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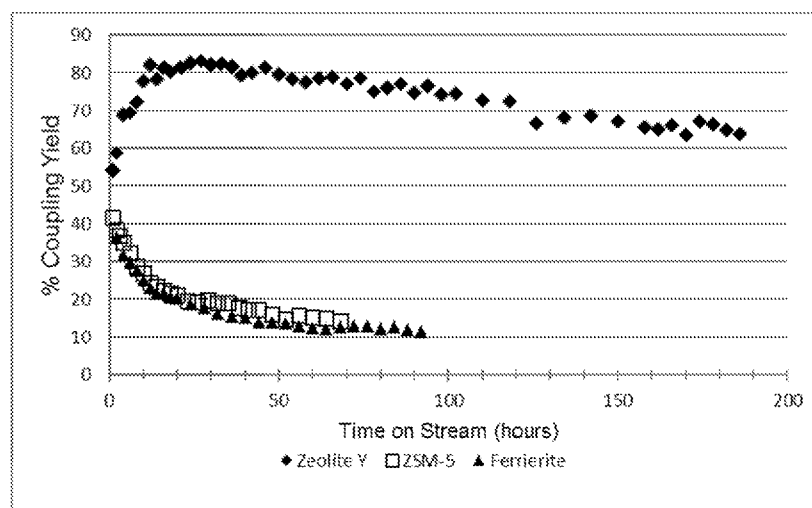
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(54) Title: A PROCESS FOR THE PRODUCTION OF AN ALKYLATED AROMATIC PRODUCT

Figure 1



(57) Abstract: A process for the production of an alkylated aromatic product comprises providing a feed stream containing an aromatic compound and an alcohol and contacting said feed stream with a solid acid catalyst to form an alkylated aromatic product. The process may be used for the alkylation of products obtained from the pyrolysis of biomass to provide fuels.



Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
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A PROCESS FOR THE PRODUCTION OF AN ALKYLATED AROMATIC PRODUCT

The invention concerns a process for the production of hydrocarbons suitable for use in the production of fuels, particularly from bio-derived sources such as wood, via a pyrolysis process.

The use of lignin-containing materials for the production of fuels has typically been carried out by pyrolysis to yield an aromatic-rich product stream of oxygenated and non-oxygenated molecules. This product stream requires further treatment in order to be suitable for the production of fuels because the hydrocarbon chain lengths of the pyrolysis product are typically too short. This problem has been addressed in the prior art. US2013/0338410 describes a method for producing linear alkylbenzene products from a bio-renewable feedstock comprising a mixture of naturally-derived hydrocarbons including separating the mixture of naturally-derived hydrocarbons into a naphtha portion and a distillate portion, reforming the naphtha portion, and using a high purity aromatics recovery process on the reformed naphtha portion to produce benzene. The method further includes separating a normal paraffins portion from the distillate portion, dehydrogenating the normal paraffins portion to produce mono-olefins and then reacting the benzene and the mono-olefins to produce the linear alkylbenzene product.

It is an object of the invention to provide an alternative process for the production of alkylbenzene products from a bio-renewable feedstock.

According to the invention, a process for the production of an alkylated aromatic product comprises the steps of providing a feed stream containing an aromatic compound and an alcohol and contacting said feed stream with a catalyst comprising a solid acid catalyst to form an alkylated aromatic product. The alcohol reacts with the aromatic compound to form an alkylated aromatic compound.

The alkylated aromatic product preferably comprises an alkylbenzene. The alkylated aromatic product may be mono-, di- or tri-alkylated.

The catalyst comprises a solid acid catalyst. Suitable solid acid catalysts include zeolites, sulphated zirconia, supported heteropolyacids such as supported tungstic acid, supported on supports such as silica, titania, alumina or another standard support. A preferred solid acid catalyst comprises a zeolite. Preferred zeolites have at least 1-dimensional pores (or channels or windows) comprising 10-membered rings or larger. More preferably, the zeolite has 2-dimensional pores in which the pores (or channels or windows) are equal to or greater than 10-membered rings. Even more preferably, the zeolite has 3-dimensional pores in which the pores (or channels or windows) are equal to or greater than 10-membered rings. Most preferably the zeolite has 3-dimensional pores in which the pores (or channels or windows) are equal to or larger than 12-membered rings. We have found that zeolites having pores (or

channels or windows) larger than 10-membered rings (approximately 0.5nm in diameter) are able to promote polyalkylation, especially dialkylated products, leading to a higher fuel value product. Preferred zeolites include zeolite Y and beta-zeolite. Zeolite Y has been found to produce high yields of coupled products and to deactivate more slowly than other zeolites such as ZSM-5 and Ferrierite. The catalyst may be in the form of a powder, granule or shaped unit. Shaped units include tablets, extrudates, spheres, rings etc. Shapes may include cylinders, lobed cylinders, pellets, stars, rings, wheels etc. Shaped units may be formed by methods such as extrusion, tableting, granulation, moulding, coating, 3-D printing or other method. The catalyst may contain other ingredients in addition to the solid acid. Such other ingredients include diluents, supports, binders, lubricants, pore-formers.

The catalyst preferably does not comprise a metal which is catalytically active for hydrogenation of aromatic rings. Therefore, in a preferred embodiment, the catalyst is essentially free of palladium, platinum, rhodium, cobalt, nickel, copper, ruthenium and iridium.

The feed stream comprises an aromatic compound and an alcohol. The feed stream may comprise more than one different aromatic compound. The aromatic compound may be substituted or unsubstituted. In preferred embodiments the aromatic compound is derived from a biomass source, such as lignin-containing materials, cellulosic materials etc. The aromatic compound may be derived from a biomass source by pyrolysis, for example by fast pyrolysis or catalytic fast pyrolysis. When the aromatic compound is derived from a biomass source, the aromatic compound typically comprises hydrocarbons (e.g. toluene) and oxygenated hydrocarbons, such as alcohols (e.g. cresol) or ethers, (e.g. anisole) etc. The aromatic compound may comprise compounds selected from the group consisting of hydrocarbons, oxygenated hydrocarbons, and mixtures of hydrocarbons and oxygenated hydrocarbons. At least 90% by weight of the aromatic compounds in the feed stream may consist of compounds selected from the group consisting of hydrocarbons and oxygenated hydrocarbons.

The feed stream may comprise more than one different alcohol. The alcohol is preferably a saturated alcohol. The alcohol may be linear, branched or cyclic. The alcohol is preferably a secondary alcohol. Primary alcohols may be useful in the process but are less preferred due to a tendency to form ethers in the reaction. Tertiary alcohols may be useful in the process but may be less reactive due to steric hindrance. The alcohol may be a C1 – C30 (or higher) alcohol, especially C1 – C12 alcohol. The alcohol may be derived from a biomass source. Bio-ethanol may be used. The alcohol may be derived from a biomass source by pyrolysis. For example, the alcohol may be derived from an aromatic alcohol which has been produced by pyrolysis of biomass. A suitable alcohol may be derived from an aromatic alcohol by hydrogenprocessing, e.g. by hydrogenation of the aromatic ring.

The feed stream may comprise a product stream from a biomass pyrolysis reaction. Such a feed stream may include the aromatic compound and the alcohol required for the production of an alkylated aromatic product by the process of the invention. The feed stream may contain water, for example up to about 50 wt% when a biomass feed is used. The feed stream may consist of or consist essentially of a product stream from a biomass pyrolysis reaction, optionally with additional alcohol and further optionally in the presence of a diluent or solvent. A suitable diluent or solvent may be selected by the skilled person. A hydrocarbon, especially an alkane such as a C6 – C20 alkane may be used as a diluent or solvent for the reactants.

The reaction may take place in the liquid phase or the vapour phase. The reaction may be carried out in a continuous or a batch reactor. Suitable reactors may be selected by the skilled person, for example a fixed bed trickle flow reactor is suitable when the feed stream is in the liquid phase. The reactor preferably has means for temperature control and heating or cooling means. The reaction may be carried out in the presence of an inert gas such as nitrogen. We have found that hydrogen is essentially inert in the present reaction, in the absence of a hydrogenation catalyst. The reaction may be carried out in the presence or absence of hydrogen. It is a particular benefit of the process of the invention that hydrogen is not required for the reaction. The reaction pressure may be in the range from about 0.1 to about 10 MPa, e.g. 0.5 – 5 MPa. The reaction is carried out at a suitable temperature. A suitable temperature range for the reaction is 100 – 400 °C, preferably 150 – 300 °C, especially 180 – 260 °C.

The process will be further described by reference to the following examples.

Trickle bed reaction Procedure

In order, the following items were added to a reactor tube (25mm inside diameter): a plug of glass wool; 95 mL of alpha-alumina chips; a mixture of the catalyst (25 mL) and SiC (46 grit) as a diluent (combined volume of 30 mL); 10 mL additional SiC. The rest of the tube was filled with alpha-alumina chips to about 5 cm below the top, then another plug of glass wool was introduced to secure the chips in place. A thermowell was located within the catalyst bed. The reactor was sealed and fitted into the reaction rig, then tested for leaks under nitrogen. The liquid feed vessel was filled with model feed solution.

The reactor was flushed with nitrogen for 20 minutes, then the gas was changed to hydrogen with a flow rate of 0.5 L/min and the pressure set to 40 barg (4 MPa). The liquid pump was started at an initial flow rate of 5 ml/min. When liquid was observed emerging at the gas-liquid separator above the collection pot, the liquid flow rate was reduced to 1.0 mL/min, the oven was turned on and the oven set to reaction temperature. The stopwatch was started when the internal reactor temperature reached reaction temperature. An automated sampling system (flow rate 0.5 ml/min) was started, with the first product sample collected after 1-2 hours of

running at the reaction temperature. Further samples were collected at regular intervals over the duration of the experiment. The samples were analysed by gas chromatography.

The following materials have been tested as catalysts:

- (a) Zeolite Y extrudates containing an alumina binder in which the zeolite Y (nominal cation = hydrogen) has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 30, unit cell size $24.28\text{\AA}$ and surface area $780\text{ m}^2/\text{g}$. Zeolite Y has a pore size of $7.35 \times 7.35 \times 7.35\text{\AA}$, according to the Database of Zeolite Structures (Structure Commission of the International Zeolite Association <http://www.iza-structure.org/databases/>).
- (b) ZSM-5 extrudates containing an alumina binder in which the ZSM-5 (nominal cation = ammonium) has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 50 and surface area $425\text{ m}^2/\text{g}$. ZSM-5 has a 3-dimensional channel system comprising 10-membered ring channels with pore sizes 5.1×5.5 and $5.3 \times 5.6\text{\AA}$, according to the Database of Zeolite Structures (Structure Commission of the International Zeolite Association <http://www.iza-structure.org/databases/>).
- (c) Ferrierite extrudates containing an alumina binder. The Ferrierite (nominal cation = ammonium) has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 20, and surface area $400\text{ m}^2/\text{g}$. Ferrierite has a 2-dimensional channel system comprising one 10-membered ring channel and one 8-membered ring channel. The 10-membered ring channel has dimensions $4.2 \times 5.4\text{\AA}$, according to the Database of Zeolite Structures (Structure Commission of the International Zeolite Association <http://www.iza-structure.org/databases/>).

These zeolites were all calcined before use to obtain the H-form. The calcination was carried out by heating in flowing air from room temperature to 150°C at $2^\circ\text{C}/\text{min}$ and then holding at 150°C for 10 hours. They were then heated from 150 to 450°C at $5^\circ\text{C}/\text{min}$ and held for 16 hours before being allowed to cool to room temperature.

Examples 1 – 3

The above-described trickle bed reaction procedure was operated using the following conditions and catalysts. The feed was $0.96\text{ mol}/\text{dm}^3$ each of cyclohexanol and m-cresol in n-dodecane, fed at $0.1\text{ mL}/\text{minute}$ (solution LHSV = 2 hr^{-1}). Reaction temperature = 220°C ; pressure = 4 MPa H_2 (inert under reaction conditions); gas flow = $0.5\text{ L}/\text{minute H}_2$.

Example 1: catalyst = Zeolite Y.

Example 2: catalyst = ZSM-5

Example 3: catalyst = Ferrierite.

The yield of coupled products was calculated from the following formula:

$$yield_{product} = \frac{[product]_{out}}{[m-cresol]_{in}} \cdot 100$$

Where $[product]_{out}$ and $[m-cresol]_{in}$ are the product concentration coming out of the reactor and the m-cresol concentration going in to the reactor and are determined by GC analysis.

Fig 1 shows the total yield of coupled products and Fig 2 shows the distribution of coupled products obtained using Zeolite Y (Example 1).

Example 4

The reaction of Example 1 was continued after the 190 hours and the temperature was varied between 180 and 240°C. The temperature was maintained at each 10°C increment for 2 hours and then at 240 °C for 24 hours. Fig 3 shows the calculated yield of the products after operation at each temperature for the stated time. The results show that the yield of coupled products and the proportion of dialkylated products increased as the temperature was raised to 220 °C.

Example 5

Example 2 was repeated with a 15 mL catalyst bed of ZSM-5 extrudates. The reaction temperature, pressure and gas flow rate were varied as shown in Table 1. The solution was fed at 1 ml/minute, giving a solution LHSV of 4hr⁻¹. The yield of coupled products is shown in Fig 4. The results show that the yield of coupled products increased as the temperature was raised to 240 °C but that the yield of dialkylated products remained low throughout the experiment. The yield of coupled products was significantly less than that achieved using Zeolite Y.

Table 1

Time on stream (hours)	0-4	5-21	24-28	32-44	48-52	55-59	62-66
Temperature (°C)	200	180	220	220	240	240	240
Pressure (MPa)	2	2	2	4	4	4	4
Gas feed (L/min)	1	1	1	1	1	0.5	1

Example 6

Example 1 was repeated using 10 v/v% m-cresol and 15 v/v% 2-octanol in n-dodecane as liquid feed. The gas and liquid flow rates, pressure and reaction temperature were the same as in Example 1. The product yield is shown in Fig 5.

Examples 7 - 12

Reaction procedure in batch autoclaves

The catalysts were weighed into a glass sample vial in a dust booth, before being transferred to a fume hood, where they were added to the autoclaves.

The autoclaves were charged with 7.5 ml m-cresol, 7.5 ml cyclohexanol and 10 ml n-dodecane and the catalysts were added. The H₂ pressure was set at 20 bar and the autoclaves were pressure checked before being purged with H₂ three times. The overhead

stirrers were set at 800 rpm and the autoclaves were heated to 200 °C in 1 hour and held at this temperature for 2 hours. They were then allowed to cool to room temperature. The composition of the product was analysed by gas chromatography.

The zeolites used were Beta (HBEA) zeolites, one having a SiO₂/Al₂O₃ mole ratio of 38 and is indicated in Table 2 as “B38”; and the second HBEA zeolite having a SiO₂/Al₂O₃ mole ratio of 75 indicated in Table 2 as “B75”. The zeolites were calcined before use to obtain the H-form as described above. Examples 10 – 12 (all comparative) show the effect of including a hydrogenation catalyst (5% Pd on carbon) in the reaction mixture.

The results in Table 2 show the concentrations of the components of the product mixture in weight %, normalised to 100%. They show that conversion of m-cresol is higher in the presence of the hydrogenation catalyst but that the hydrogenation of the aromatic ring is significant, shown by the amount of cyclohexane and cyclohexane derivatives in the product mixture.

Table 2

Example	7	8	9	10	11	12
Zeolite catalyst	B38	B75	B75	B38	B75	B75
Weight zeolite	104	99	1248	101	103	1250
5 wt% Pd/C (mg)	-	-	-	26	24	27
Cyclohexane (wt%)	12.5	16.58	1.5	44.4	45.5	49.1
Cyclohexene (wt%)	24.0	16.3	1.1	-	-	-
Cyclohexanol (wt %)	2.4	1.7	-	0.5	1.0	-
m-cresol (wt%)	49.4	48.6	36.9	11.0	15.7	27.5
Alkylated products	2.2	4.2	9.9	-	-	1.9
Dialkylated products	9.5	12.7	50.7	4.2	5.2	14.4
Methylcyclohexane	-	-	-	4.9	4.9	3.2
methylcyclohexanone	-	-	-	34.9	27.7	3.9

Examples 13 - 18

The autoclaves were charged with the reactants (as shown in Table 3) and 20 mL of n-dodecane and the catalysts were added. Zeolite Y and HBEA Zeolite “B38” were used in powder form. Nitrogen was used as headspace gas and, after pressure checking, was set to a pressure of 2 MPa. The overhead stirrers were set at 800 rpm and the autoclaves were heated to 220 °C in 1 hour and held at this temperature for 2 hours. They were then allowed to cool to room temperature. The composition of the product was analysed by gas chromatography and the composition is shown in Table 3 as a percentage (mol %). The “total alkylated products” is shown as the sum of “alkylated products” and dialkylated products.

The results show that zeolite Y converts more of the starting aromatic compound than the beta zeolite. Furthermore, Zeolite Y shows greater selectivity to dialkylated products than H-Beta. Dialkylated product has more fuel value than monoalkylated products so this is a benefit of using Zeolite Y.

Table 3

Example	13	14	15	16	17	18
Reactants						
toluene (mL)	2.5	-	-	2.5	-	-
3-methylanisole (mL)	-	3.0	-	-	3.0	-
m-cresol (mL)	-	-	2.5	-	-	2.5
2-octanol (mL)	4.0	4.0	4.0	4.0	4.0	4.0
Catalyst	Zeolite Y	Zeolite Y	Zeolite Y	B38	B38	B38
Catalyst mass (mg)	257.8	244.1	255.3	253.1	244.9	255.9
Products (mol %)						
octene	4.1	3.4	2.2	13.5	22.3	11.7
Toluene	23.3	-	-	47.9	-	-
3-anisole	-	8.1	-	-	48.8	-
m-cresol	-	0.7	8.6	-	-	20.4
Alkylated product	48.0	59.7	59.3	38.6	28.9	67.9
Dialkylated product	24.6	28.1	29.9	-	-	-
Total alkylated product	72.5	87.8	89.1	38.6	28.9	67.9

Claims

1. A process for the production of an alkylated aromatic product comprising the steps of providing a feed stream containing an aromatic compound and an alcohol and contacting said feed stream with a solid acid catalyst to form an alkylated aromatic product.
2. A process as claimed in claim 1, wherein said alkylated aromatic product comprises an alkylbenzene.
3. A process as claimed in claim 1 or claim 2, wherein the alkylated aromatic product is mono-, di- or tri-alkylated.
4. A process as claimed in any one of the preceding claims wherein the solid acid catalyst is selected from the group consisting of zeolites, sulphated zirconia and supported heteropolyacids.
5. A process as claimed in claim 4 wherein the solid acid catalyst comprises a zeolite.
6. A process as claimed in claim 5, wherein the zeolite has at least 1-dimensional pores, channels or windows comprising 10-membered rings or larger.
7. A process as claimed in claim 6, wherein the zeolite has at least 2-dimensional pores in which the pores, channels or windows are equal to or greater than 10-membered rings.
8. A process as claimed in claim 7, wherein the zeolite has 3-dimensional pores in which the pores, channels or windows are equal to or greater than 10-membered rings.
9. A process as claimed in claim 8, wherein the zeolite has 3-dimensional pores in which the pores, channels or windows are equal to or larger than 12-membered rings.
10. A process as claimed in any one of the preceding claims, wherein the catalyst comprises zeolite Y or BEA.
11. A process as claimed in any one of the preceding claims, wherein the catalyst is essentially free of a hydrogenation catalyst.
12. A process as claimed in any one of the preceding claims, wherein the feed stream contains a diluent.
13. A process as claimed in claim 10, wherein the diluent is a C6 – C20 aliphatic hydrocarbon.
14. A process as claimed in any one of the preceding claims, wherein the reaction pressure is in the range from 0.1 to 10 MPa.

15. A process as claimed in any one of the preceding claims, wherein the reaction temperature is in the range from 100 – 400 °C.
16. A process as claimed in any one of the preceding claims, wherein at least a portion of the feed stream is derived from biomass.

Figure 1

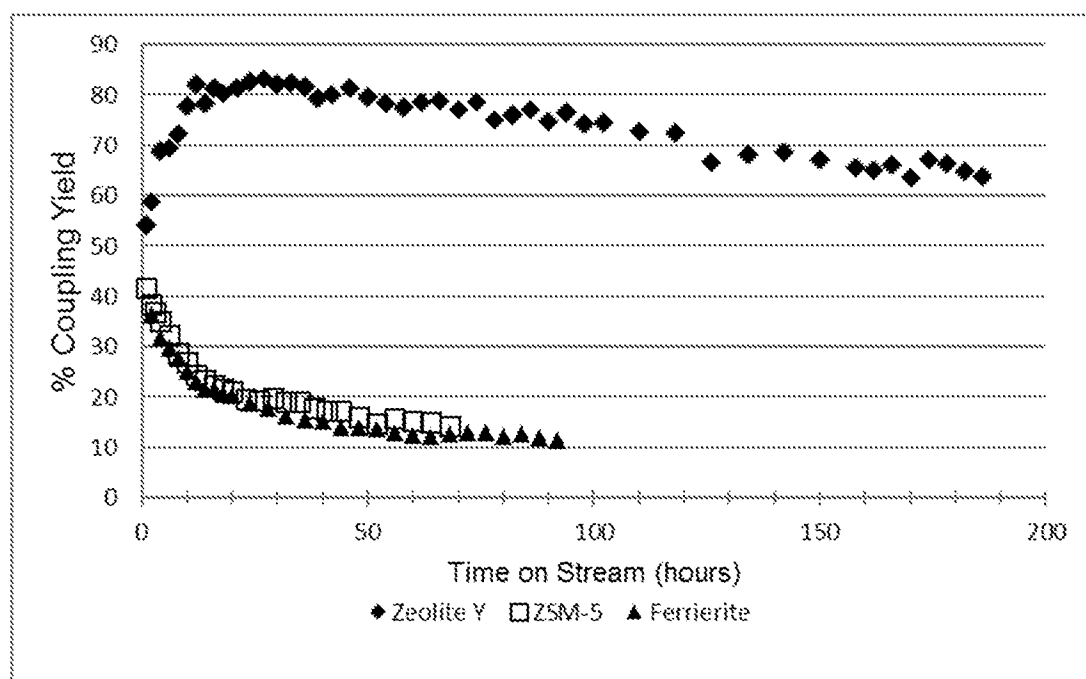


Figure 2

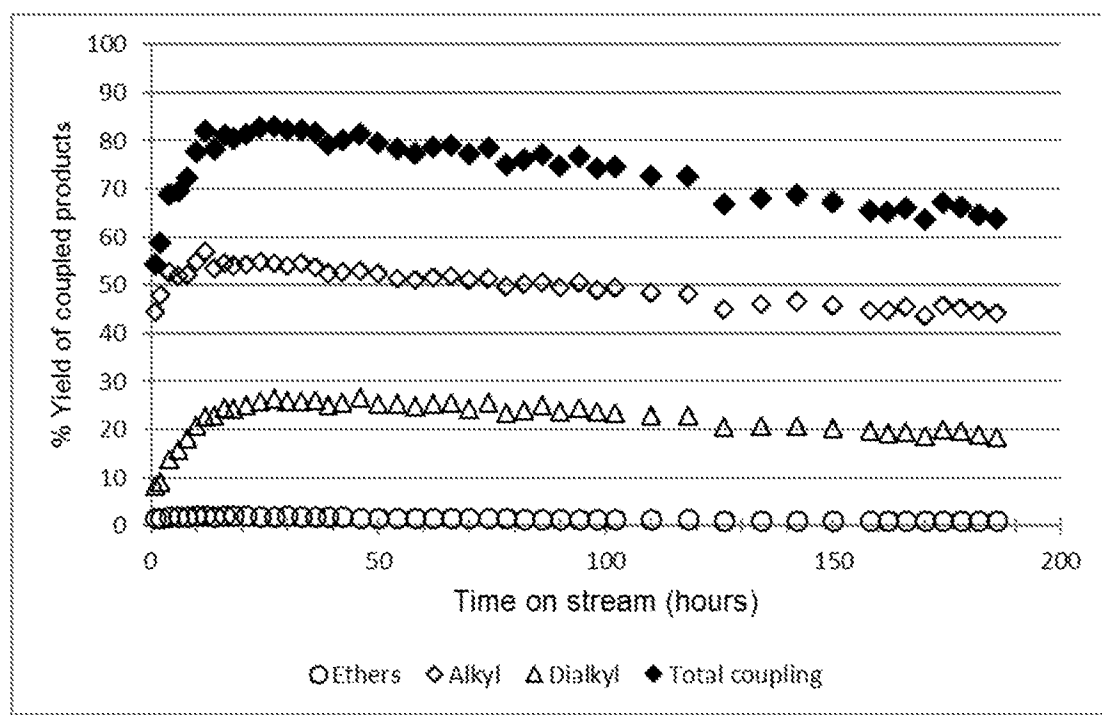


Figure 3

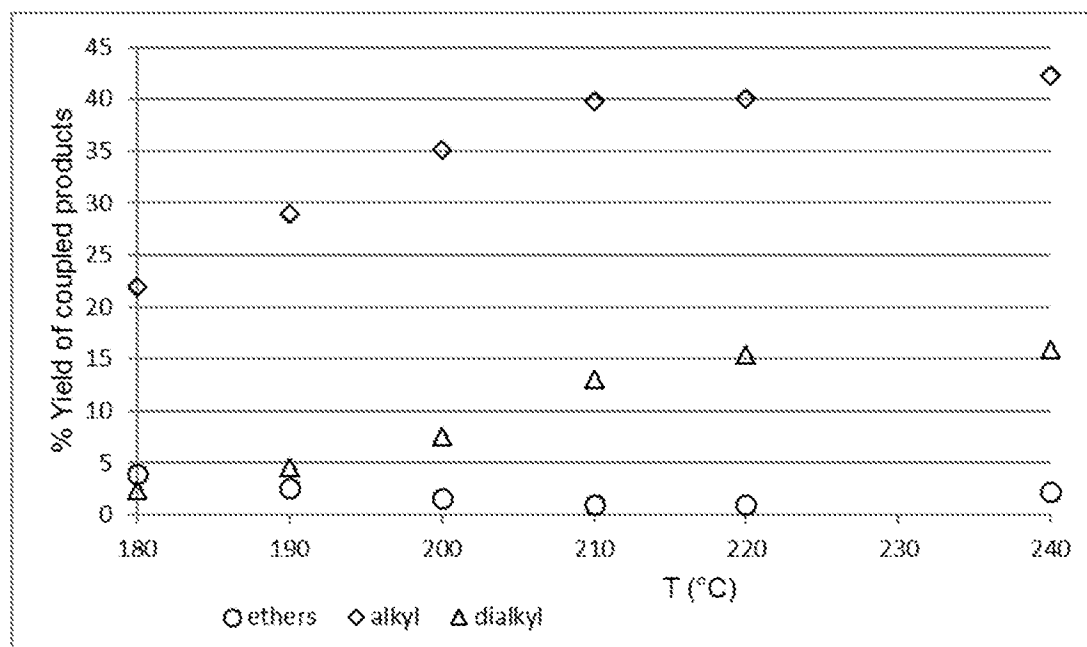


Figure 4

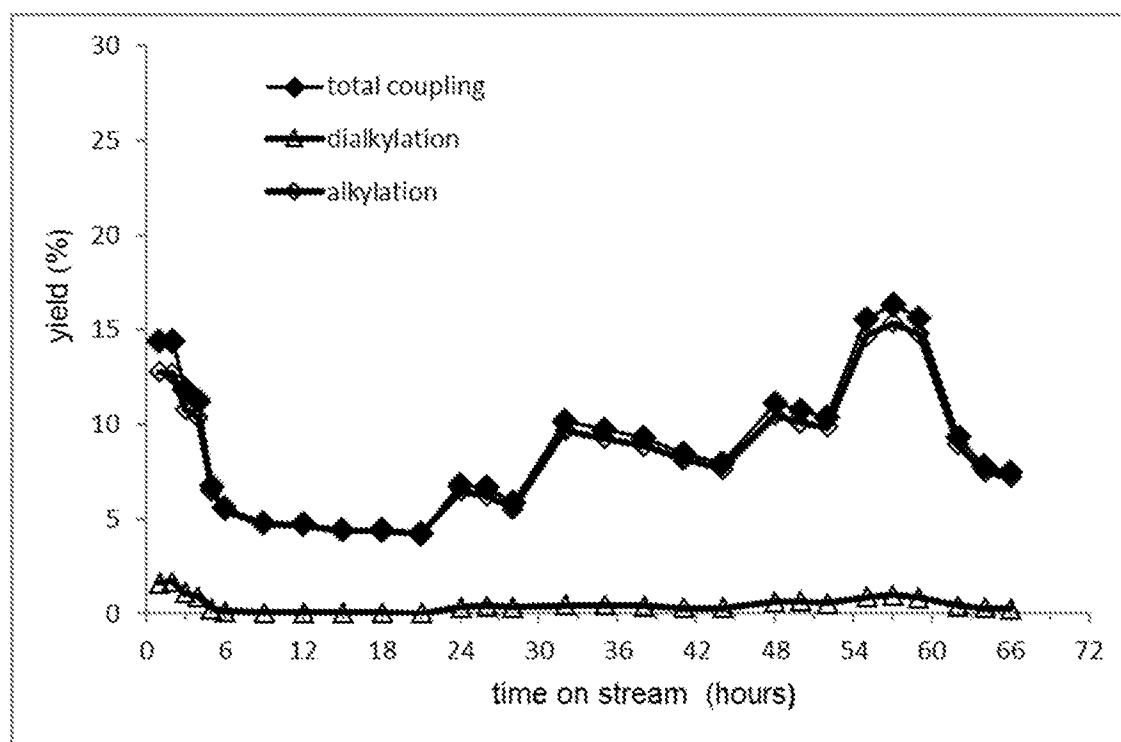
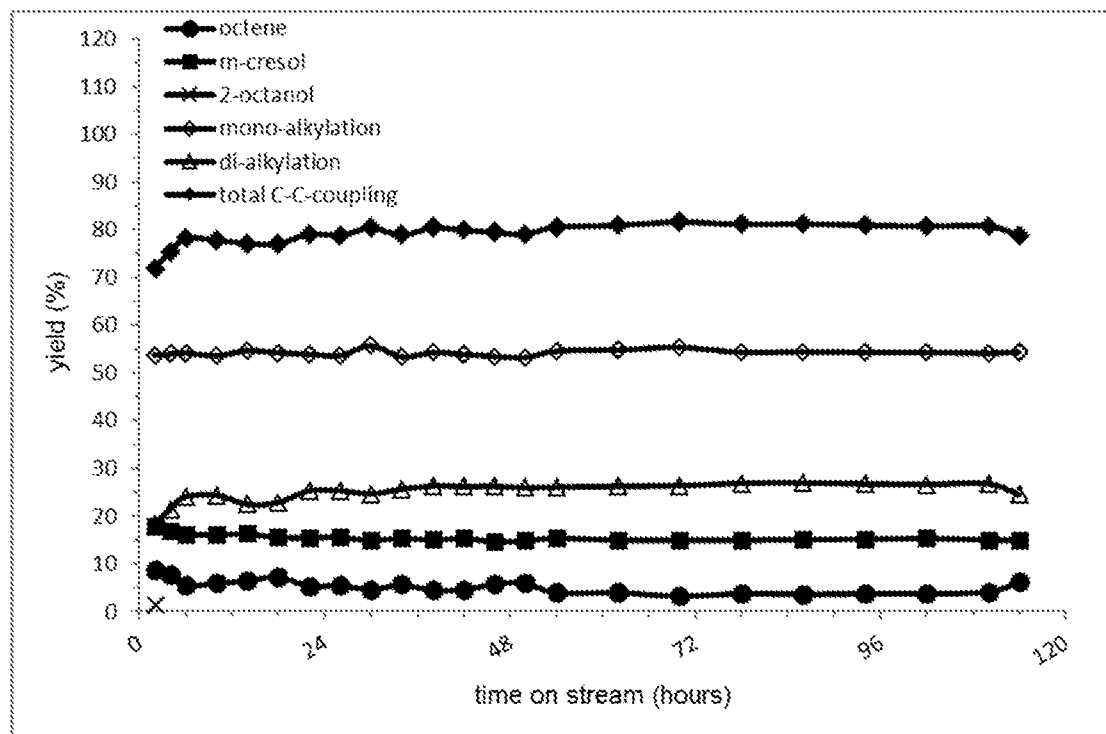


Figure 5



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/052669

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C39/07 C07C43/205 C07C2/86 C07C11/02 C07C15/08
C07C15/107 C07C15/113

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)

C07C

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BRENDAN COUGHLAN ET AL: "Alkylation reactions over ion-exchanged molecular sieve zeolite catalysts. Part 1.-Alkylation of toluene with methanol: consideration of the effects of reaction parameters on catalyst deactivation and the extent of polysubstitution", JOURNAL OF THE CHEMICAL SOCIETY. FARADAY TRANSACTIONS, vol. 79, no. 2, 1 January 1983 (1983-01-01), pages 281-296, XP055417067, GB ISSN: 0300-9599, DOI: 10.1039/f19837900281 table 4 ----- -/-	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

1 November 2017

Date of mailing of the international search report

08/11/2017

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2017/052669

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/000767 A1 (EXXONMOBIL CHEM PATENTS INC [US]; MOHR GARY D [US]; BUCHANAN SCOTT J []) 31 December 2003 (2003-12-31) tables 1-17 examples 1-6 claim 23 page 15, paragraph 3 -----	1-15
X	PATRA C R ET AL: "Isopropylation of Xylenes Catalyzed by Ultrastable Zeolite Y (USY) and Some Other Solid Acid Catalysts", JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 212, no. 2, 10 December 2002 (2002-12-10), pages 216-224, XP027233548, ISSN: 0021-9517 [retrieved on 2002-12-10] tables 1-6 abstract -----	1-12,14, 15
X	MARTIN KUB°U ET AL: "Three-dimensional 10-ring zeolites: The activities in toluene alkylation and disproportionation", CATALYSIS TODAY, vol. 259, 1 January 2016 (2016-01-01), pages 97-106, XP055417068, AMSTERDAM, NL ISSN: 0920-5861, DOI: 10.1016/j.cattod.2015.05.019 abstract table 1 paragraph [02.5] -----	1-12,14, 15
X	US 2011/009682 A1 (MATSUSHITA KOICHI [JP] ET AL) 13 January 2011 (2011-01-13) paragraph [0071] - paragraph [0117] tables 1-6 -----	1-9, 11-15
X	US 2005/240070 A1 (GHOSH ASHIM K [US] ET AL) 27 October 2005 (2005-10-27) paragraph [0003] * examples * ----- -/--	1-9, 11-15

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2017/052669

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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