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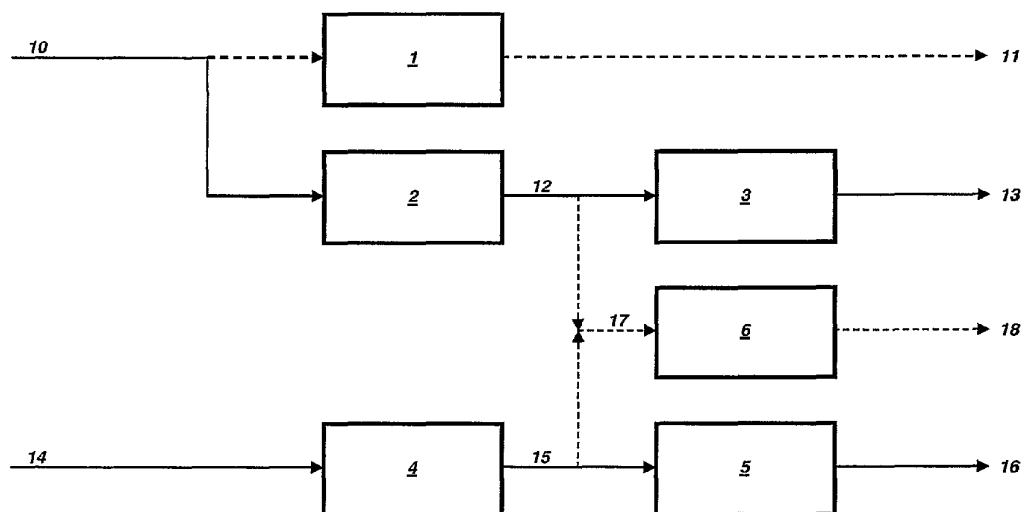
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(54) Title: FUEL FOR HOMOGENEOUS CHARGE COMPRESSION IGNITION (HCCI) SYSTEMS AND A PROCESS FOR PRODUCTION OF SAID FUEL



Summary of Processing Requirements for Synthetic HCCI Fuels

(57) Abstract: The invention provides a HCCI fuel or fuel component, which fuel includes at least n-paraffins and iso-paraffins having from 7 to 14 carbon atoms, and which fuel has an ignition delay of less than 7 ms, according to ASTM D6890. A process for preparing a HCCI fuel or fuel component.

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FUEL FOR HOMOGENEOUS CHARGE COMPRESSION IGNITION (HCCI) SYSTEMS AND A PROCESS FOR PRODUCTION OF SAID FUEL

5 Field of the Invention

The invention relates to a fuel for Homogeneous Charge Compression Ignition (HCCI) systems and to a process for producing such a fuel.

10 Background to the Invention

The HCCI engine is a relatively new concept under development by several institutions and companies. The principle of HCCI combustion is that a dilute, premixed, homogenous mixture of fuel and air reacts and burns volumetrically throughout the cylinder as it is compressed by the piston. Combustion reactions start when the mixture reaches a sufficiently high temperature to autoignite. These reactions initiate at multiple locations simultaneously, proceed very quickly, and there is a complete absence of localized high-temperature regions or flame-fronts.

In essence, the HCCI combustion process seeks to combine the low nitrogen oxides (NOx) exhaust emissions associated with the gasoline engine, with the high thermal efficiency associated with the diesel or compression ignition (CI) engine. In theory, HCCI offers the potential for sootless combustion and very low emissions of nitrogen oxides (NOx), together with an energy efficiency that can exceed that of the CI engine.

Successful implementation of HCCI combustion would therefore increase the competitiveness of the internal combustion (IC) engine against emerging technologies such as fuel cells, thereby extending its lifespan.

Because HCCI is effectively an evolution of the IC engine, there are no external barriers to its implementation, and the gradual adoption of this technology may see it eventually being implemented in the majority of automotive IC engines, in one form or another. A 2001 report by the US Department of Energy to the US Congress

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speculated that, with successful R&D, passenger car HCCI engines might be commercialised by 2010.

Thus a need exists for a fuel for HCCI systems and engines.

5 Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

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Summary of the Invention

20 According to one aspect of the invention, there is provided a HCCI fuel or fuel component, which fuel includes at least n-paraffins and iso-paraffins having from 7 to 14 carbon atoms, and which fuel has an ignition delay of less than 7 ms according to ASTM D6890, which fuel has ASTM D86 distillation range from 90 °C to 260 °C.

The fuel may be substantially cyclo-paraffins free. Thus, the fuel may have less than 5 mass%, typically less than 1 mass% cyclo-paraffins.

Moreover, it preferably contains less than 1 wt % of aromatic and negligible levels of sulphur.

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In this specification, the ignition delay is measured using the ASTM Method D6890 in a constant volume combustion bomb, Ignition Quality Tester (IQT™)

The ignition delay of the fuel may be less than 5 ms.

The ignition delay of the fuel may be between 2 and 5 ms.

- 5 The weight % of the n-paraffins may exceed that of any other single component in the fuel.

The n-paraffins may be in excess of 25% by weight of the fuel

The n-paraffins may be in excess of 50% by weight of the fuel.

The n-paraffins may be in excess of 80% by weight of the fuel.

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The n-paraffins may be in the order of 95% by weight of the fuel.

The n-paraffins may be Fischer-Tropsch (FT) reaction derived n-paraffins.

The iso-paraffins may be FT reaction derived iso-paraffins.

The fuel may include olefins.

- 5 The HCCI fuel may include oxygenates.

The HCCI fuel may be substantially free of heteroatoms such a nitrogen, sulphur and oxygen.

The HCCI fuel may be substantially sulphur free.

The HCCI fuel may be substantially oxygenate free.

- 10 The fuel may include a lubricity improver or other fuel additives to make meeting product specifications possible.

An aspect of the invention relates to the use of the fuel or fuel component as a blending component with conventional fuel.

- 15 The invention extends to a process for preparing a HCCI fuel or fuel component, which fuel or fuel component includes at least n-paraffins and iso-paraffins, which fuel has an ignition delay of less than 7 ms, said process including:

- a) hydrotreating at least a Condensate fraction of a Fischer-Tropsch (FT) synthesis reaction product, or a derivative thereof;
- 20 b) hydroconverting a Wax fraction of the FT synthesis product or a derivative thereof;

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- c) fractionating in a single unit or in separate units, one or more of the hydrotreated Condensate fractions of step a) and the hydroconverted fraction of step b) to obtain the desired HCCI fuel or fuel component having 7 to 14 carbon atoms, and which fuel has an ASTM D86 distillation range from 90 °C to 270 °C; and
- 5 d) optionally, blending two or more of said components from step c) in a desired ratio to obtain the desired HCCI fuel.

The hydroconversion may be by way of hydrocracking.

The properties of the fuel made according to the process may be as disclosed above
5 and elsewhere in the specification.

The blending of step d) may be the blending of FT condensate derivative and hydroconverted FT wax derivative from 1:99 to 99:1 by volume

10 The table below gives a typical composition of the two fractions.

Typical FT product after separation into two fractions (vol % distilled)

	FT Condensate (< 270°C fraction)	FT Wax (> 270°C fraction)
C ₅ -160°C	44	3
160-270°C	43	4
270-370°C	13	25
370-500°C		40
> 500°C		28

The >160°C fraction, contains a considerable amount of hydrocarbon material, which
15 boils higher than the normal naphtha range. The 160°C to 270°C fraction may be regarded as a light diesel fuel. This means that all material heavier than 270°C needs to be converted into lighter materials by means of a catalytic process often referred to as hydroprocessing, for example, hydrocracking.

20 Catalysts for this step are typically of the bifunctional type; i.e. they contain sites active for cracking and for hydrogenation. Catalytic metals active for hydrogenation include group VIII noble metals, such as platinum or palladium, or a sulphided Group VIII base metals, e.g. nickel, cobalt, which may or may not include a sulphided Group VI metal, e.g. molybdenum. The support for the metals can be any refractory
25 oxide, such as silica, alumina, titania, zirconia, vanadia and other Group III, IV, V and

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VI oxides, alone or in combination with other refractory oxides. Alternatively, the support can partly or totally consist of zeolite.

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Specific Description and Examples

The following table summarises the origin and carbon number ranges for the proposed fuels usable in HCCI engines:

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Class	Typical (LTFT) Feedstock	Composition	Carbon Number range		
			C ₇ -C ₉	C ₇ -C ₁₄	C ₁₀ -C ₁₄
SR FT	FT Condensate	Paraffins, olefins and oxygenates	X	X	X
HT SR FT	FT Condensate	Mostly linear paraffins	X	X	X
HX FT	FT Wax	Mostly iso-paraffins	X	X	X
GTL	FT Condensate and Wax	Fully paraffinic	X	X	X

Definitions

- SR FT Straight Run Fischer-Tropsch
- HT SR FT Hydrotreated Straight Run Fischer-Tropsch
- 5 ▪ HX FT Hydrocracked Fischer-Tropsch
- GTL Hydroconverted Product as expected from a Fischer-Tropsch Gas-to-Liquid plant

The fuel contains hydrocarbon species having from 7 to 14 carbon atoms and has been found to define unique characteristics with respect to vapour pressure and ignition delay.

- 10 Moreover, the criteria also made consideration to the highly paraffinic nature of the fuel as well as the high linearity of the hydrocarbon species.

The C7 to C14 carbon number range has been found to exclude hydrocarbons like pentane or hexane that have high vapour pressures. Adequate volatility is important to establish a homogeneous gaseous charge in the combustion chamber, with enough

15 cetane character (propensity to auto-ignite) to effect the homogeneous ignition throughout the whole volume.

Furthermore, the C7 to C14 carbon number range has been found to exclude hydrocarbons like n-hexadecane that conventionally has cetane number of 100. The

cetane number of the HCCI fuel must not be too high and its ignition delay not too short to ensure controlled in-cylinder combustion.

The inventors believe that the abovementioned twelve options cover almost all practical options for FT-based synthetic HCCI fuels.

The key quality requirements for these fuels are summarised in Table 1.

Table 1 Selected Quality Characteristics of Synthetic FT HCCI Fuels

	Desired Range	Analytical Procedure
Distillation Range	90-270°C	ASTM D86
Density	0.65-0.78 kg/l	ASTM D1298
Composition	hydrocarbon	GC-FID
Ignition delay (IQT)	2-7 ms	ASTM D6890-03
Cetane Number	25-75	ASTM D613-03a
Aromatics content	<1.0% wt	ASTM D5186-99 ASTM D6591-00
Sulfur content	< 1 ppm wt	ASTM D5453
Oxygen content	<5000 ppm	GC-TCD

The ignition delay is a good indication of the elevated pressure, high temperature autoignition characteristics of the fuel and can be correlated to the distillation range and cetane number of the fuel, which in turn relate to its chemical composition. The conditions at which the ignition delay is determined in the IQTTM; at 22.4 bar air pressure and 565 °C, are comparable to the conditions that an HCCI fuel could experience in an HCCI engine, thus the ignition delay (ID) can be used as an appropriate yardstick for HCCI fuel ignition quality. The implications are that fuels with a high propensity for autoignition under compression will have short ignition delays (~2-4 ms), while fuels with increased resistance against autoignition (equivalent to high octane spark ignition gasoline) will have longer ignition delays (~7-11ms).

Since the resistance against autoignition is no different to a resistance against oxidation at the specific pressure and temperature conditions to which the fuel is exposed in an HCCI engine's combustion chamber, it follows that those sulphur (S)

and nitrogen (N) heteroatoms present in crude oil derived HCCI fuel will act as oxidation inhibitors, leading to longer ignition delays and a lower propensity towards autoignition.

- 5 FT fuels are virtually sulphur free, with lower levels of nitrogen-containing compounds, and the absence of these naturally occurring anti-oxidants represent a benefit when FT fuels are applied in HCCI engines. This results in FT fuels outperforming conventional fuels in terms of their propensity to autoignite under HCCI conditions.

10 Process Scheme

A generic block diagram flow scheme is included as figure 1. The process options for all four classes of HCCI fuels are shown in a simple format. The following table 2 summarises the basic processing for these fuels and feeds.

15

Table 2 Generic Requirement for FT Feedstock Processing

Process Step	Process Description	Reference
Distillation	Atmospheric Distillation	(1)
Hydrotreatment	<ul style="list-style-type: none"> ▪ H₂ saturation of olefinic double bonds. ▪ H₂ saturation of oxygen-containing hydrocarbons with formation of water ▪ Other hydroconversion reactions 	US 6,475,375
Hydrocracking	<ul style="list-style-type: none"> ▪ Cracking of heavy molecules (mostly paraffinic) ▪ H₂ saturation of olefinic double bonds. ▪ H₂ saturation of oxygen-containing hydrocarbons with formation of water ▪ Other hydroconversion reactions 	EP 1129155

- 20 (1) There are many references for this unit operation. For example, refer to PA Schweitzer, Handbook of Separation Techniques for Chemical Engineers (McGraw-Hill, 1979) or RH Perry and CH Chilton, Chemical Engineers' Handbook (McGraw-Hill, 5th Edition, 1973)
- 25 The production of the synthetic HCCI fuel components can be achieved following at least four process configurations. The selection of one for a specific plant is an

exercise in process synthesis that demands additional site and market specific information.

5 A first group of HCCI fuels – named SR FT in this description – can be produced by fractionation of a light synthetic FT hydrocarbon stream 10 in Distillation unit 1. The operation of this fractionation unit to the required product specification results in the group of products 11.

10 A second group of HCCI fuels – named SR HT FT in this description - can be obtained from a light synthetic FT hydrocarbon stream 10 which is first hydrogenated in hydrogenation unit 2 to saturate the olefinic double bonds and remove the oxygen from the oxygenate species. Then the hydrogenated products can be fractionated in fractionation unit 3 to the required specification, obtaining the group of products 13.

15 A third group of HCCI fuels – named HX FT in this description – can be obtained from a heavy synthetic FT hydrocarbon stream 14 which is hydrocracked in hydrocracking unit 4 to result in lighter saturated hydrocarbon species. Then the hydrocracked products can be fractionated in fractionation unit 5 to the required specification, obtaining the group of products 16.

20 An alternative to produce a fourth group of HCCI fuels – named GTL (GTL = gas to liquid) in this description – can be produced by direct blending of the hydrotreated and hydrocracked products described above. This can be done in an optimised way by using a common fractionator unit 6 to the required specification, obtaining the group of
25 products 18.

It is also possible to blend the products 11 and 16, either by sharing a common fractionator or after fractionation to also obtain synthetic HCCI fuels.

30 In all of these process options there is co-production of non-HCCI hydrocarbon stream, both lighter and heavier than the designed HCCI synthetic products. The former can be described as a light naphtha and the latter as a heavy diesel stream. These can be used in fuel and non-fuel applications.

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All fuels in any of these four groups can be used as blends components for final HCCI fuels.

Emissions Performance of the Synthetic FT HCCI Fuels

- There is wide acceptance to the fact that the synthetic FT fuels produce less noxious emissions than conventional fuel. This point has been brought into the public domain several times – for example refer to *"Processing of Fischer-Tropsch Syncrude and Benefits of Integrating its Products with Conventional Fuels"* presented at the National Petrochemical & Refiners Association Annual Meeting held in March 2000 in San Antonio, Texas – paper AM-00-51. This document makes reference to both FT naphthas and FT
- 5
- 10

Typical Quality of Synthetic FT HCCI Fuels

Table 3 contains the typical quality of synthetic FT HCCI fuels produced as described in accordance with the invention and generally conforming to the selected requirements. Table 4 shows a comparison between HT SR FT fuel and crude derived fuel.

15 **Table 3 Typical Quality of Synthetic FT HCCI Fuels**

	Desired Range		SR FT			HT SR FT		
			C ₇ -C ₉	C ₇ -C ₁₄	C ₁₀ -C ₁₄	C ₇ -C ₉	C ₇ -C ₁₄	C ₁₀ -C ₁₄
Distillation Range	90-270	°C	103-183	103-251	164-251	90-160	90-254	165-254
Density	0.65-0.78	kg/l	0.67	0.71	0.76	0.71	0.74	0.76
Composition								
▪ n-paraffins		wt %	52.5	63.1	68.4	94.6	94.9	95.1
▪ i-paraffins		wt %	0.4	1.6	2.2	5.4	5.1	4.9
▪ Olefins		wt %	38.5	26.5	20.5	0	0	0
▪ Oxygenates		wt %	8.6	8.8	8.9	0	0	0
Ignition delay (IQT™)	2-7	ms	3.34	2.79	2.60	3.44	2.74	2.54
Cetane Number	30-70		60	75	83	58	77	86
Aromatics content	<1.0 %	wt %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sulphur content	< 1 ppm	wt	<1	<1	<1	<1	<1	<1
Oxygen content	<5000	ppm (wt)	700	2000	2150	<80	<80	<80

	Desired Range		HX			GTL		
			C ₇ -C ₉	C ₇ -C ₁₄	C ₁₀ - C ₁₄	C ₇ -C ₉	C ₇ -C ₁₄	C ₁₀ - C ₁₄
Distillation Range	90-270	°C	80-163	80-250	135-250	90-163	90-250	155-250
Density	0.65-0.78	kg/l	0.68	0.72	0.74	0.69	0.72	0.75
Composition								
▪ n-paraffins		wt %	46.0	30.7	26.6	57.5	41.0	38.0
▪ i-paraffins		wt %	54.0	69.3	73.4	42.5	59.0	62.0
▪ Olefins		wt %	0	0	0	0	0	0
▪ Oxygenates		wt %	0	0	0	0	0	0
Ignition delay (IQT™)	2-7	ms	4.92	4.06	3.50	4.55	3.34	3.08
Cetane Number	30-70		41	49	57	44	60	66
Aromatics content	<1.0%	wt %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sulphur content	< 1 ppm	wt	<1	<1	<1	<1	<1	<1
Oxygen content	<5000	ppm (wt)	<80	<80	<80	<80	<80	<80

Table 4 Comparison between equivalent synthetic FT Fuel for HCCI Fuels and Crude Derived Fuels

	Desired Range		HT SR FT			Crude Derived Fuels		
			C ₇ -C ₉	C ₇ -C ₁₄	C ₁₀ -C ₁₄	C ₇ -C ₉	C ₇ -C ₁₄	C ₁₀ -C ₁₄
Distillation Range	90-270	°C	90-160	90-254	165-245	80-159	80-257	151-257
Density	0.65-0.78	kg/l	0.71	0.74	0.76	0.7329	0.7715	0.7961
Composition								
▪ n-paraffins		wt %	94.6	94.9	95.1	28.2	23.8	24.7
▪ i-paraffins		wt %	5.4	5.1	4.9	32.8	53.0	55.3
▪ Olefins		wt %	0	0	0	0.4	0.4	0.5
▪ Oxygenates		wt %	0	0	0	0	0	0
▪ Aromatics		wt %	0	0	0	10.3	14.2	18
▪ Naphthenes		wt %	0	0	0	28.3	8.6	1.5
Ignition delay (IQT™)	2-7	ms	3.44	2.74	2.54	6.17	5.22	4.79
Cetane Number	30-70		58	77	86	34.1	39.0	42.0
Sulphur content	< 1	ppm wt	<1	<1	<1	50	50	50

5

Table 5 below presents an example of the quality characteristics of blends of the C7-C9 GTL HCCI fuel with an equivalent Petroleum fraction. The benefits of including synthetic FT fuel in conventional blends are quite evident.

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Table 5 Quality of blends of the C7-C9 GTL HCCI fuel with an equivalent Petroleum fraction

		GTL Fuel Content				
		0%	25%	50%	75%	100%
Density	kg/l	0.733	0.722	0.711	0.700	0.690
Composition						
n-paraffins	wt %	28.2	35.4	42.8	50.1	57.5
i-paraffins	wt %	32.8	35.1	37.6	40.0	42.5
Olefins	wt %	0.4	0.3	0.2	0.1	0.0
Oxygenates	wt %	0.0	0.0	0.0	0.0	0.0
Aromatics	wt %	10.3	7.8	5.2	2.6	0.0
Naphthenes	wt %	28.3	21.3	14.2	7.1	0.0
Total	wt %	100.0	99.9	100.0	99.9	100.0
Ignition delay (IQT™)	ms	6.17	5.75	5.22	4.75	4.55
Cetane Number		34.1	36.0	39.1	41.9	44.0
Sulphur content	ppm	50	38	25	13	<1

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Claims

1. A HCCI fuel or fuel component, which fuel includes at least n-paraffins and iso-paraffins having from 7 to 14 carbon atoms, and which fuel has an ignition delay of less than 7 ms, according to ASTM D6890, which fuel has ASTM D86 distillation range from 90 °C to 270 °C.
2. A fuel or fuel component as claimed in claim 1, which fuel contains less than 1% wt of aromatic and negligible levels of sulphur, in an amount less than 1ppm.
3. A fuel or fuel component as claimed in any one of the preceding claims, which fuel has an ignition delay of less than 5 ms.
4. A fuel or fuel component as claimed in any one of the preceding claims, which fuel has an ignition delay of between 2 and 5 ms.
5. A fuel or fuel component as claimed in any one of the preceding claims, wherein the mass % of the n-paraffins exceeds that of any other single component in the fuel.
6. A fuel or fuel component as claimed in any one of the preceding claims, wherein the mass % of the n-paraffins is in excess of 25% by mass of the fuel
7. A fuel or fuel component as claimed in any one of the preceding claims, wherein the mass % of the n-paraffins is in excess of 50% by mass of the fuel.
8. A fuel or fuel component as claimed in any one of the preceding claims, wherein the mass % of the n-paraffins is in excess of 80% by mass of the fuel.
9. A fuel or fuel component as claimed in any one of the preceding claims, wherein the mass % of the n-paraffins is in the order of 95% by mass of the fuel.

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10. A fuel or fuel component as claimed in any one of the preceding claims, wherein the n-paraffins are Fischer-Tropsch (FT) reaction derived n-paraffins.
11. A fuel or fuel component as claimed in any one of the preceding claims, wherein the iso-paraffins are FT reaction derived iso-paraffins.
12. A fuel or fuel component as claimed in any one of the preceding claims, which fuel includes one or more of: olefins, lubricity improver, and oxygenates.
13. A fuel or fuel component as claimed in any one of claims 1 to 11, which fuel is substantially free of heteroatoms such as nitrogen, sulphur and oxygen.
14. Use of an HCCI fuel or fuel component as claimed in any one of claims 1 to 13 as a blending component with conventional fuel.
15. A process for preparing a HCCI fuel or fuel component, which fuel or fuel component includes at least n-paraffins and iso-paraffins, which fuel has an ignition delay of less than 7 ms, said process including:
 - a) hydrotreating at least a Condensate fraction of a Fischer-Tropsch (FT) synthesis reaction product, or a derivative thereof;
 - b) hydroconverting a Wax fraction of the FT synthesis product or a derivative thereof;
 - c) fractionating in a single unit or in separate units, one or more of the hydrotreated Condensate fractions of step a) and the hydroconverted fraction of step b) to obtain the desired HCCI fuel or fuel component having 7 to 14 carbon atoms and which fuel has ASTM D86 distillation range from 90 °C to 270 °C; and
 - d) optionally, blending two or more of said components from step c) in a desired ratio to obtain the desired HCCI fuel.

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16. A process as claimed in claim 15, wherein the hydroconversion is by way of hydrocracking.

17. A process as claimed in claim 15 or claim 16, wherein the blending of step d) is the blending of FT condensate derivative and hydroconverted FT wax derivative in a blending ratio of from 1:99 to 99:1 by volume.

18. A HCCI fuel or fuel component as claimed in claim 1, substantially as herein described and with reference to the examples.

19. A process as claimed in claim 15, substantially as herein described and illustrated.

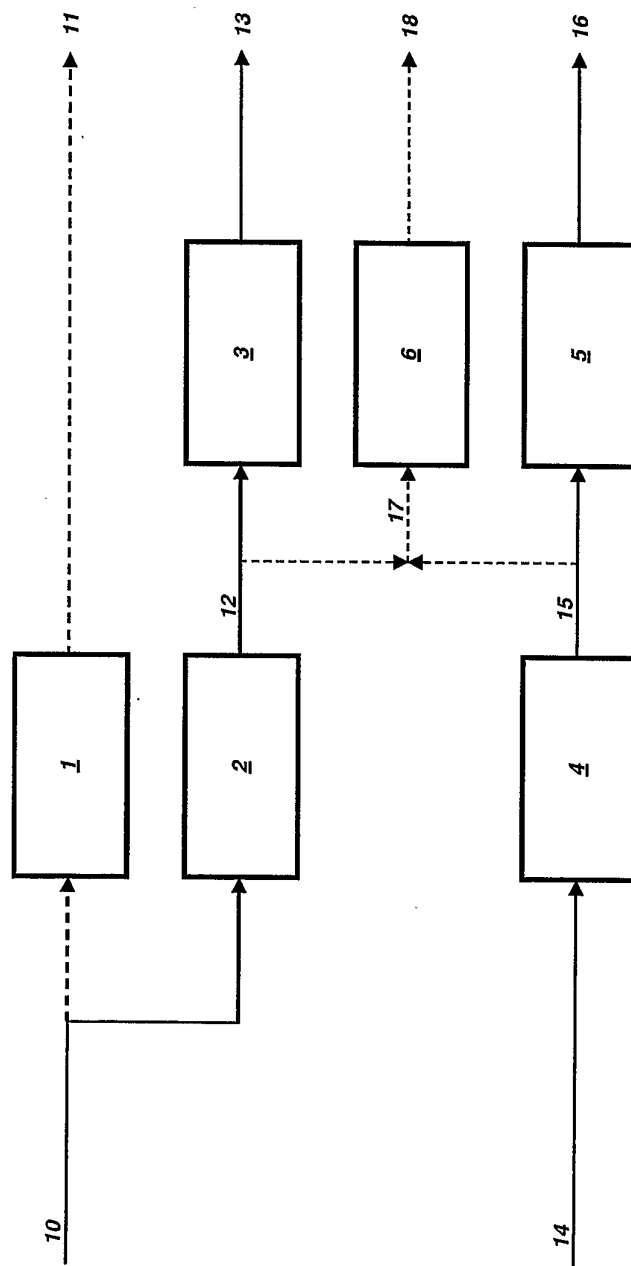


Figure 1 – Summary of Processing Requirements for Synthetic HCCI Fuels