metal from 0.01% to 2% by weight, based on the total weight of the catalyst. The catalyst can also include a promoter

element from Group IIIA or Group IVA. These metals include gallium, germanium, indium, tin, thallium and lead.

[0042] Experiments were performed with an LHSV of 1.7 hr⁻¹, at the elevated temperature, for comparison with a normal operation of LHSV of 1.1 hr⁻¹. The data, as presented in Figures 1-12, shows a significant increase in aromatics, hydrogen and C5+ liquid product when the same catalyst is operated at a higher temperature, but the same catalyst is operated at different space velocities. The experiments with run with a dehydrogenation catalyst, UOP's DEH-5 catalyst, comprising 0.5 wt% Pt, 1.03 wt% Cl on a support. The density of the catalyst was 0.31 g/cc. Figure 1 shows the weight check with added sulfur during hours on stream (HOS) v. LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 2 shows the C8 aromatics increase for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 3 shows the C5+ content of the product streams for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 4 shows the aromatics increase in the product streams for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 5 shows the hydrogen generation during the process for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 6 shows the average reaction block temperature for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 7 shows the average reaction block temperature vs. catalyst life (BPP), for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). The BPP is a normalized time of operation, or barrels of feed per pound of catalyst. Figure 8 shows the total aromatics vs. catalyst life for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 9 shows the hydrogen produced vs. catalyst life, for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 10 shows the C5+ wt. % in the product stream vs. the catalyst life, for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). Figure 11 shows the C8 aromatics generated in the product stream vs. the catalyst life, for the two runs, LHSVs of 1.1 (diamonds) and 1.7 (squares). This increase is expected at the higher temperature due to a decrease in activity through a reduced chloride content on the catalyst.

[0043] The increases due to higher temperatures allow for increased throughputs, or increased federates, and produces more aromatic products at a lower cost.

[0044] An embodiment of the present invention includes a reformer, as shown in Figure 12, comprises four reactor beds, and an additional tail reactor bed. The system includes the flow from a combined feed exchanger 12 to the charge heater 10. The heated feed 14 can

pass to a first reactor 30, and some of the feed can be directed to a second reactor 40 through a bypass device 16. The first reactor effluent 32 is passed to the first interheater 20 to generate a heated second reactor feed 22. A second bypass device 24 can direct some of the second reactor feed 22 to a third reactor 50. The second reactor effluent 42 is passed to a
5 second interheater 60 to generate a heated third reactor feed 62. A third bypass device 64 can direct some of the third reactor feed 62 to a fourth reactor 70. The third reactor effluent 52 is passed to a third interheater 80 to generate the fourth reactor feed 82. The effluent 72 from the fourth reactor bed is heated to a greater temperature through a tail heater 100, and to a temperature of at least 540°C, and is then passed to a tail reactor 110. The tail reactor 110 is
10 operated at the higher temperature and at a higher LHSV to insure a lower contact time. The tail reactor 110 also receives heated catalyst 112 from a separate transfer system to the regenerator, and returns spent catalyst 114 to the regenerator. The tail reactor 110 is operated at a higher temperature, so the catalyst will have a short contact time and a relatively short residence time in the reactor for more frequent regeneration. This increases the yields of
15 aromatics, and especially aromatics in the C6 to C8 range.

[0045] While the invention has been described with what are presently considered the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

CLAIMS:

1. A process for the generation of aromatic compounds from a hydrocarbon feedstream comprising:

passing a regenerated catalyst to a first reformer;

5 passing the hydrocarbon feedstream to the first reformer operated at an elevated temperature, to create a first effluent stream, and a catalyst effluent stream;

passing the first effluent stream to a first fractionation unit, thereby creating an overhead stream comprising light gases, and a bottoms stream comprising reformate;

10 passing the reformate to an aromatics extraction unit to generate a purified aromatics product stream.

2. The process of claim 1 wherein the elevated temperature includes a temperature greater than 540°C.

15 3. The process of claim 1 wherein the first reformer operating conditions include space velocity is between 0.6 hr⁻¹ and 10 hr⁻¹.

4. The process of claim 1 wherein the catalyst has a residence time in the first reformer between 0.5 hours to 36 hours.

20

5. The process of claim 1 wherein the reformer is coated with a non-coking coating.

6. The process of claim 1 further comprising:

25 passing the hydrocarbon feedstream to a second fractionation column prior to the first reformer, to generate an overhead stream comprising C7 and lighter hydrocarbons, and a bottoms stream comprising C8 and heavier hydrocarbons;

passing the overhead stream to the first reformer, thereby creating a first process stream;

30 passing the bottoms stream to a second reformer operates at a second set of reaction conditions, thereby creating a second process stream; and

passing the first and second process streams to a reformat splitter to generate a reformat overhead stream, and a reformat bottoms stream.

5 7. The process of claim 6 wherein the catalyst in the second reformer has a longer residence time then the catalyst in the first reformer.

8. The process of claim 1 wherein the reformer is made with a high chromium content stainless steel.

10 9. The process of claim 8 wherein the chromium content in the stainless steel is at least 17% by weight.

10. The process of claim 1 further comprising the injection of sulfur into the feedstream.

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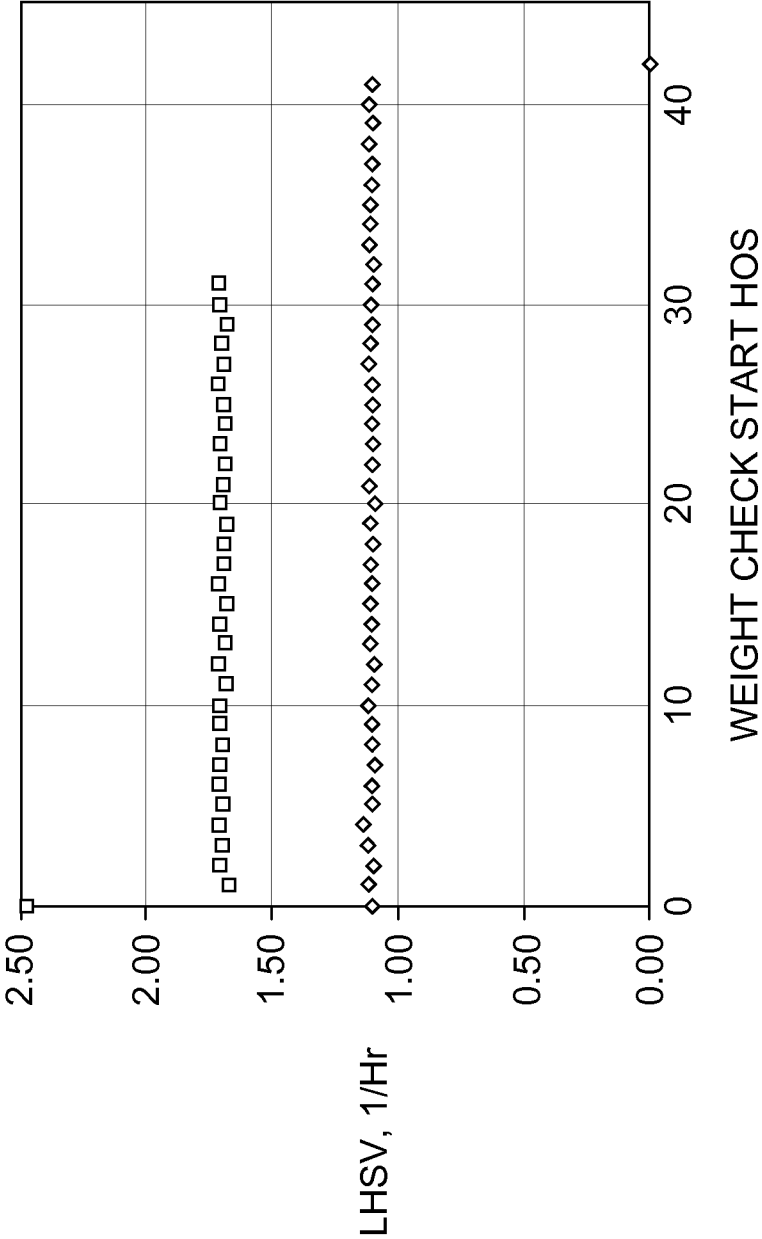


FIG. 1

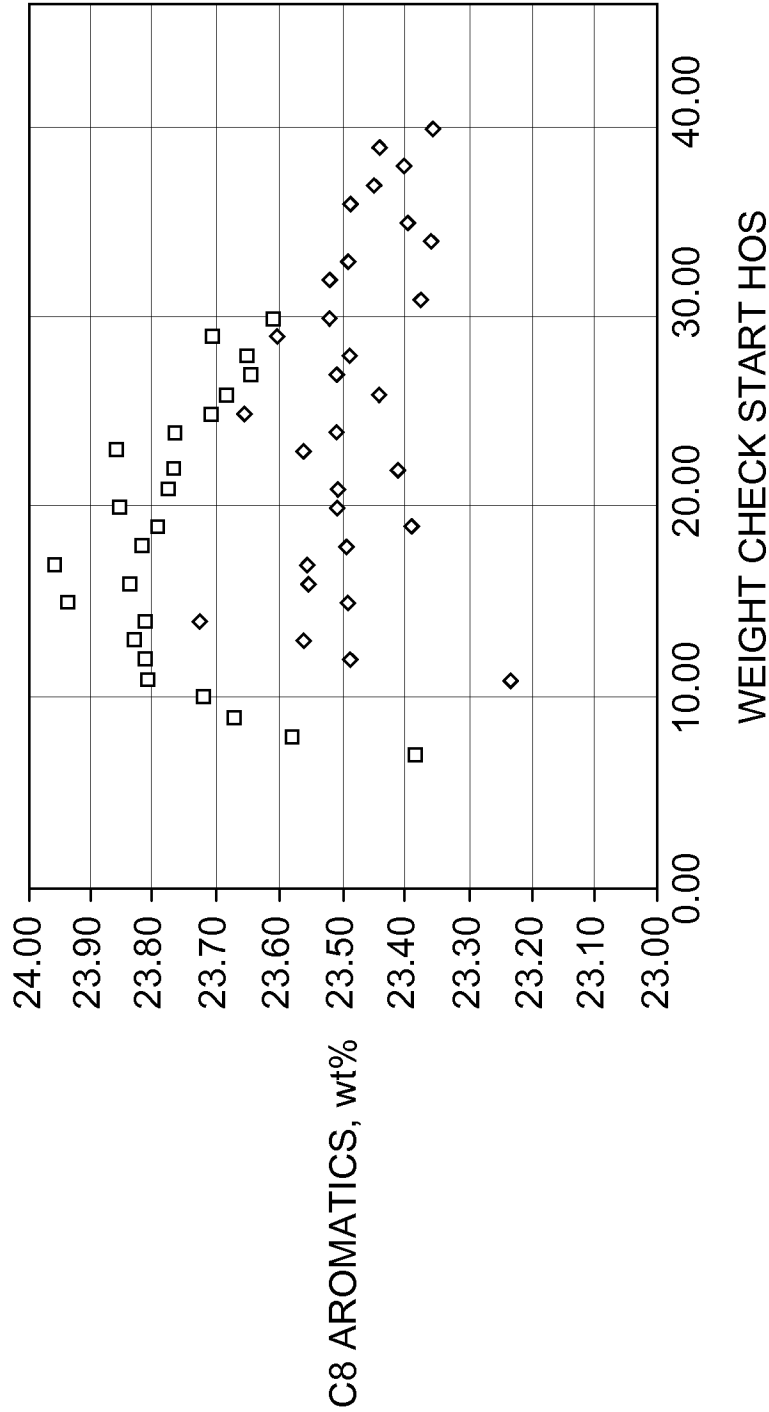


FIG. 2

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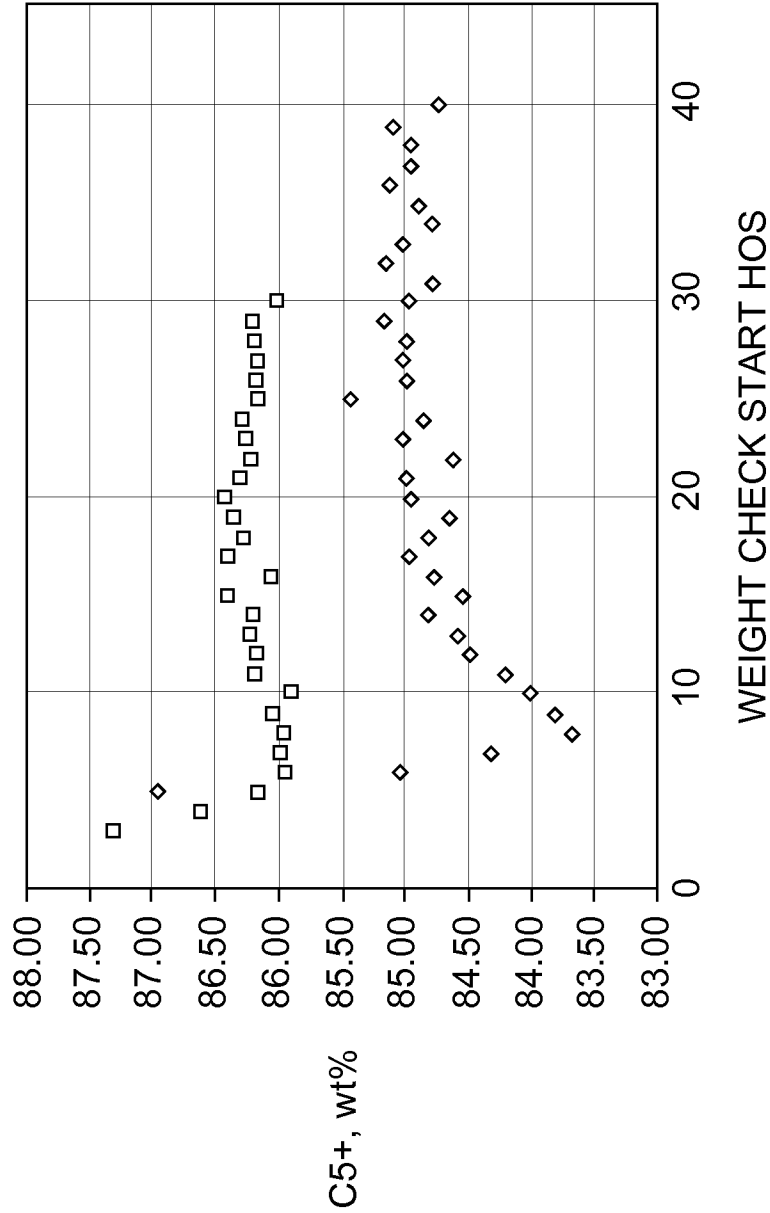


FIG. 3

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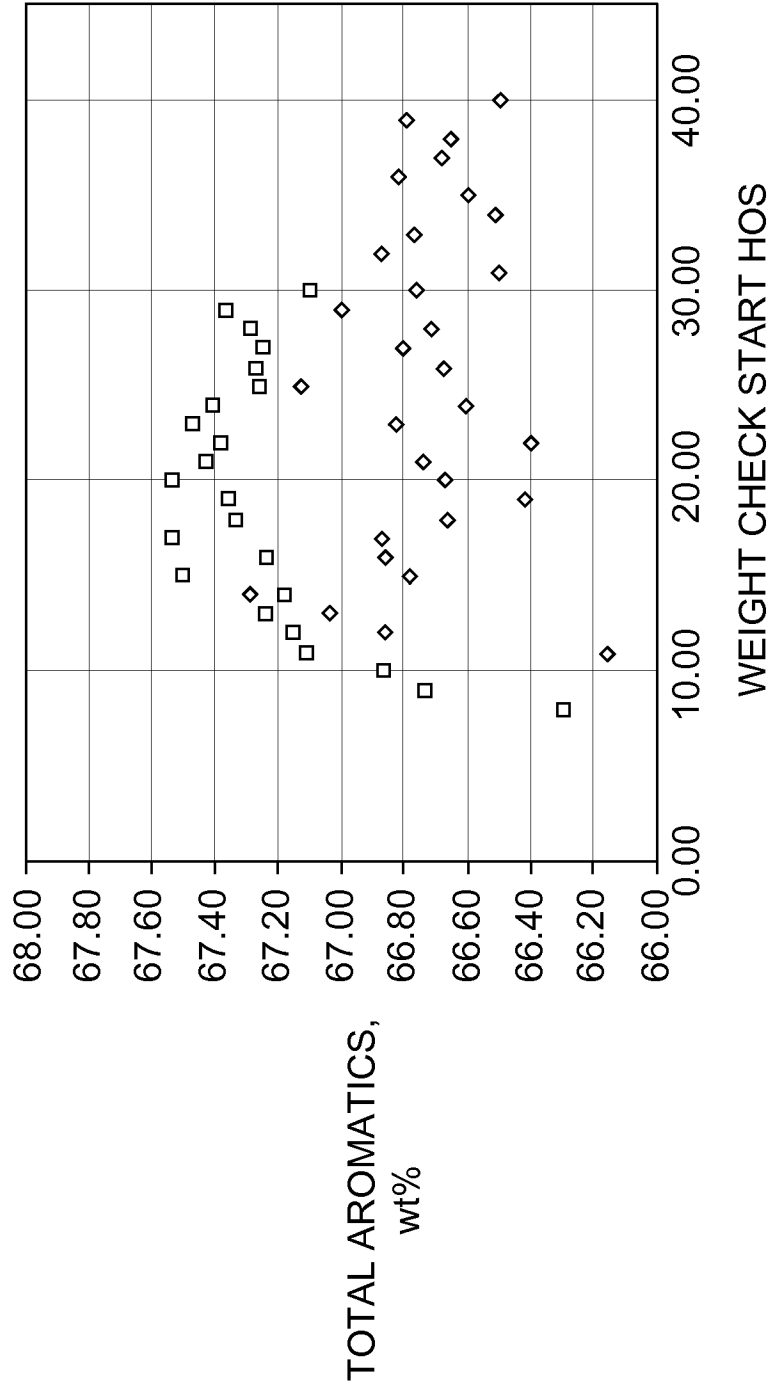


FIG. 4

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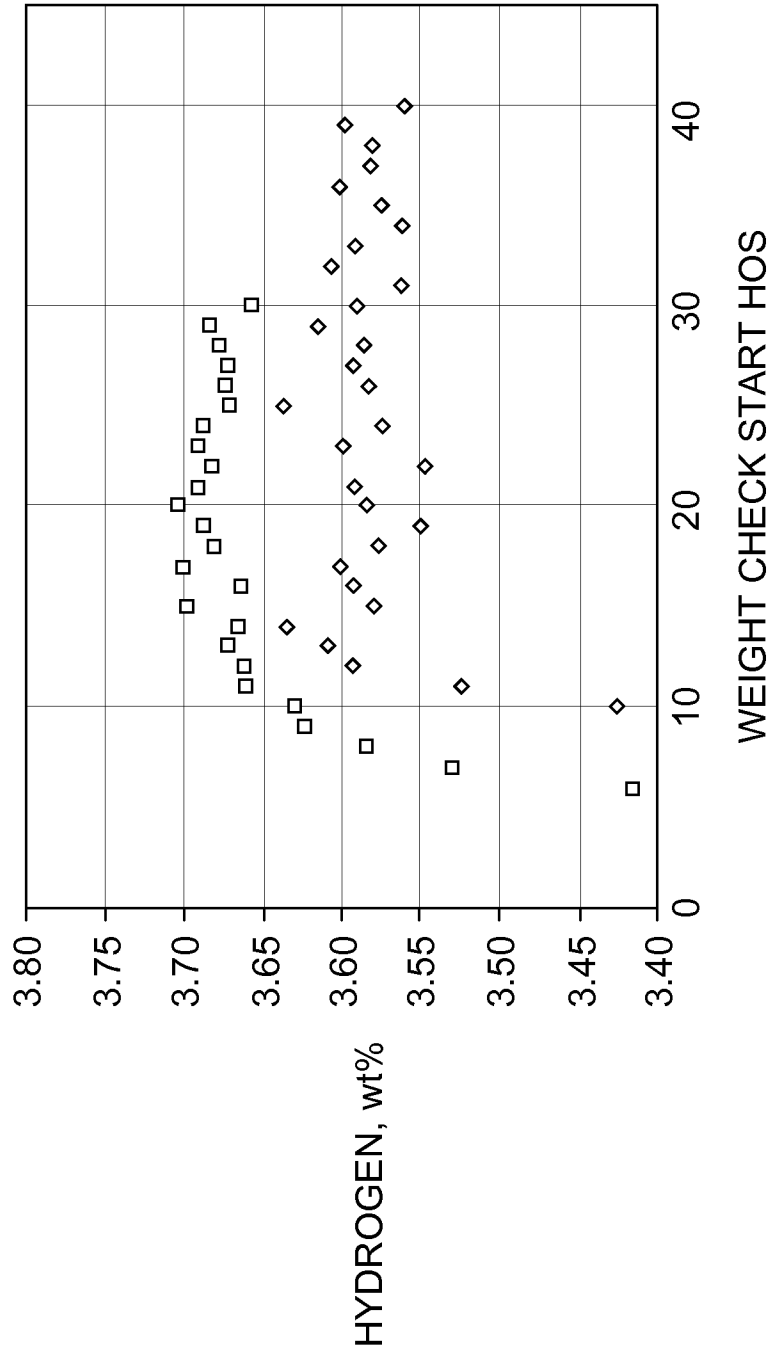


FIG. 5

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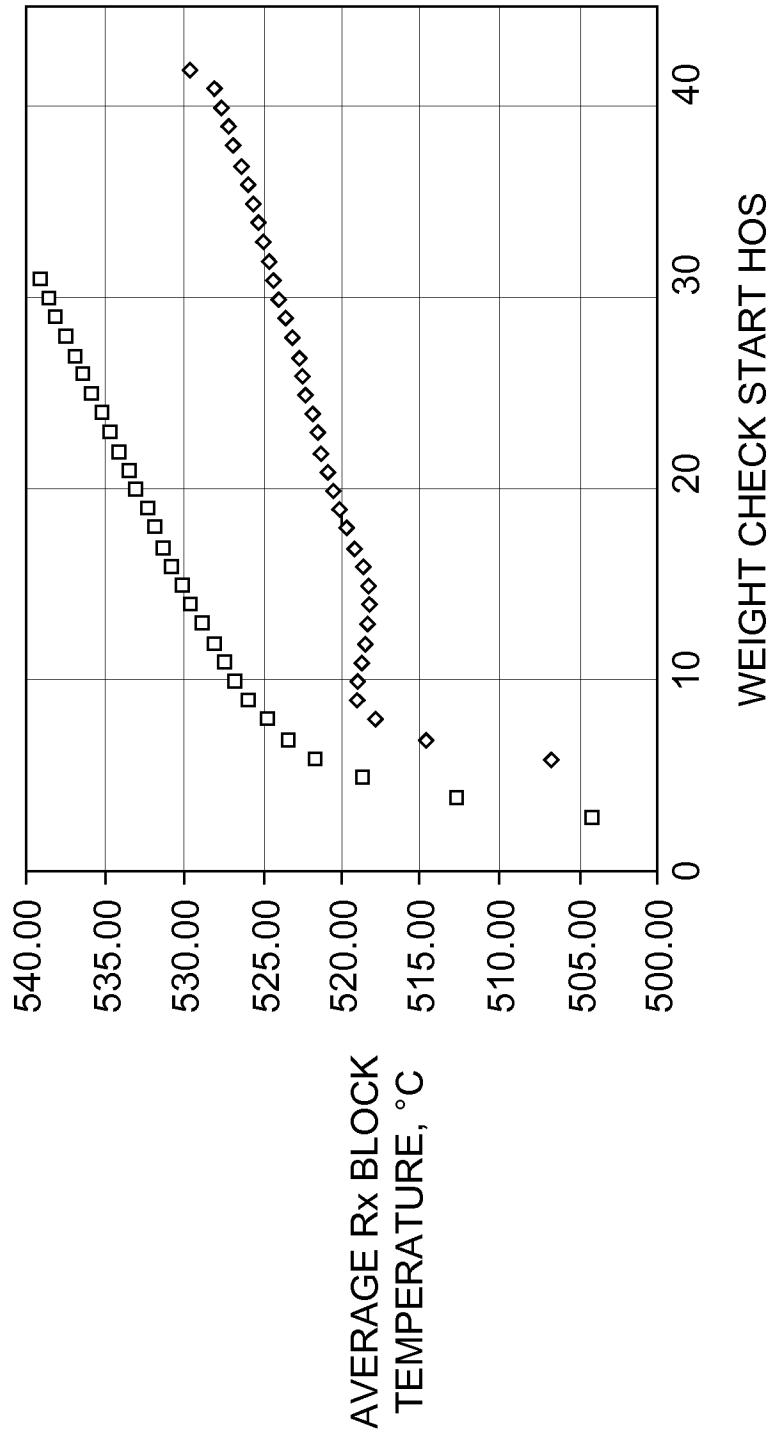


FIG. 6

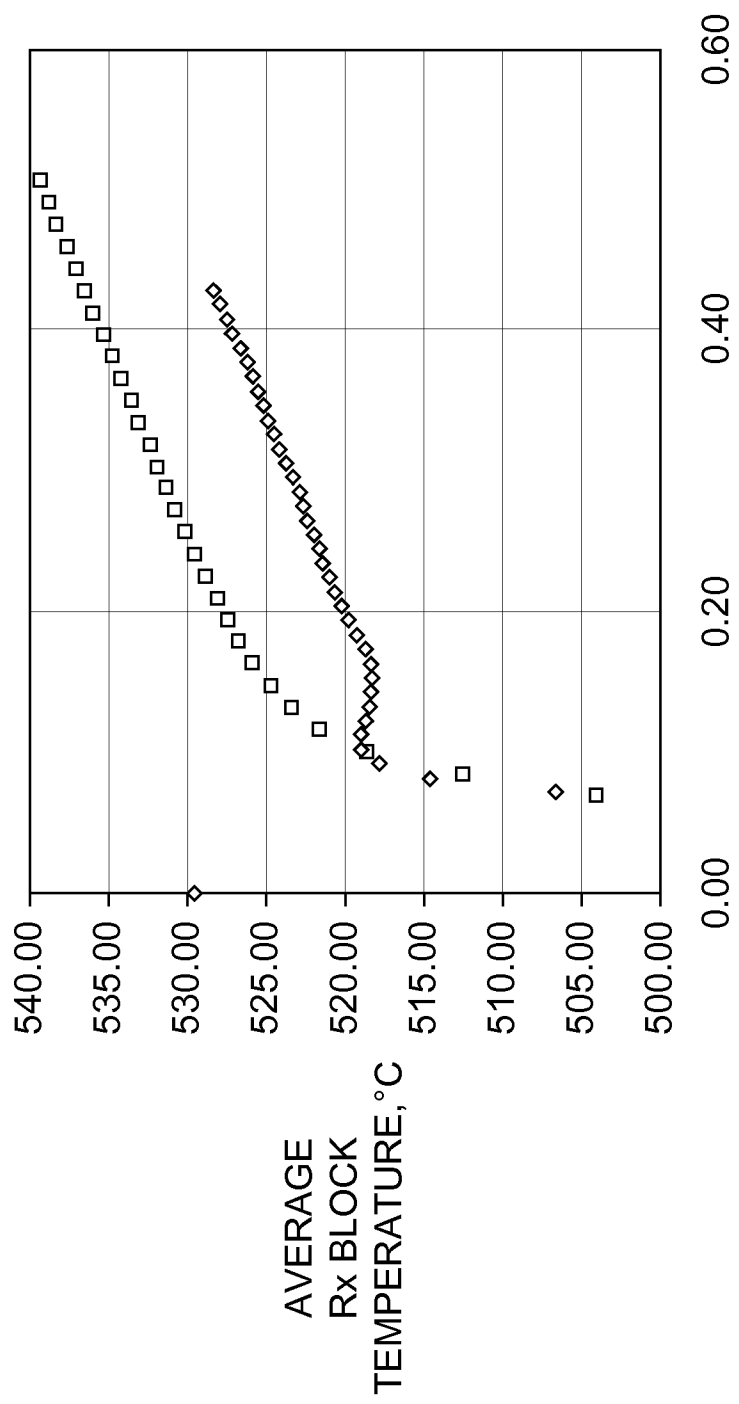


FIG. 7

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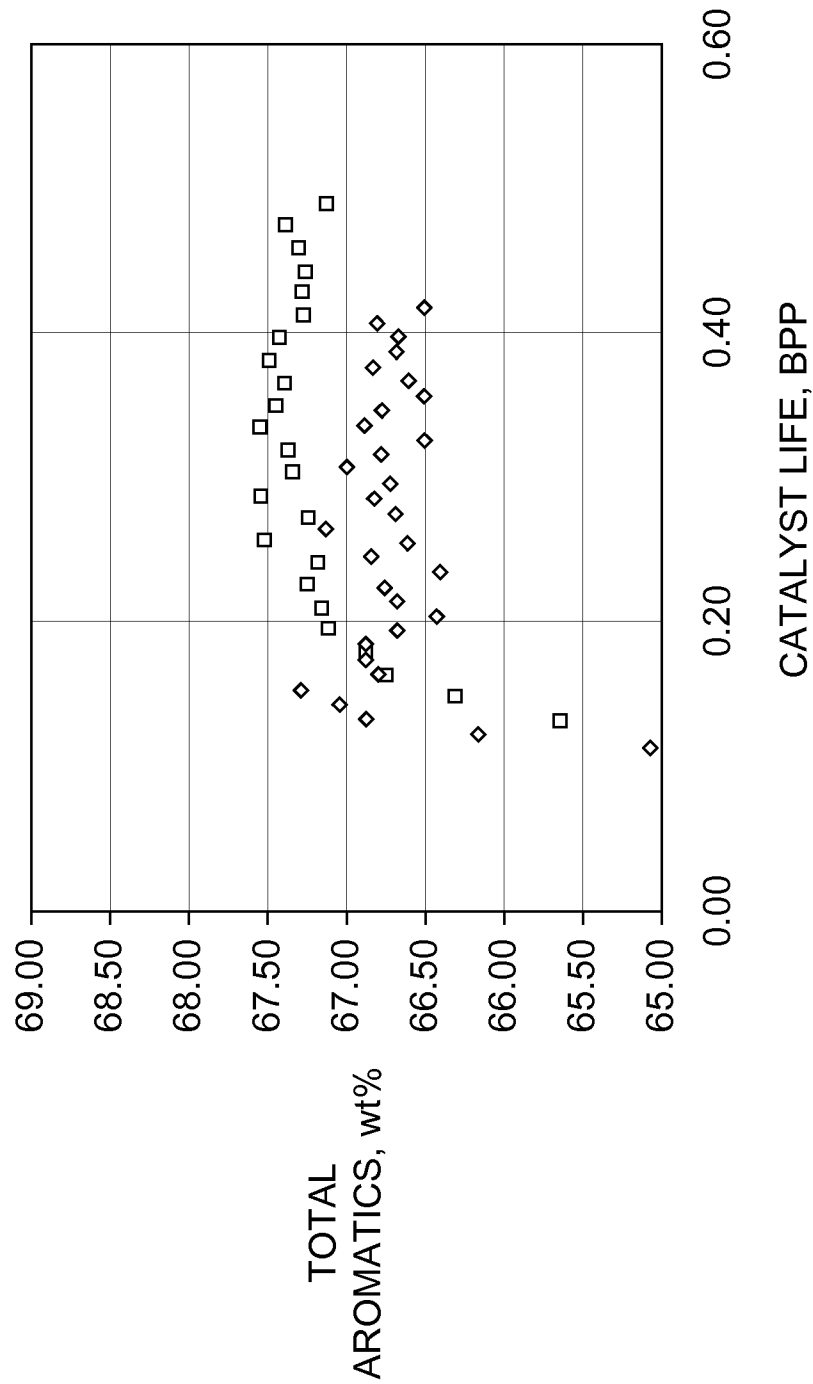
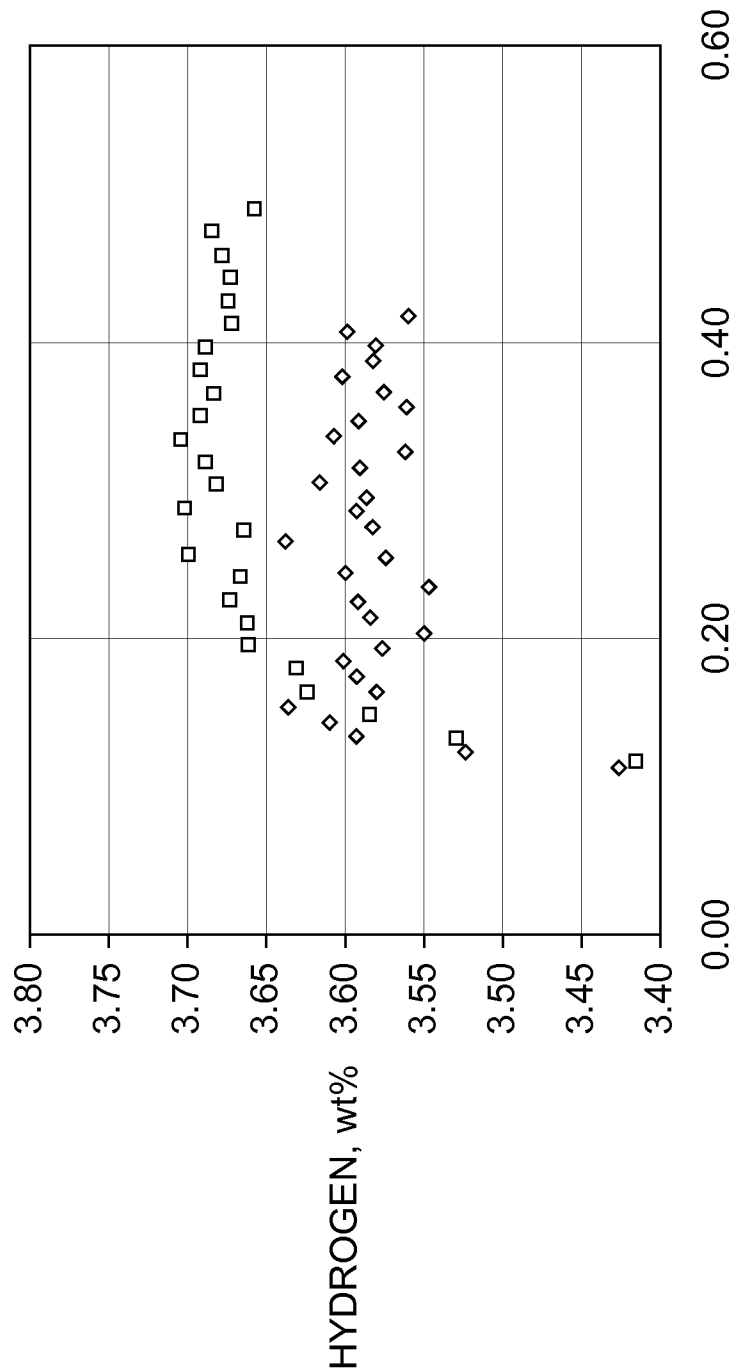


FIG. 8

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CATALYST LIFE, BPP

FIG. 9

10/12

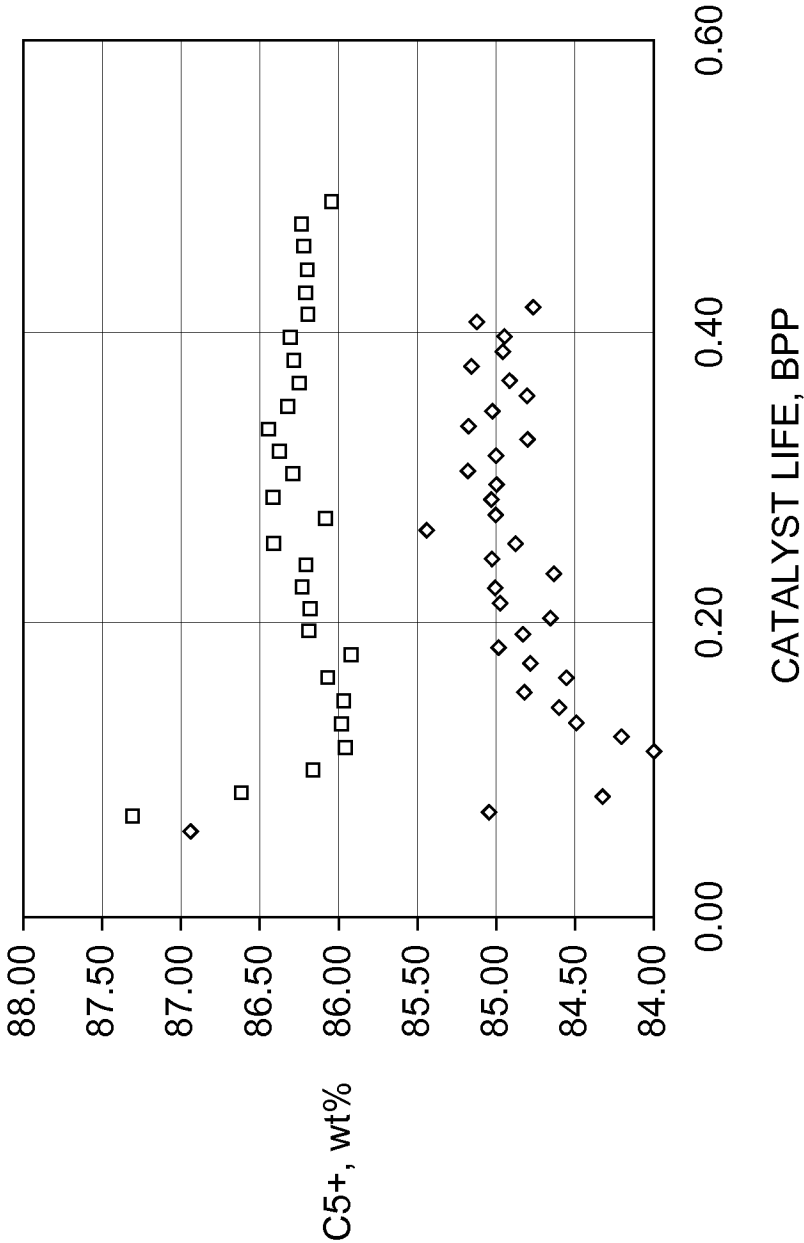


FIG. 10

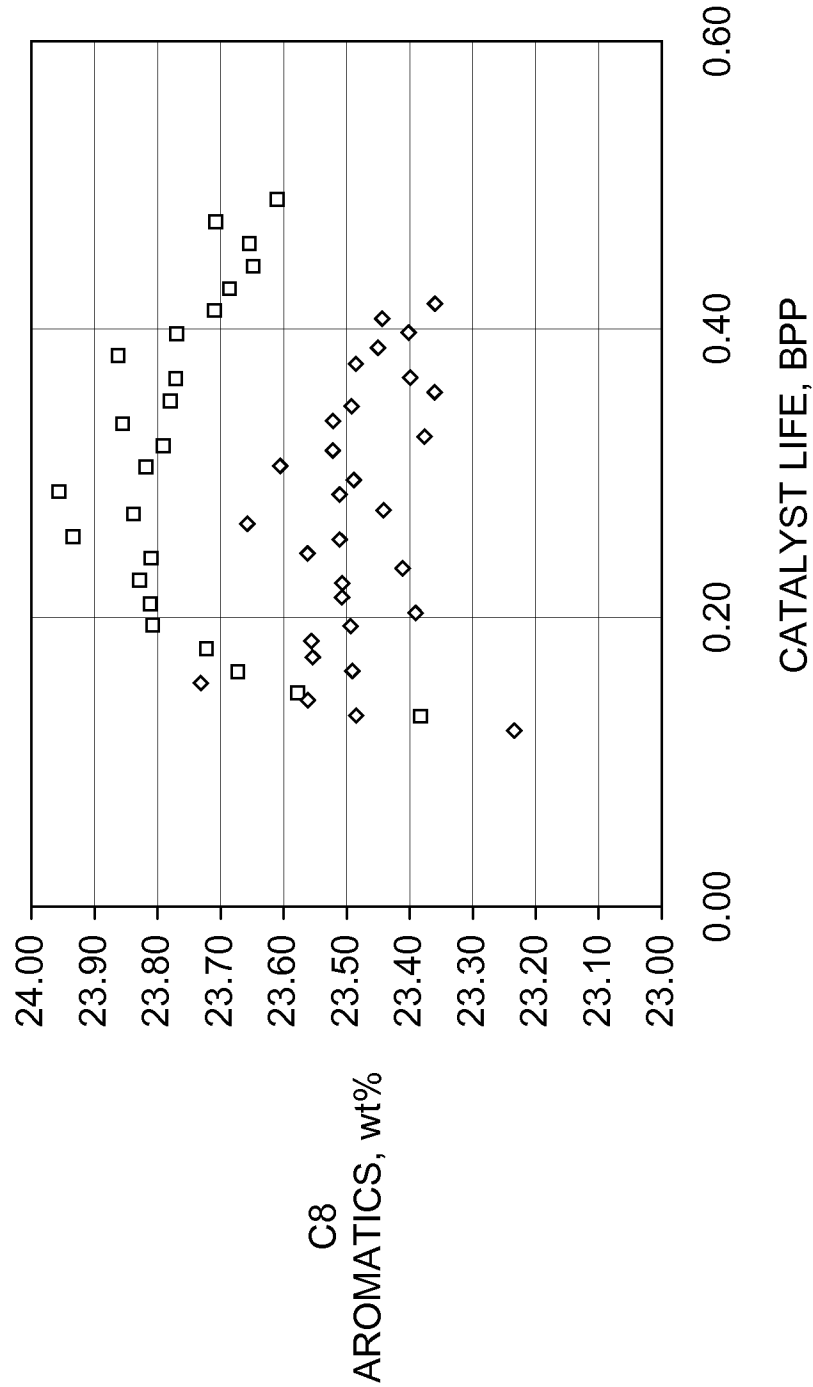


FIG. 11

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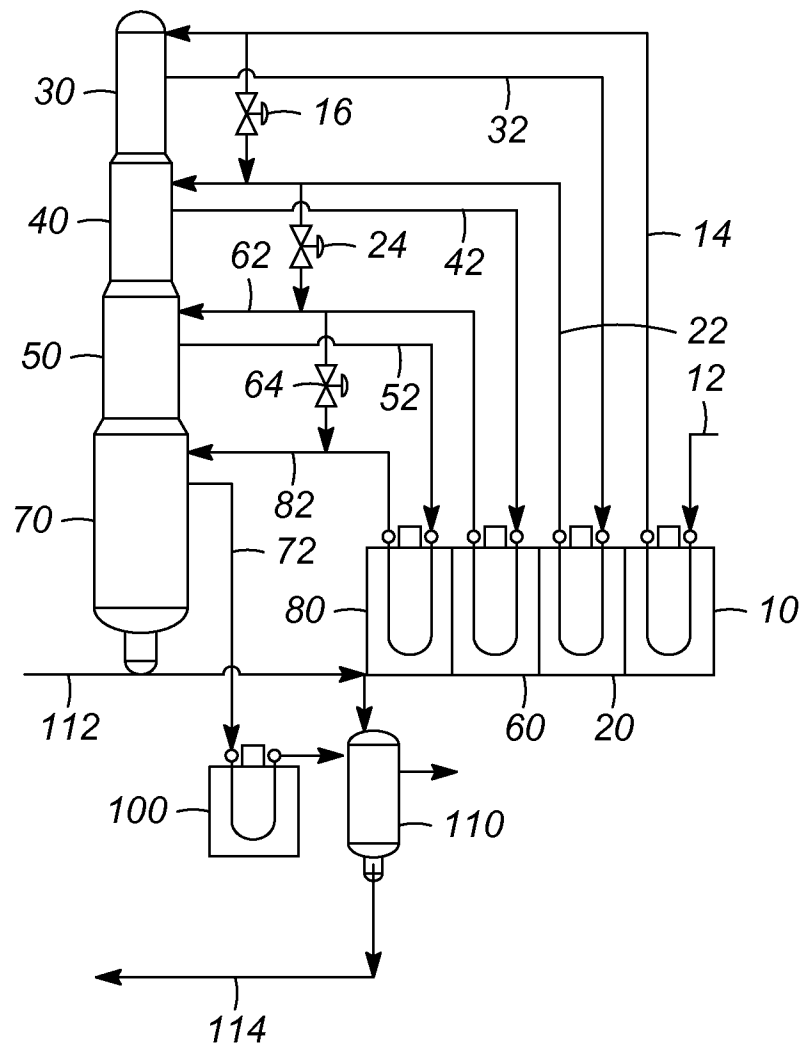


FIG. 12