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(54) **Gasoline composition and method for its preparation.**

(57) A novel gasoline additive is described comprising a mixture of methanol, *iso*-propanol, methyl *t*-butyl ether and, optionally, a C_5- isomerate, typically in amounts of, per 100 parts by weight of additive, from about 5 to about 90 parts by weight methanol, from about 3 to about 35 parts by weight *iso*-propanol, from about 3 to about 35 parts by weight mthyl *t*-butyl ether, and from 0 to 35 parts by weight of C_5- isomerate. A process is described for producing such an additive from natural gas streams by isomerising *n*-butane component thereof to *iso*-butane, dehydrogenating propane component of the natural gas stream to propylene and *iso*-butane formed by isomerisation of *n*-butane to *iso*-butene respectively, converting resulting propylene to *iso*-propanol, etherifying resulting *iso*-butene with methanol to form methyl *t*-butyl ether, and blending resulting *iso*-propanol and methyl *t*-butyl ether with methanol, and optionally with a C_5- isomerate formed by isomerising C_5 and heavier hydrocarbons present in the natural gas stream, to form the additive.

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PROCESS AND PRODUCT

TITLE MODIFIED
see front page

This invention relates to a process for the production from natural gas of a novel gasoline additive and to the additive itself.

Gasoline is essentially a mixture of hydrocarbons containing usually 4 and more carbon atoms. For satisfactory performance in a motor car engine a gasoline must have a sufficiently high "octane rating". To this end it has been customary to add to gasoline an "anti-knock" compound such as lead tetra-ethyl. However, there is increasing concern at the damage to health and to the environment caused by emission of lead compounds in the exhaust gases of motor car engines and many countries now have laws limiting the permissible amount of lead in petrol. In addition anti-pollution legislation in many countries now limits the permissible levels of carbon monoxide, nitrogen oxides and hydrocarbons in exhaust gas emissions and has led to the adoption of catalytic converters as a part of motor car exhaust gas systems. Such converters utilise noble metal catalysts whose effectiveness is destroyed by the use of lead-containing gasoline. Hence there is for a variety of reasons a move towards the use of lead-free gasoline.

Several ways have been adopted for producing lead-free gasoline. For example, aromatic compounds can be added to the gasoline in order to improve its octane rating. Benzene is, however, a known carcinogen and if too much aromatic material is added the hydrocarbon emission in the exhaust gas tends to increase. Moreover the available quantities of aromatic compounds are limited by the nature of the crude oil used as gasoline feedstock. In addition it is expensive to cyclise and dehydrogenate linear aliphatic hydrocarbons in order to produce aromatic compounds for use as gasoline additives and production

of aromatic compounds in this way represents a loss of aliphatic hydrocarbons which could otherwise be used as such in gasoline.

A certain improvement in octane rating can also be attained by isomerising linear alkanes to iso-compounds and similar branched chain compounds. However this requires the use of an extra processing unit in the refinery and the resulting isomerate cannot be used to produce lead-free gasolines, since its octane rating is not sufficiently high.

Another approach involves addition of oxygenated compounds such as alcohols and ethers, the most important compounds heretofore suggested for this purpose being methanol and methyl t-butyl ether. Besides methanol and methyl t-butyl ether, proposals have been also made to use t-amyl methyl ether; see, for example, British Patent Specification No. 2010323A and United States Patent Specification No. 4193770. There have also been suggestions to use mixtures of ethers and alcohols as gasoline additives. Thus, for example, German Offenlegungsschrift No. 2809481 suggests use of a mixture of methanol, n- or iso-butanol, and optionally methyl t-butyl ether. British Patent Specification No. 2043098A and United States Patent Specification No. 4207077 use methyl or ethyl t-butyl ether to solubilise ethanol in gasoline-hydrous ethanol mixtures. Mixtures of one or more C_4-alcohols and either or both of methyl and ethyl t-butyl ethers are suggested for incorporation in gasoline compositions in British Patent Specification No. 1461966. Azeotropic alcohol-ether mixtures are proposed as gasoline additives in Canadian Patent Specification No. 958213; amongst azeotropic mixtures exemplified are mixtures containing:

methanol and methyl t-butyl ether;

methanol and methyl t-amyl ether;

iso-propanol and di-iso-propyl ether; and

iso-propyl t-butyl ether and iso-propanol.

German Offenlegungsschrift No. 2626883 proposes a motor fuel consisting of a mixture of petrol and methanol, with additions of iso-propanol and motor oil.

As examples of other oxygenated compounds that have been proposed as gasoline additives there can be mentioned acetals, and mixtures thereof with alcohols, (see United States Patent Specification No. 3869262) and a mixture of a methyl-substituted phenol, e.g. p-cresol, and an ether, e.g. methyl methoxymethyl propane, optionally together with a C_1 to C_4 acyclic alcohol (see United States Patent Specification No. 3976437).

Conventionally methyl t-butyl ether is made by etherification of methanol by reaction with iso-butene, which is usually a product of oil refinery operations, e.g. in the by-product stream from steam crackers, and fluidised bed crackers (see, for example British Patent Specification No. 2049693A and French Patent Specifications Nos. 2371408 and 2283116) However, such iso-butene is also required for production of alkylate petroleum and chemical products. The supply of iso-butene from conventional oil refinery sources is limited and is inadequate to satisfy the potential market for methyl t-butyl ether as well as to meet the demands for its use in alkylate petroleum production.

In most oil fields natural gas is found in gas reservoirs and in association with crude oil, often in very large quantities. Such natural gas contains mainly methane and some carbon dioxide but also variable amounts of ethane, propane, n-butane, n-pentane, and higher hydrocarbons. Although some progress has been made towards utilising this natural gas in some parts of the world, often no convenient use can be found for the gas which is simply flared off or re-compressed and re-injected into

the oil-bearing geological formation. This represents a tremendous waste of fuel values or of potential chemical feedstock. Even where an end use can be found for natural gas, possibly after separation of L.P.G. (liquefied petroleum gas), no use can be found for the pentane and higher hydrocarbon content.

British Patent Specification No. 1493754 and German Offenlegungsschrift No. 2620011 describe a process for producing methyl t-butyl ether for use as a gasoline additive by processing a stream of n-butane, the n-butane first being partially isomerised to iso-butane, and the resulting n-butane/iso-butane mixture being dehydrogenated to form a mixture of n-butenes and iso-butene. This dehydrogenated mixture is then etherified with excess methanol so as to convert iso- butene to methyl t-butyl ether. Unreacted methanol is extracted with water from the reaction mixture, whilst the remaining C_4 hydrocarbons are separated by distillation from the ether and returned to the dehydrogenation stage. Because of the necessary presence of n-butane which is a feature of this process it is necessary to increase the size of the plant for a given throughput in order to allow the n-butane to be circulated through the plant. Moreover, since n-butenes are recycled to the dehydrogenation stage, it is possible for butadiene to be formed as by-product which can lead to disruption in operation of the plant and which would have to be prevented from appearing in the methyl t-butyl ether product so as to obviate the risk of gum formation in the final gasoline composition. In addition the use of water extraction to separate the product ether from unreacted methanol is disadvantageous since methanol has to be recovered from the aqueous phase and the ether has to be dried.

British Patent Specification No. 1443745 and German Offenlegungsschrift No. 2248841 propose the

production of a water-free mixture of iso-propanol, di-iso-propyl ether and by-products, suitable for use as a gasoline additive, by catalytic hydration of propylene in the gas phase. Propylene is usually available as a by-product of catalytic cracking or similar oil refinery operations.

The present invention seeks to provide a novel gasoline additive and a process for the production thereof from natural gas which utilises the components of natural gas to optimum advantage.

According to the present invention there is provided a novel gasoline additive comprising a mixture of methanol, iso-propanol, methyl t-butyl ether and, optionally a C_{5+} isomerate. A preferred additive comprises, per 100 parts by weight of additive, from about 5 to about 90 parts by weight methanol, from about 3 to about 35 parts by weight of iso-propanol, from about 3 to about 35 parts by weight of methyl t-butyl ether, and from 0 to about 35 parts by weight of a C_{5+} isomerate. Such an additive can be admixed with a gasoline precursor in amounts of, for example, from about 1 to about 10 parts by weight or more of additive, e.g. up to about 50 parts by weight of additive, per 100 parts by weight of gasoline precursor to form a gasoline composition.

Suitable gasoline precursors include gasoline itself or a component which is substantially miscible with the additive mixture and with gasoline, is substantially immiscible with water, and does not have a deleterious effect on a gasoline. Hence the gasoline precursor may include a proportion of aromatic compounds e.g. up to about 30% by weight of benzene, toluene, xylene(s), ethyl benzene, or a mixture of two or more thereof. The use as gasoline precursor of alkylates, of natural gas condensates, and of naphtha is also contemplated in the preparation of the gasoline compositions of the invention.

Hence there can be used alkylates, reformates, fluid-cracked light and heavy naphthas, isomerates, naphthas from hydrocracking units and the like. Typical additive mixtures within the scope of the invention include those listed below in Table I:

TABLE I

	Parts by weight			
Additive	A	B	C	D
Methanol	86	60	33.3	20
MTBE	7	20	33.3	35
IPA	7	20	33.3	35
C_{5+} isomerate	0	0	0	10

Note: MTBE = methyl t-butyl ether.
IPA = iso-propanol

Typical gasoline compositions within the scope of the invention include those listed below in Table II:

TABLE II

Parts by weight

Composition	I	II	III	IV	V
Additive A	30	7	0	0	0
" B	0	0	30	0	0
" C	0	0	0	20	0
" D	0	0	0	0	20
Gasoline fraction	70	93	70	80	80

In accordance with the invention there is further provided a process for the production of a gasoline additive comprising a mixture of methanol, methyl t-butyl ether and iso-propanol which comprises isomerising n-butane component of a natural gas stream to iso-butane,

dehydrogenating propane component of the natural gas stream to propylene and iso-butane formed by isomerisation of n-butane to iso-butene respectively, converting resulting propylene to iso-propanol, etherifying resulting iso-butene with methanol to form methyl t-butyl ether, and blending resulting iso-propanol and methyl t-butyl ether with methanol to form the gasoline additive.

A particularly preferred process in accordance with the invention comprises splitting a natural gas stream containing C_1 to C_4 hydrocarbons to provide a C_{1-2} hydrocarbon-containing stream, a C_3 hydrocarbon-containing stream and a C_4 hydrocarbon-containing stream, catalytically dehydrogenating propane in the C_3 hydrocarbon-containing stream to propylene, converting resulting propylene to iso-propanol, isomerising n-butane in the C_4 hydrocarbon-containing stream to form iso-butane, catalytically dehydrogenating resulting iso-butane to form an iso-butane/iso-butene mixture, converting natural gas hydrocarbons to methanol, etherifying a portion of the resulting methanol with iso-butene in the iso-butene/iso-butane mixture to form methyl t-butyl ether, separating iso-butane from the etherification mixture, recycling separated iso-butane to the iso-butane dehydrogenation stage, and blending at least a portion of the non-etherified methanol, iso-propanol and methyl t-butyl ether to form the gasoline additive. In a preferred process the C_{1-2} hydrocarbon-containing stream is steam reformed to form a synthesis gas and resulting synthesis gas is catalytically converted to methanol. Such methanol can be used without extensive purification, the sole purification step necessary being separation from any excessive amount of water in order to avoid miscibility problems. Furthermore it is not necessary to purify the iso-propanol except to separate largely from water; further details of a suitable

process for the conversion of propylene to iso-propanol can be obtained, for example, from British Patent Specification No. 1443745 and German Offenlegungsschrift No. 2248841.

Purification of methyl t-butyl ether is not necessary prior to incorporation in the gasoline additive of the invention.

In the process of the invention the C_3 and C_4 hydrocarbons need not be separated prior to the isomerisation step, in which n-butane is isomerised to iso-butane, so that dehydrogenation of propane and of iso-butane to propylene and to iso-butene respectively can be carried out simultaneously in the same reactor or reactors. Preferably, however, separation of the C_3 and C_4 hydrocarbons is effected prior to the n-butane isomerisation step and iso-butane and n-butane are separated prior to the iso-butane dehydrogenation step.

Natural gas usually contains varying amounts of C_5 and heavier hydrocarbons. If the natural gas contains little or no C_{7+} hydrocarbons any C_5 and C_6 hydro- carbons are preferably separated from the C_4 hydrocarbons of a C_{4+} hydrocarbon-containing stream, which is formed as bottom product during separation of the C_3 hydrocarbon- containing stream, and the resulting C_5 and C_6 hydrocarbons are then subjected to isomerisation, using a conventional catalyst such as platinum. Alternatively the C_4 and C_{5+} hydro-carbons separated from the natural gas can be passed together through the same isomerisation reactor or reactors and then separated into C_4 and C_{5+} hydro-carbon streams, the latter of which is then subjected to isomerisation. If, on the other hand, the natural gas contains significant quantities of C_{7+} hydrocarbons, it will usually be preferable to separate such C_{7+} hydro-carbons from the C_{5+} hydrocarbon fraction prior

to isomerisation of the latter. The resulting C_{5+} isomerate produced by isomerisation of the C_5 and C_6 hydrocarbon components of the natural gas can then be blended in any order with the other essential components of the gasoline additive, i.e. methanol, iso-propanol and methyl t-butyl ether, and also, if desired, with the gasoline precursor. Any C_{7+} hydrocarbons from the natural gas can also be blended at this stage into the gasoline additive or into the gasoline composition as part of the gasoline precursor.

In carrying out the process of the invention the olefins propylene and iso-butene are produced by dehydrogenation of propane and iso-butane respectively. Further C_4 olefins can be produced by dehydrogenating n-butane. Such C_3 and/or C_4 olefins can be alkylated by reaction with iso-butane to form C_{7+} hydrocarbon alkylates in the presence of a conventional catalyst, such as hydrofluoric acid or sulphuric acid. The resulting alkylate can be used as, or as part of, the gasoline precursor.

In order that the invention may be clearly understood and readily carried into effect a preferred form of plant for the production of a gasoline additive by the process of the invention will now be described, by way of example only, with reference to Figure 1 of the accompanying drawings which is a diagrammatic flow sheet of the plant.

It will be appreciated by those skilled in the art that certain items of equipment that would be necessary for operation of an actual plant, e.g. pumps, heaters, reboilers, valves, temperature sensors, and the like, have been omitted from the drawing. Such additional items of equipment would be provided in an actual plant in accordance with standard chemical engineering practice.

Referring to Figure 1, a mixed gaseous

hydrocarbon feedstock, for example a natural gas which has been pretreated for removal of H_2O, H_2S and CO_2 therefrom, is supplied by way of line 1 to a rectifier or stripping column 2 in which the mixture is separated by distillation into a C_{1-2} stream and a C_{3+} stream. The C_{1-2} stream passes overhead and is supplied by way of line 3 to the reformer tubes of a reformer furnace 4. Steam is also supplied to the reformer tubes by way of line 5 so as to provide a predetermined steam:carbon ratio in the hydrocarbon/steam mixture supplied to the reformer tubes. As is conventional in steam reformer furnaces, the reformer tubes, which may be made for example of an alloy steel are packed with a suitable catalyst, e.g. a supported nickel oxide catalyst. Suitable preheaters (not shown) are provided to raise the C_{1-2} stream to a suitable inlet temperature e.g. about 350°C prior to entry to the reformer tubes. The bottom fraction from column 2, consisting of C_3 and heavier hydrocarbons, passes through line 6 to a column 7 in which the C_3 fraction is distilled overhead whilst C_4 and higher hydrocarbons are removed through line 8 as bottom product and are passed to a further column 9 in which the C_4 fraction is distilled overhead and C_5 and higher hydrocarbons are removed through line 10 as bottom product. The C_4 fraction, which consists mainly of n-butane, passes through line 11 to a de-iso-butanisation column 12 in which the C_4 hydrocarbons are split into an iso-butane fraction and an n-butane fraction. The n-butane is drawn off as bottom product through line 13 and is supplied to a catalytic isomerisation reactor 14, in which n-butane is partially isomerised to iso-butane by passage, for example, over a platinum-containing catalyst at 150 to 200°C. The iso-butane/n-butane mixture is removed from the reactor 14 through line 15 and is freed from C_{1-3} hydrocarbons

in a depropanisation column 16, the C_{1-3} hydrocarbons and hydrogen being discharged overhead by way of line 17. The bottom product of the column 16 consists essentially of a mixture of n-butane and iso-butane and is returned to the de-iso-butanisation column 12 through line 18.

The high percentage iso-butane leaves the de-iso-butanisation column as overhead product by way of line 19, is heated in heat exchanger 20 and, after expansion and being combined with re-cycled iso-butane in line 21, is fed into one of a number of catalytic dehydrogenation reactors of which two only are shown, i.e. reactors 22a and 22b. These reactors, e.g. 22a, 22b, are supplied in turn with the iso-butane stream and the other reactors that are switched off at any time are simultaneously regenerated with hot air which burns off coke deposited on the catalyst. Dehydrogenation may be effected, for example, by passage of the iso-butane stream over a chromium oxide/aluminium oxide catalyst at a temperature in the range of from about 540°C to about 640°C. The product gas from the reactors 22a, 22b consists essentially of an iso-butane/iso-butene/hydrogen mixture and is passed via line 23 to a cooling system 24 in which it is cooled. The cooled iso-butene/iso-butane/hydrogen mixture then flows through line 27 to a multi-stage compressor 28 with intermediate cooling by means of which the pressure of the mixture is raised to a pressure of, for example, 12 bar. The compressed mixture then travels by way of line 29 into an absorption column 30, in which iso-butene and iso-butane are washed out of the gas mixture with an absorption oil. Hydrogen and light hydrocarbons which are formed as dehydrogenation by-products remain in the gas phase and are recovered overhead in line 31. The cold absorption oil, now loaded with iso-butene and iso-butane, passes via line 32 into a

stripper 33, in which the iso-C_4 hydrocarbons are driven off by heating the absorption solution. The regenerated absorption oil is fed through line 34 and is cooled, e.g. by heat exchange with the iso-C_4 hydrocarbons laden oil in line 32 and possibly also by further cooling against cooling water, before being returned to the top of the absorption column 30. The gas mixture, consisting essentially of iso-butene and iso-butane, leaves the stripper 33 through line 35.

In the reformer furnace 4 the C_{1-2} hydrocarbons supplied in line 3 are steam reformed to form a synthesis gas which is then compressed in compressor 36 and passed via line 37 to a methanol synthesis reactor 38, in which methanol formation takes place in the presence of a catalyst. The methanol formed is separated from the unreacted synthesis gas by condensation in a condenser (not shown), whilst the unreacted synthesis gas is recirculated via lines 39 and 37 to the methanol synthesis reactor. Line 40 serves for discharge of the purge gas from the synthesis gas loop. The crude methanol is passed, after water removal, along lines 41 and 42 and is combined with the iso-C_4 hydrocarbons mixture in line 35 and with a methanol/methyl t-butyl ether mixture in line 43. The resulting mixture is fed via line 44 and a preheater (not shown) to a catalytic etherification reactor 45. Reactor 45 contains a solid bed catalyst, e.g. an acidic ion exchange resin having $-SO_3H$ or - COOH groups, and cooling means for dissipating the heat of reaction. In the reactor the iso-butene introduced in the mixed iso- butene/iso-butane stream in line 35 reacts with methanol to form methyl t-butyl ether.

A mixture consisting essentially of methyl t-butyl ether, iso-butane and excess methanol leaves reactor 45 and is supplied through line 46 to a first pressurised column 47 in which iso-butane distils off

overhead and is combined by way of line 21 with the feed stream in line 19 for the C_4 dehydrogenation reactors 22a, 22b. The bottom product of column 47 is a mixture of methyl t-butyl ether and methanol and is fed by way of line 48 to a second pressurised column 49. An azeotrope, consisting of methanol and methyl t-butyl ether, is recovered overhead from column 49 and is recycled to the etherification reactor 45 by way of lines 43 and 44. Methyl t-butyl ether is recovered as bottom product from column 49 through line 50.

The overhead product from column 7 consists essentially of C_3 hydrocarbons, mainly n-propane, and is recovered in line 51. This C_3 hydrocarbon stream is combined with propane recycled through line 52 and the combined stream flows on through heater 53 to a plurality of C_3 dehydrogenation reactors, of which two only are shown, i.e. reactors 54a, 54b which are charged with a suitable dehydrogenation catalyst, e.g. a chromium oxide/aluminium oxide catalyst. As with the iso-butane dehydrogenation reactors 22a, 22b, the reactors 54a, 54b are fed in turn with the C_3 hydrocarbon feed stream whilst the other reactors are regenerated with hot air to burn off coke deposited on the catalyst. Typical dehydrogenation temperatures in reactors 54a, 54b range from about 540°C to about 640°C.

The resulting propylene/propane gas mixture flows on by way of line 55 to an iso-propanol plant 56 in which propylene is catalytically hydrated in the gas phase to iso-propanol. Further details of the construction and operation of plant 56 can be obtained, for example, from German Offenlegungsschrift No. 2248841. Unreacted propylene and propane from plant 56 pass along line 57, to a propane/propylene splitter 58 in which propane and propylene are essentially separated from each other, the propane being returned by way of line 52 to the

dehydrogenation reactors 54a, 54b, while the propylene is recycled to the iso-propanol plant 56 by way of line 59.

The product from plant 56 is a water-free mixture of iso-propanol, di-iso-propyl ether and by-products and is suitable for use, without further purification, as a gasoline additive. This is passed along line 60.

The C_{5+} hydrocarbon stream in line 10 is heated in heater 61 and passed to a reactor 62 charged with an isomerisation catalyst, such as a platinum-containing catalyst, and maintained at a temperature of, for example 150°C to 200°C. The resulting C_{5+} isomerate passes on via line 63 to a condenser 64. The resulting condensate is recovered in line 65.

The capacity of methanol plant 38 exceeds the requirements of the methyl t-butyl ether synthesis section of the illustrated plant. This excess methanol passes on through line 66 and then is either exported beyond plant limits in line 67 or is passed forward for blending with the other products of the illustrated plant by way of line 68.

Methyl t-butyl ether in line 50 can either be exported beyond plant limits by way of line 69 or can be passed forward for blending with the other products of the illustrated plant by way of line 70.

In a similar manner the water-free crude iso-propanol in line 60 can be passed forward for blending via line 71 or exported beyond plant limits in line 72.

C_{5+} isomerate in line 65 can likewise be passed forward for blending in line 73 whilst any excess is exported beyond plant limits in line 74.

The resulting blend in line 79 contains methyl t-butyl ether, iso-propanol, methanol and C_{5+} isomerate, can be used as a gasoline additive and has valuable octane rating improving qualities.

The streams of hydrogen and C_{1-3} hydrocarbons in lines 17 and 31 are combined in line 75 and pass on for use as fuel in reformer furnace 4, the stream in line 75 being mixed with the purge gas stream in line 40 from the methanol plant 38 and with a purge gas stream in line 76 from iso-propanol plant 56. Further fuel, e.g. natural gas, is supplied through line 77 to the burners of reformer furnace 4. Reference numeral 78 indicates the line for supplying combustion air to reformer furnace 4.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight, unless otherwise stated.

Examples

The following mixtures were made up as shown below in Table III:

TABLE III

Parts by weight

Mixture	A	B	C	D	E	F
MTBE	6.73	32.4	0.49	10.13	1.43	6.82
IPA	6.98	33.7	0.51	10.51	1.48	7.08
Methanol	86.29	33.9	8.04	10.58	18.33	7.13
Distillate	-	-	90.96	68.78	-	-
Gasoline	-	-	-	-	78.76	78.97

Notes:

1. MTBE = methyl t-butyl ether
2. IPA = iso-propanol
3. The distillate was a 60-120°C cut of hydrocarbon feedstock made up of oil from the Ninian field and mixtures of naphthas, the aromatics content being 12-14%.
4. The gasoline was a commercial 2-star petrol

with an octane number of 92 and a lead content of 0.4-0.45g/litre.

These mixtures were subjected to the following tests:

1. I.P. 123/58: the distillation curves obtained are shown in Figure 2 to 5 of the accompanying drawings. Figures 2 and 3 illustrate the results obtained with Mixtures C and D respectively, together in each case with the corresponding curve for the distillate. In Figures 4 and 5 there are plotted the results for Mixtures E and F respectively; the corresponding curve for the gasoline is also given. Other data are set out in Table IV:

TABLE IV

Mixture/ Component	C	D	Distillate	E	F	Gasoline
Initial b.p. °C	56.0	57.5	82.5	33.0	30.5	30.0
Dry point °C	138.5	138.0	140.0	170.0	168.0	170.0
Final b.p. °C	139.0	145.0	145.0	171.0	171.0	172.0

2. Octane numbers: the research octane number (RON) and motor octane number (MON) of the gasoline and of the distillate used in preparation of Mixtures A to F numbers were determined by standard methods. The results are given in Table V together with the results for Mixtures C to F.

TABLE V

Sample	Octane Number			Effect of additive on base fuel			Theoretical octane number (calculated on volume basis)			Difference between determined and theoretical octane number			Blending value of additives	
	RON	MON	$\frac{(RON+MON)}{2}$	ΔRON	ΔMON	$\Delta\frac{(RON+MON)}{2}$	RON	MON	$\frac{(RON+MON)}{2}$	ΔRON	ΔMON	$\Delta\frac{(RON+MON)}{2}$	RON	MON
Gasoline	92.9	85.9	89.4											
Distillate	56.1	55.8	56.0											
Mixture C	63.8	61.5	62.7	+ 7.7	+ 5.7	+ 6.7	59.6	58.4	59.0	+ 4.2	+3.1	+ 3.7	166.1	137.3
Mixture D	82.7	76.7	79.7	+26.6	+20.9	+23.7	71.7	67.6	69.7	+11.0	+9.1	+10.0	144.8	125.5
Mixture E	100.2	88.4	94.3	+ 7.3	+ 2.5	+ 4.9	95.5	87.2	91.4	+ 4.7	+1.2	+ 2.9	129.4	98.4
Mixture F	98.5	87.8	93.2	+ 5.6	+ 1.9	+ 3.8	95.9	87.8	91.9	+ 2.6	0	+ 1.3	120.9	95.4

Notes:

Octane ratings of additives taken as :

	RON	MON
Isopropyl alcohol	104	95
Methanol	105	92
MTBE	115	98

3. Haze Point: the method IP 15/60 for cloud point determination was used in order to determine the haze point for formulations using both the gasoline and distillate as received and the same base fuels after saturation with water. In addition, experiments were carried out to see how much water had to be added in order to raise the haze point of the mixtures tested to that of the base fuel. The results are listed in Table VI

TABLE VI

	Haze Points		
Sample	As blended	Base Fuel saturated with water	Water Added to give equivalent haze point (ppm vol/vol)
Gasoline	-90°F	34°F	
Distillate	-70°F	41°F	
Mixture C	N.D.	40°F	N.D. (Nil)
Mixture D	-96°F	-96°F	8,800
Mixture E	N.D.	-23°F	2,200
Mixture F	-96°F	-96°F	5,600

Note: N.D. = Not Determined

CLAIMS

1. A gasoline additive comprising in admixture methanol, methyl t-butyl ether and another alcohol, characterised in that the additive contains, in addition to methanol and methyl t-butyl ether, iso-propanol and, optionally, a C5+ isomerate.

2. A gasoline additive according to Claim 1, characterised in that the additive comprises, per 100 parts by weight of additive, from about 5 to about 90 parts by weight methanol, from about 3 to about 35 parts by weight of iso-propanol, from about 3 to about 35 parts by weight of methyl t-butyl ether, and from 0 to about 35 parts by weight of a C5+ isomerate.

3. A process for preparing a gasoline additive according to Claim 1, characterised in that it comprises isomerising n-butane component of a natural gas stream to iso-butane, dehydrogenating propane component of the natural gas stream to propylene and iso-butane formed by isomerisation of n-butane to iso-butene respectively, converting resulting propylene to iso-propanol, etherifying resulting iso-butene with methanol to form methyl t-butyl ether, and blending resulting iso-propanol and methyl t-butyl ether with methanol to form the gasoline additive.

4. A process according to Claim 3, characterised in that isomerisation of n-butane component to iso-butane is carried out without prior separation of C_3 and C_4 hydrocarbons and dehydrogenation of propane and of iso-butane to propylene and to iso-butene respectively are carried out simultaneously in the same reactor or reactors.

5. A process according to Claim 3, characterised in that separation of C_3 and C_4 hydrocarbons is effected prior to isomerisation of n-butane component and iso-butane and n-butane are separated prior to dehydrogenation of iso-butane.

6. A process according to Claim 3, characterised in that it comprises splitting a natural gas stream containing C_1 to C_4 hydrocarbons to provide a C_{1-2} hydrocarbon-containing stream, a C_3 hydrocarbon-containing stream and a C_4 hydrocarbon-containing stream, catalytically dehydrogenating propane in the C_3 hydrocarbon-containing stream to propylene, converting resulting propylene to iso-propanol, isomerising n-butane in the C_4 hydrocarbon-containing stream to form iso-butane, catalytically dehydrogenating resulting iso-butane to form an iso-butane/iso-butene mixture, converting natural gas hydrocarbons to methanol, etherifying a portion of the resulting methanol with iso-butene in the iso-butene/iso-butane mixture to form methyl t-butyl ether, separating iso-butane from the etherification mixture, recycling separated iso-butane to the iso-butane dehydrogenation stage, and blending at least a portion of the non-etherified methanol, iso-propanol and methyl t-butyl ether to form the gasoline additive.

7. A process according to Claim 6, characterised in that the C_{1-2} hydrocarbon-containing stream is steam reformed to form a synthesis gas and resulting synthesis gas is catalytically converted to methanol.

8. A process according to any one of Claims 3 to 7, characterised in that C_5 and heavier hydrocarbons are separated from the natural gas stream, C_5 and C_6

hydrocarbons separated from the natural gas are subjected to isomerisation and resulting C_{5+} isomerate is incorporated in the gasoline additive.

9. A gasoline composition characterised in that it comprises an additive according to Claim 1 or Claim 2 or prepared by a process according to any one of Claims 3 to 8 in admixture with a gasoline precursor.

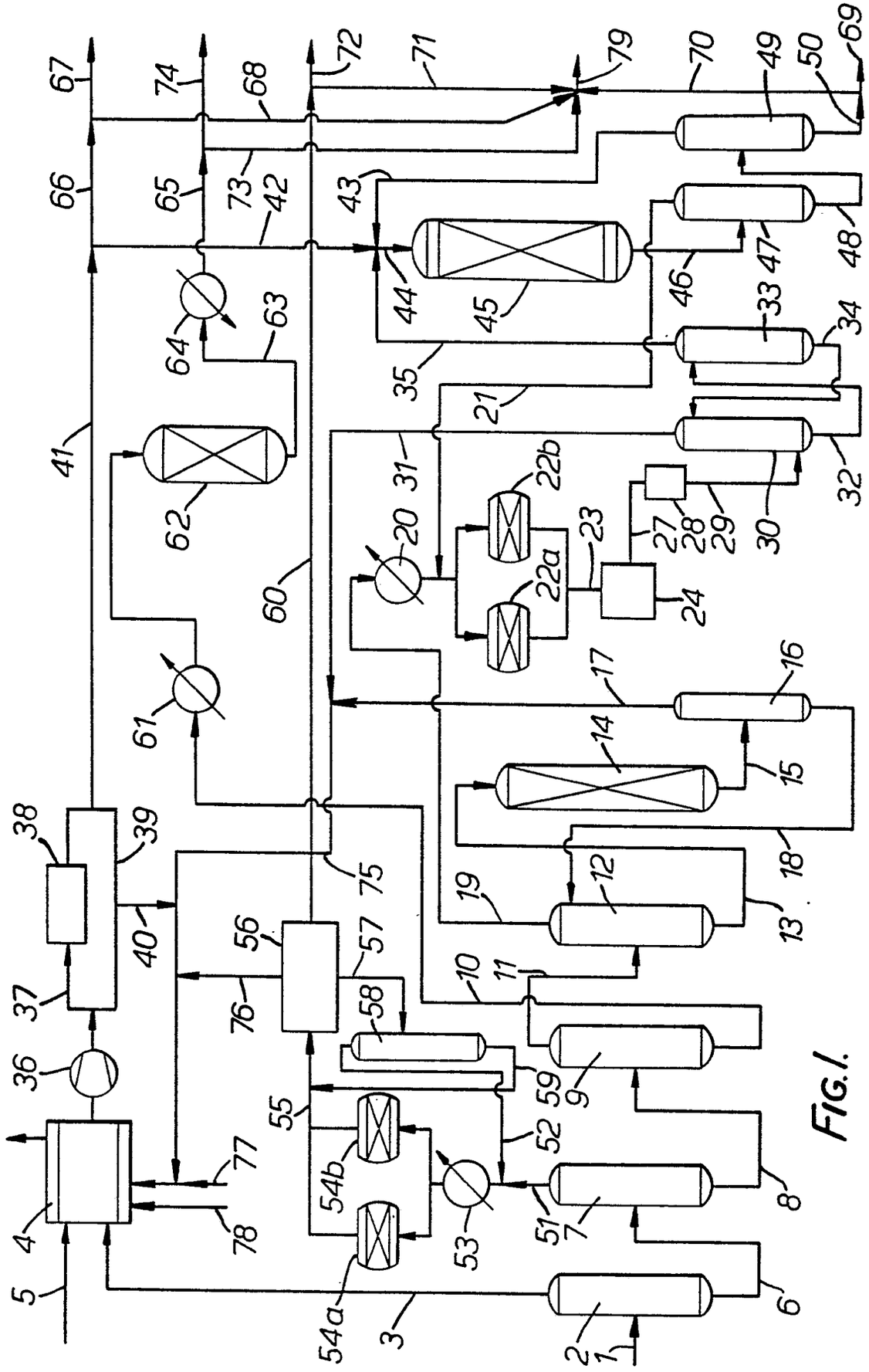
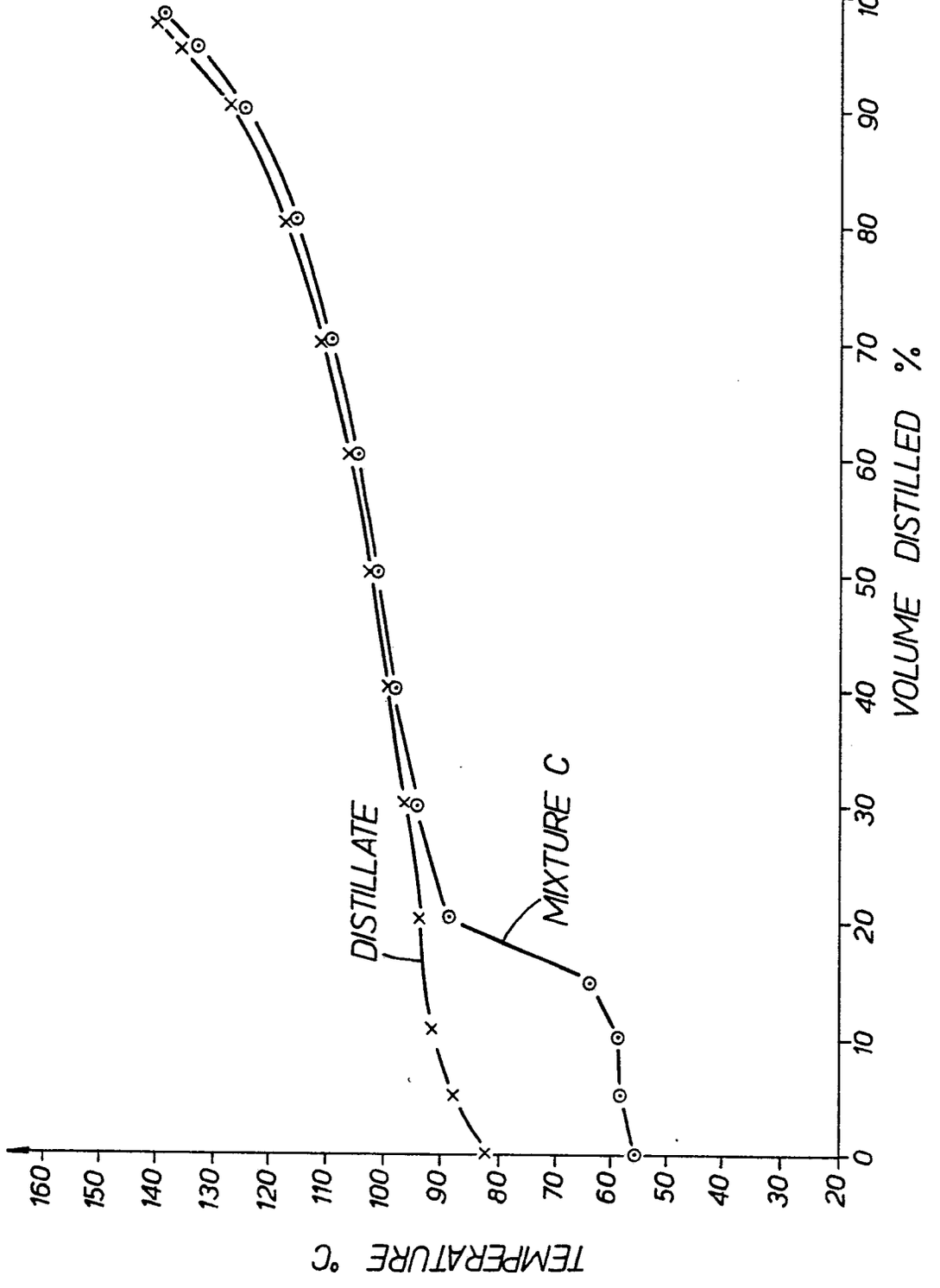


FIG. 1.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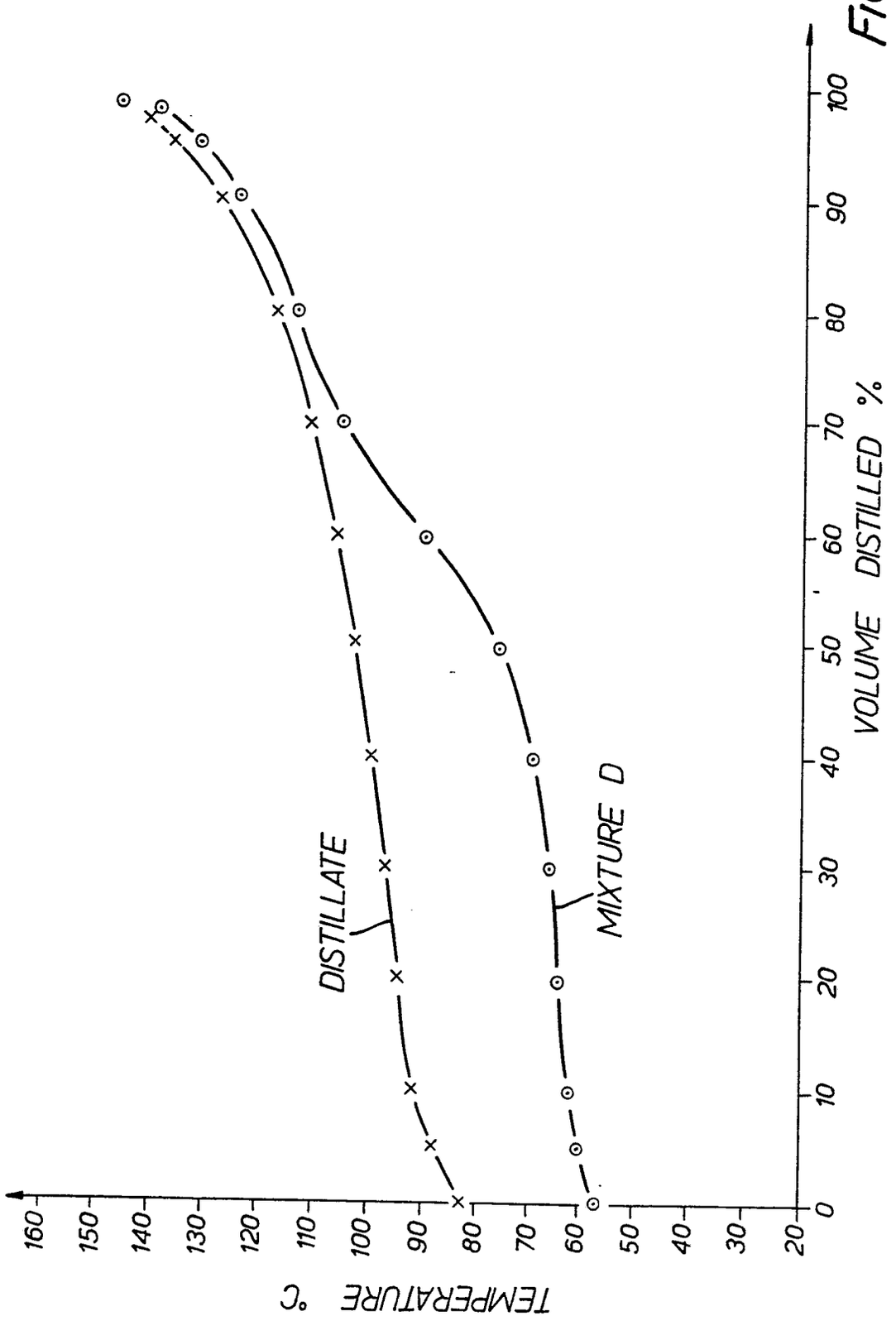
VOLUME DISTILLED %
DISTILLATE
MIXTURE C

FIG. 2.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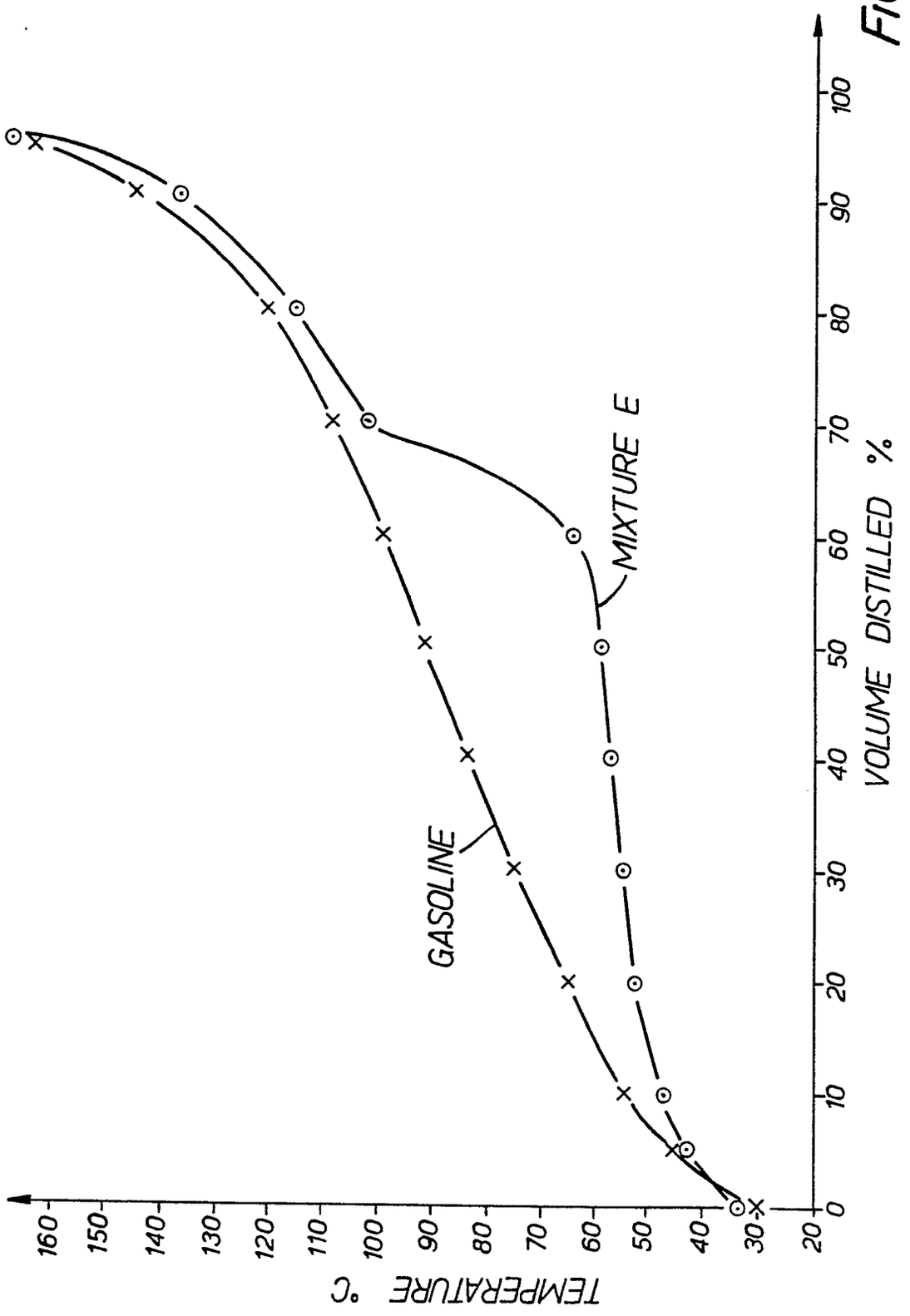
VOLUME DISTILLED %
DISTILLATE
MIXTURE D

FIG. 3.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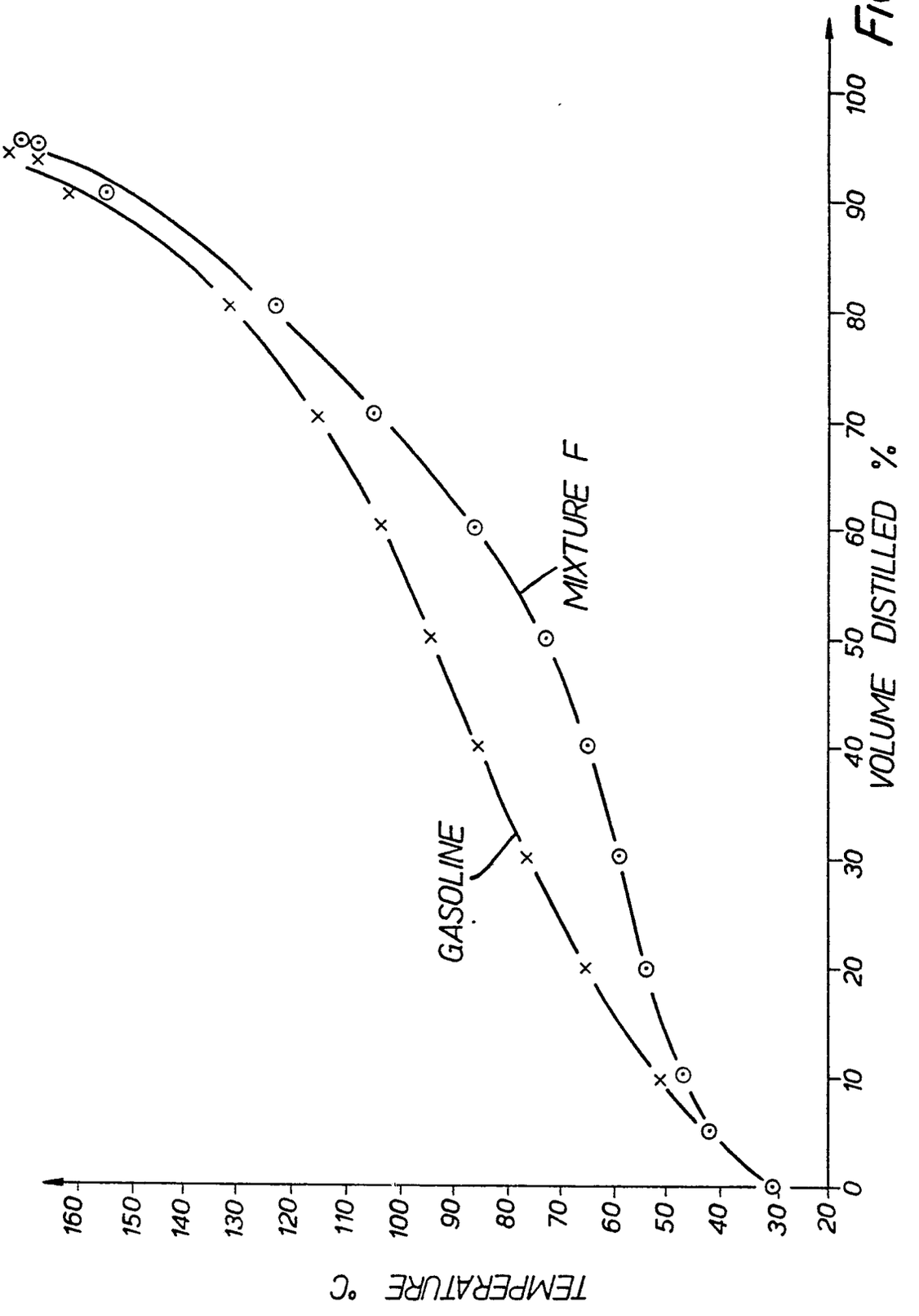
VOLUME DISTILLED %
GASOLINE
MIXTURE E

FIG. 4.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100
VOLUME DISTILLED %
GASOLINE
MIXTURE F

FIG. 5.

0049995

Application number

EP 81 30 4627

European Patent Office

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	DE - A - 2 419 439 (CHEMISCHE WERKE HULS)	
DA	GB - A - 1 493 754 (TEXACO)	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 10 L 1/02

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 10 L 1/02
1/18

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	18-01-1982	OSWALD DE HERDT