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(54) **Title:** ALKYLBENZENES DERIVED FROM FISCHER-TROPSCH HYDROCARBONS AND THEIR USE IN DRILLING FLUIDS

(57) **Abstract:** The invention provides for the use of Fischer-Tropsch hydrocarbons for the production of alkyl benzenes, detergents and drilling fluids having advantageous branching properties.

ALKYLBENZENES DERIVED FROM FISCHER-TROPSCH HYDROCARBONS AND THEIR USE IN DRILLING FLUIDS

Field of the Invention

The invention relates to the use of Fischer-Tropsch hydrocarbons for the production of alkyl benzene (AB) and drilling fluid compositions.

Background to the Invention

The Fischer–Tropsch process is a well known process for the production of hydrocarbons from carbon monoxide and hydrogen i.e from syngas.

The prior art, in US 3 674 885, teaches that AB derived from Fischer-Tropsch process products is almost entirely linear as the AB derivation feedstock from the Fischer-Tropsch process comprises of almost entirely linear paraffins and olefins with very small amounts, if any, of branched-chain compounds. In recent years this was believed to be very positive as linear alkyl benzene (LAB) were preferred in the production of bio-degradable detergents.

Summary of the Invention

Surprisingly, after extensive research and experimentation, it has now been found by the inventors that the AB derived from Fischer-Tropsch process products although having substantial branching has acceptable biodegradability and cold water detergency.

The Fischer-Tropsch reaction for the production of the hydrocarbons, such as olefins, may be effected in a fixed bed, in a slurry bed, or in a fluidised bed reactor. The Fischer-Tropsch reaction conditions may include utilising a reaction temperature of between 190°C and 340°C, with the actual reaction temperature being largely determined by the reactor configuration. Thus, when a fluidised bed reactor is used, the reaction temperature is preferably between 300°C and 340°C; when a fixed bed reactor is used, the reaction temperature is preferably between 200°C and 250°C; and when a slurry bed reaction is used, the reaction temperature is preferably between 190°C and 270°C.

An inlet synthesis gas pressure to the Fischer-Tropsch reactor of between 1 and 50 bar, preferably between 15 and 50 bar, may be used. The synthesis gas may have a H_2:CO molar ratio, in the fresh feed, of 1,5:1 to 2,5:1, preferably 1,8:1 to 2,2:1. A gas recycle may optionally be employed to the reaction stage, and the ratio of the gas recycle rate to the fresh synthesis gas feed rate, on a molar basis, may then be between 1:1 and 3:1, preferably between 1,5:1 and 2,5:1. A space velocity, in m^3 (kg catalyst)$^{-1}$, of from 1 to 20, preferably from 8 to 12, may be utilised in the reaction stage.

In principle, an iron-based, a cobalt-based or an iron/cobalt-based Fischer-Tropsch catalyst can be used in the Fischer-Tropsch reaction stage, however, an iron-based catalyst is preferred.

Thus, according to a first aspect of the invention, there is provided an alkyl benzene (AB) composition derived from Fischer-Tropsch process products, said AB composition including from 10% to 90% branched alkyl chain AB, said alkyl chain having branches of from 1 to 2 carbon atoms.

Generally, the AB of the AB composition is predominantly linear.

Typically, the AB composition includes between 10% and 49% branched alkyl chain AB.

The AB composition includes about 25% branched alkyl chain AB.

In most embodiments the branched alkyl chain AB portion of the AB composition is predominantly mono-methyl branched. However, the branched alkyl chain AB portion of the AB composition may include di-methyl and/or ethyl branched alkyl chain AB.

The branching on the alkyl chain of the AB is predominantly on the C4+ carbon atoms, with some branching on the C2 carbon atom of the alkyl chain.

Typically, the branching on the alkyl chain of the AB is at least 70% on the C4+ carbon atoms.

The branching on the alkyl chain of the AB may exceed 90% on the C4+ carbon atoms.

The AB of the AB composition may be obtained by alkylation of benzene with Fischer-Tropsch process products.

For purposes of detergent production, the AB composition may include AB having between 10 and 14 carbon atoms on the alkyl chain. However, in some cases the AB of the AB composition may have up to 16 carbon atoms on the alkyl chain.

The alkylation of the benzene may proceed under conventional or novel process conditions using conventional or novel catalysts. Typical catalysts for alkylation of the benzene include homogeneous Lewis acids including metal halides such as aluminium trichloride, Bronsted acids such as hydrogen fluoride, sulphuric acid, and phosphoric acid, and heterogeneous catalysts such as amorphous and crystalline silica alumina.

Methyl branching on the alkyl side chain leads to the formation of quaternary carbons which decreases biodegradeability. Surprisingly, narrow pore zeolites, such as dealuminated mordenite, offretite and Beta zeolite, give higher selectivity to alkylation towards the end positions of the alkyl chain, typically on the 2-position of the alkyl chain. This leads to a reduction in the amount of quaternary carbons formed after alkylation and hence improves the biodegradation qualities of the product.

The AB composition requires no work up to increase or decrease the linearity and utilises as feedstock for production thereof the products of the Fischer-Tropsch process. Typically, the feedstock is an olefinic product stream from a high temperature Fischer-Tropsch process, although the invention is not limited to any particular Fisher-Tropsch process conditions.

The inventors believe that the direct use of the high temperature Fischer-Tropsch process products for the derivation of AB has economic advantages over other AB production processes in that the peculiar branched to linear ratios of the high temperature Fischer-Tropsch derived AB, as well as the peculiar branch types and branch positions allow for process steps such as delinearization or linearization to be omitted. Furthermore, the inventors believe that the AB composition of the invention is suitable as a substitute for presently used AB without extensive adjustment of detergent formulations.

According to a second aspect of the invention, there is provided a drilling fluid composition derived from Fischer-Tropsch process products, the drilling fluid composition including between 10% and 90% branched hydrocarbons having branches of from 1 to 2 carbon atoms.

Generally, the hydrocarbons of the drilling fluid composition are predominantly linear.

Typically, the hydrocarbons of the drilling fluid composition are α-olefins.

Typically, the drilling fluid composition includes between 10% and 49% branched hydrocarbons.

The drilling fluid composition includes between about 25% branched hydrocarbons.

In most embodiments the branched hydrocarbons portion of the drilling fluid composition is predominantly mono-methyl branched. However, the branched hydrocarbons portion of the drilling fluid composition may include di-methyl and/or ethyl branched hydrocarbons.

The hydrocarbons of the drilling fluid composition may be obtained from high temperature Fischer-Tropsch process products.

For purposes of drilling fluid production, the drilling fluid composition may include hydrocarbons having from 12 to 18 carbon atoms. However, in some cases the hydrocarbons of the drilling fluid composition may have from 14 to 16 carbon atoms.

The hydrocarbons may either be used directly as drilling fluids or used to alkylate benzene to form alkylated benzenes usable as drilling fluids.

The inventors believe that the direct use of the high temperature Fischer-Tropsch process products for the derivation of hydrocarbons for drilling fluid compositions has economic advantages over other drilling fluid composition production in that the peculiar branched to linear ratios of the high temperature Fischer-Tropsch derived hydrocarbons as well as the peculiar branch types and branch positions allow for preliminary and intermediate process steps such as delinearization or linearization to be omitted.

EXAMPLES

Example 1 – Alkyl Benzene

Alkylation of benzene with C_{11} to C_{12} Fischer-Tropsch olefins.

A mixture of Benzene and an olefin containing Fischer-Tropsch stream of carbon range 11 to 12 with an olefin benzene molar ratio of 1:5 was treated with anhydrous aluminium trichloride, 5 mass%, in a round bottomed flask at a temperature range of 60 °C to 80 °C and at atmospheric pressure for 6 hours.

Removal of a light fraction at 120 °C and a vacuum of up to 5 mbar and subsequent distillation of the remaining reaction mixture at a temperature of 135 °C and a vacuum of up to 1 mbar gave C_{11} to C_{12} alkylated benzene.

Example 2

An olefinic C_{11}/C_{12} Fischer-Tropsch feedstock was used to alkylate benzene to produce alkyl benzenes (AB's) .

For the alkylation of benzene with the Fischer-Tropsch product, 1 mole of the α-olefins, 10 mole of benzene and 10 wt% based on the olefin mixture of a shape selective Beta – zeolite, amorphous silica, and ultra stable Y-zeolite (USY)catalyst, were added in three separate runs to a stainless steel autoclave. The autoclave was purged with N_2 and then charged to 8 bar(g) N_2. The mixture was stirred and heated to about 150°C for 16 hours. It was then cooled and removed from the autoclave. The reaction mixture was in each case filtered to remove the catalyst and the unreacted benzene was removed in vacuo using a rotary evaporator.

The product was sulfonated with an equivalent of chlorosulfonic acid using methylene chloride as solvent. The methylene chloride was distilled away. The sulfonated product was neutralized with sodium methoxide in methanol and the methanol was evaporated to give alkyl benzene sulfonate, sodium salt mixture.

The above runs are set out in tables 1 to 4below.

In Table 1, an olefinic C11/C12 feed is used to alkylate benzene in the presence of the amorphous silica-alumina catalyst for 24 hours. The overall reaction of C11/C12 to AB is 37.6 % of the C11/C12 feed.

In Tables 2, 3 and 4, the olefinic C11/C12 feedstock is reacted in the presence of the three catalyst types with benzene to form alkyl benzene's. An analysis of the AB's to determine the position of the phenyl group on the alkyl chain of the AB's indicates that the 2 position is favoured in all cases, with a marked favouring when beta-zeolite catalyst is used.

Table 1: Alkylation of Benzene with C11/C12 Olefins

	Feed %	Product %
Benzene	69.56	73.58
C_{11} / C_{12} olefins	30.12	18.80
AB's (alkyl benzene)	0.00	7.10
Other	0.32	0.52
C_{11} / C_{12} reacted		37.6

Table 2 Alkylation of Benzene with C11/C12 Olefins in the presence of three different catalysts

	Feed %	Amorphous Si-Al Catalyst	ß-zeolite Catalyst	Ultra stable y-zeolite Catalyst
Benzene	77.0	77.1	81.6	73.4
$C_{11} - C_{12}$	22.5	9.5	11.1	11.1
AB's (alkyl benzene)	0.0	13.1	6.9	14.0
Other	0.5	0.4	0.4	1.5
C_{11} / C_{12} reacted	0.0	58.0	50.8	50.5

Table 3: Analysis of C11 Alkyl Benzene produced in the presence of three different catalysts

Isomer (indicating position of phenyl group)	Amorphous Si-Al Catalyst	ß-zeolite Catalyst	Ultra stable y-zeolite Catalyst
C11 / 6-Ph	16.12	10.06	23.25
C11 / 5Ph	11.09	6.76	15.15
C11 / 4 Ph	14.45	11.04	17.51
C11 / 3 Ph	23.45	21.86	19.93
C11 / 2 Ph	34.89	50.28	24.16

Table 4: Analysis of C12 Alkyl Benzene produced in the presence of three different catalysts

Isomer (indicating position of phenyl group)	Amorphous Si-Al Catalyst	ß-zeolite Catalyst	Ultra stable y-zeolite Catalyst
C12 / 6-Ph	10.01	5.68	16.81
C12 / 5Ph	11.61	6.57	17.82
C12 / 4 Ph	15.63	13.10	21.42
C12 / 3 Ph	25.17	23.93	20.86
C12 / 2 Ph	37.58	50.72	23.08

Example 3 – Drilling Fluids

C_{16} Fischer-Tropsch α-olefins were obtained by metathesis and were useable as a drilling fluid composition.

The drilling fluid composition included about 75% linear α-olefins and about 25% branched α-olefins, which α-olefins were predominantly mono-methyl, di-methyl and ethyl branched.

The drilling fluid compositions in accordance with the invention had the following physical properties:

The properties are for a typical C_{12}-C_{16} internal linear and branched combination of olefinic product made in accordance with the present invention:

Viscocity: 1-2 cSt @ 100'C

Flash point: >90'C

Linear:branch ratio 1:1 to 5:1

Pour Point: < 0'C

Examples of the α-olefins useful as drilling fluids include:

1) A drilling fluid including:

A linear component making up about 75.1% of the composition; and

A mono-methyl branched component making up about 24.9% of the drilling fluid composition.

2) A drilling fluid composition including:

A linear component of mainly hexadec-1-ene in amounts of between 2 and 40%, depending on process conditions; and

A mono-methyl branched component of between 60% and 98% of the drilling fluid composition.

Claims

1. An alkyl benzene (AB) composition derived from Fischer-Tropsch process products, said AB composition including from 10% to 90% branched alkyl chain AB, said alkyl chain having branches of from 1 to 2 carbon atoms.

2. An alkyl benzene composition as claimed in claim 1, wherein the alkyl chains of the AB of the AB composition are predominantly linear.

3. An alkyl benzene composition as claimed in claim 1 or claim 2, wherein the AB composition includes between 10% and 49% branched alkyl chain AB.

4. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the AB composition includes 25% branched alkyl chain AB.

5. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branched alkyl chain AB portion of the AB composition is predominantly mono-methyl branched.

6. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branched alkyl chain AB portion of the AB composition includes di-methyl and/or ethyl branched alkyl chain AB.

7. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branching on the alkyl chain of the AB is predominantly on the C4+ carbon atoms of the alkyl chain.

8. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branching on the alkyl chain of the AB includes branching on the C2 carbon atom of the alkyl chain.

9. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branching on the alkyl chain of the AB is at least 70% on the C4+ carbon atoms of the alkyl chain.

10. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the branching on the alkyl chain of the AB is at least 90% on the C4+ carbon atoms of the alkyl chain.

11. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the AB of the AB composition is obtained by alkylation of benzene with Fischer-Tropsch process products.

12. An alkyl benzene composition as claimed in any one of the preceding claims, which includes AB having an alkyl chain of from 10 to 16 carbon atoms.

13. An alkyl benzene composition as claimed in any one of the preceding claims, which includes AB having an alkyl chain of from 10 to 14 carbon atoms.

14. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the phenyl group of the AB is predominantly towards the end positions of the alkyl chain.

15. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the phenyl group of the AB is predominantly in the second position of the alkyl chain.

16. An alkyl benzene composition as claimed in any one of the preceding claims, wherein the feedstock for the production of the alkyl chain is an olefininc product stream from a high temperature Fischer-Tropsch process.

17. A drilling fluid composition derived from Fischer-Tropsch process products, the drilling fluid composition including between 10% and 90% branched hydrocarbons having branches of from 1 to 2 carbon atoms.

18. A drilling fluid composition as claimed in claim 17, wherein the hydrocarbons of the drilling fluid composition are predominantly linear.

19. A drilling fluid composition as claimed in claim 17 or 18, wherein the hydrocarbons of the drilling fluid composition are predominantly α-olefins.

20. A drilling fluid composition as claimed in any one of claims 17 to 19, which includes between 10% and 49% branched hydrocarbons.

21. A drilling fluid composition as claimed in any one of claims 17 to 19, which includes 25% branched hydrocarbons.

22. A drilling fluid composition as claimed in any one of claims 17 to 21, wherein the branched hydrocarbons of the drilling fluid composition are predominantly mono-methyl branched.

23. A drilling fluid composition as claimed in any one of claims 17 to 22, wherein the branched hydrocarbons of the drilling fluid composition include di-methyl and/or ethyl branched hydrocarbons.

24. A drilling fluid composition as claimed in any one of claims 17 to 23, wherein the hydrocarbons are obtained from high temperature Fischer-Tropsch process products.

25. A drilling fluid composition as claimed in any one of claims 17 to 24, which includes hydrocarbons having from 12 to 18 carbon atoms.

26. A drilling fluid composition as claimed in any one of claims 17 to 24, which includes hydrocarbons having from 14 to 16 carbon atoms.

27. A drilling fluid composition as claimed in any one of claims 17 to 26, wherein the hydrocarbons are used to alkylate benzene to form alkylated benzenes usable as drilling fluids.

28. An alkyl benzene composition, substantially as herein described and illustrated.

29. A drilling fluid composition, substantially as herein described and illustrated.

30. A new alkyl benzene composition or a new drilling fluid composition, substantially as herein described and illustrated.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C15/107 C09K7/06

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)
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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 practical, 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	GB 990 744 A (UNIVERSAL OIL PRODUCTS COMPANY) 28 April 1965 (1965-04-28) page 3, line 53 -page 4, line 19; claims	1-16
X	US 3 674 885 A (GRIESINGER WILLIAM K ET AL) 4 July 1972 (1972-07-04) cited in the application claims	1-16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 3674885 A	04-07-1972	ZA 7100287 A	27-10-1971

Form PCT/ISA/210 (patent family annex) (July 1992)