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TITLE: **THE OCTAMIX PROCESS**

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<u>OBJECTIVE:</u> To develop a process for the production of mixed alcohols that can be used as a component for motor fuels.

<u>TECHNICAL APPROACH:</u> During ongoing development work for the LURGI Low Pressure Methanol Process a catalyst type was discovered which showed tendency to yield to higher alcohols. Encouraged by the commonly practice of adding so-called oxygenates to gasoline LURGI pursuit to develop a process for production of mixed alcohols in a single synthesis step.

To determine the optimal parameters and to prove the quality of the selected catalyst extended pilot plant tests using a water cooled tubular reactor were performed for more than 12 000 hours.

Product from the PDU operation was added to gasoline for several test programs in the United States and in Europe.

<u>SIGNIFICANT ACCOMPLISHMENTS:</u>

- Identified and demonstrated the effectiveness of a catalyst for mixed alcohol synthesis.
- A demonstration unit designed by LURGI for the production of about 2 tpd OCTAMIX is currently under commissioning.
- Process routes for economical production of synthesis gas for the OCTAMIX synthesis were developed.
- Promising results from tests with OCTAMIX blended gasolines available.
- Granting the EPA "Waiver" for OCTAMIX as a gasoline additive through "Texas Methanol Corpration, USA".
- OCTAMIX process ready for commercial application.

1. Introduction

First test runs aiming at fuel methanol production were made already at the beginning of the seventies with a catalyst type which was singled out during the screening tests for an improvement of the Lurgi methanol catalyst because it tended to stimulate the formation of higher alcohols.

As alcohol mixes containing methanol were becoming more and more important as motor gasoline components also in Europe, Lurgi began, in 1981, to intensify its efforts to develop a process aiming at direct catalytic production of a mixture of methanol and higher alcohols from synthesis gas under economically justifiable conditions.

An extensive catalyst screening programme was implemented in cooperation with the catalyst manufacturer SÜD-CHEMIE AG, and investigations with modified methanol test reactors were made at the same time to determine the influences resulting from the reaction parameters and from syngas composition.

A semi-industrial pilot plant was designed on the basis of a water-cooled tubular reactor - a type that had proven its merits in Lurgi's methanol synthesis plants before. This plant was then operated with the selected catalyst for a total of approx. 12,000 hours.

By selecting an appropriate temperature range and using a syngas with a surplus of CO, the test team succeeded in

- reaching a long service life of the copper catalyst,
- largely suppressing the water reaction by shifting the CO to CO_2 and hydrogen, and
- ensuring a satisfactory space/time yield and a high percentage of higher alcohols.

Lurgi used these results to design an Octamix demonstration plant for an output of more than 2 tpd which is currently being commissioned.

2. OCTAMIX Synthesis

Figure 1 shows the configuration of the synthesis loop, which differs from that in a methanol synthesis unit only by the inclusion of a CO_2 scrubber stage. Syngas with an H_2/CO ratio of approx. 1.0 is mixed with recycled gas. Then its CO_2 content is reduced to something like 1 % by the CO_2 scrubber in the loop. After preheating, this mixture is fed to the synthesis reactor, which - as for Lurgi low-pressure methanol synthesis - is of tubular design. Conversion takes place at temperatures between 250 and 300°C over a catalyst that differs from the Lurgi methanol catalyst mainly by a somewhat different pore structure. As the reaction temperature is somewhat higher than during methanol production, the boiling water used to cool the reactor is turned into steam of 80 to 100 bar. On leaving the reactor, the mixture of alcohols, other oxygenates and unreacted gas is cooled down in the gas/gas exchanger and further in a trim cooler to about 40°C so that alcohols, other oxygenates and traces of water are condensed. They are separated from the uncondensed gases which are recompressed into the loop by means of the recycle compressor. Mainly depending on plant capacity the optimal operation pressure is in the range between 50 and 100 bar.

The crude product is fed to a stabilizing column to remove dissolved gases and components whose boiling point is lower than that of methanol. The bottoms of the stabilizing column constitute the finished product, which, depending upon the H_2/CO ratio of the syngas contains about 50 - 70 wt.% of methanol. The rest are C_2 to C_8 alcohols and other oxygenates. The product contains 0.1 to 0.3 wt.% of water. The hydrocarbon content is almost negligible. Some 2.0 to 2.2 kg of steam are produced from the reaction heat per ton of OCTAMIX.

The composition of the product may be varied by changing the H_2/CO ratio or the reaction temperature. A low ratio and a high reaction temperature do not only increase the percentage of higher alcohol and other oxygenates, but also shift the product range towards higher alcohols and higher percentages of other oxygenates. Apart from the adjustment of the H_2/CO ratio and the reaction temperature there are other possibilities of, so to speak, custom tailoring the product over a fairly wide range.

If, for instance, the H_2/CO ratio cannot be adjusted economically to the required low ratio, an OCTAMIX will be produced with a low content of say 30 % of higher alcohols. By overhead extraction not only of dissolved gases and low-boiling components but even parts of the methanol itself, an OCTAMIX can be produced with the required higher alcohol content. The overhead methanol can then be conventionally distillated to pure methanol of grade AA and sold.

Recycling the low boilers and methanol to the synthesis reactor results in a product mix with 60 % and more higher alcohols. This recycling of low boilers and methanol, in combination with a low H_2/CO ratio and a higher reaction temperature, allows to combine the advantage of a considerably reduced methanol proportion, with the production of a high percentage of higher alcohols with a smaller C6+ content.

Figure 2 summarizes 3 different product mixes in a table, indicating the relevant H_2/CO ratio, the operating temperatures and the recycled quantities of low boilers and methanol.

3. Integration of Gas Production and Synthesis

3.1 Feedstock: Natural Gas

For maximum production of higher alcohols, the H_2/CO ratio of the synthesis gas should be around 1.0 or lower. If natural gas is used as a feedstock, this can be achieved by steam reforming of the natural gas with carbon dioxide addition.

On the assumption, however, that OCTAMIX production will probably be practical only in plants designed for 2000 tpd or more, the LURGI Combined Reforming Process or partial oxidation may offer economic advantages and avoids carbon dioxide addition from an external source.

3.1.1 Combined Reforming

Figure 3 shows a complete natural gas-based plant for fuel methanol production. Part of the natural gas is routed through steam reforming. The balance of the gas together with the reformed gas from the steam reformer and oxygen from the air separation unit are sent to the autothermal reformer where a synthesis gas with the desired H_2/CO ratio is produced. The synthesis gas is compressed in the makeup gas compressor, mixed with the recycle gas and sent to a CO_2 scrubber. CO_2-lean gas enters the synthesis section to be converted into OCTAMIX. Carbon dioxide from the CO_2 removal unit is recycled to the autothermal reformer.

3.1.2 Partial Oxidation

Partial oxidation of natural gas is an alternative for the production of a synthesis gas with the required H_2/CO ratio (Figure 4).

Natural gas, oxygen and recycled carbon dioxide are sent to the partial oxidation unit where make-up gas is produced at pressures up to 60 bar. After mixing it with recycle gas it is fed into a CO_2 scrubber to remove carbon dioxide which is recycled to the partial oxidation unit.

3.2 Feedstock: Heavy Residue Oil

Figure 5 shows the production of OCTAMIX from heavy residues. The residue is gasified by partial oxidation with steam and oxygen. The carbon formed during gasification is removed from the gas and remixed to the feedstock. The crude gas is mixed with the recycle gas, freed from sulfur and carbon dioxide and fed into the synthesis unit. Due to the high carbon content of the feedstock, no CO_2 recycling is required.

3.3 Feedstock: Coal

Syngas can be produced from coal by various methods ranging from pressure gasification at relatively low temperatures to the newly developed partial oxidation process operating with dry coal dust as a feedstock.

Since coal, if used for OCTAMIX production, will always have a carbon surplus, an on-specification syngas can be obtained with all these processes. No CO_2 recycling is required.

3.4 Thermal Efficiency

Figure 6 shows the thermal efficiency of OCTAMIX production from various feedstocks. The figures are based on the lower heating values and include oxygen production.

4. OCTAMIX Properties

The OCTAMIX properties have been investigated by specialized firms in the USA and the Federal Republic of Germany. With a view to the proposed applications, the extensive tests were made on blends of motor gasoline and OCTAMIX.

For a more meaningful evaluation, the properties of mixtures made up of motor gasoline and a blending component consisting of methanol and tertiary butyl alcohol were derived for comparison. This gasoline blending component is known on the world market by the brand name of Oxinol.

Various types of gasolines representative of the European market were tested, as the results obtained with the mix are influenced also by the properties of the motor gasolines used. Three types of gasolines of different origins as shown in Fig. 7 were considered, one being a cat cracker type (Type I), the second a reformate type (Type II) and the third being a mix containing a considerable proportion of petrochemical products. For each type, both the regular and the premium versions were studied. The lead content in all gasolines considered was 0.15 g/l.

Three different types of OCTAMIX as shown in the table in Figure 2 were used as blending components. Two consisted of OCTAMIX 40, type A being produced without and type B with recycling of methanol and low boilers, and one was OCTAMIX 50, which had been produced without recycling methanol. Unless stated otherwise, all gasoline/alcohol mixes were adjusted to a methanol content of 3 vol.% in the mix.

The following OCTAMIX and blend properties have been determined and will be described in the following sections:

- Density and blending density
- Boiling behaviour
- Reid vapor pressure
- Octane boosting capacity
- Water tolerance

4.1 Density and blending density

Figure 8 shows the density of OCTAMIX and its blending density. The blending density is some 2 % higher than the corresponding density figure for oxygenates, because mixing of oxygenates with gasoline is associated with a minor reduction in volume. For the blending rates selected for the studies, the density of the gasoline/oxygenate mix is only about 0.5 - 0.7 % higher than that of gasoline alone.

4.2 Boiling behaviour

Figure 9 shows the boiling characteristics of gasoline/alcohol mixtures contrasted with the boiling curve for pure gasoline. The figure shows that the 70°C point, which is essential for the refineries, is exactly the same for a mixture of 5 % OCTAMIX 40 B with 95 % of gasoline Type I and for this gasoline alone. Only about 28 % have boiled-off at 70°C. The figures for the methanol/TBA blend are slightly less favorable where as the blend with methanol exhibits a clearly negative effect.

4.3 Influence of Alcohol Blending on REID Vapor Pressure

Figure 10 shows the influence of alcohol blending on Reid vapor pressure. The change in the Reid vapor pressure of the gasoline caused by the admixture of oxygenates is of particular importance because any increase in this vapor pressure reduces the butane blending capacity. Past studies have shown that an admixture of 5 vol.% pure methanol leads to an increase in vapor pressure of about 0.25 bar on an average. However, this figure varies considerably, depending on the type of the base gasoline. Figure 10 shows to what extent the percentage of higher alcohols offsets the undesired effect of methanol. For instance, if the methanol percentage in the oxygenate mix is limited to 50 % as in the case of OCTAMIX 50, the increase in vapor pressure is of the same order as for a methanol/TBA blend, ranging between 12 and 25 %. The only exception is gasoline of Type II for which the increase in vapor pressure caused by oxygenate blending is highest in all cases - both for the regular and for the premium versions. For oxygenate blends containing 60 % methanol - for instance for OCTAMIX 40 - the most favorable value for the increase in vapor pressure is about 28 % and the most unfavorable about 40 %.

4.4 Octane Boosting Capacity

Adding OCTAMIX to gasoline increases the octane rating of the mix.

Fig. 11 contrasts the measured RON and MON figures for the mixes with different gasoline types with the calculated blending octane number. A striking result is that the blending octane number for mixes of OCTAMIX and regular gasoline is clearly higher than for premium gasoline. The different gasoline types, on the other hand, are of little influence. The road octane number (RON + MON)/2 for a mixture of 95 % regular gasoline and 5 % OCTAMIX 40 increases from 86.8 to 88, whereas the same percentage of OCTAMIX 40 mixed with premium gasoline boosts the octane rating only from 93.2 to 93.7.

Fig. 12 illustrates the blending octane numbers calculated from measured values for various OCTAMIX blends and for TBA/methanol.

4.5 Water Tolerance

Phase segregation problems may be encountered with blends of methanol and hydrocarbons especially at low temperatures. OCTAMIX with its content of higher alcohols enhances the water tolerance of gasoline/alcohol blends.

The top half of Fig. 13 shows the water tolerance of a blend consisting of reformate-type regular gasoline mixed with the three OCTAMIX grades and with a methanol/TBA mix. It illustrates clearly that the higher the percentage of higher alcohols, the better will be the water tolerance of the blend.

As shown by the two bottom diagrams of Fig. 13, it is particularly the olefin and aromatics content of the base gasoline that influences the water tolerance of the gasoline/alcohol blend. On the left, two regular gasolines with almost the same aromatics content - one being a cat cracker and the other a reformate type - are contrasted with each other. The cat cracker gasoline with its high olefin content is much less tolerant to water than the reformate type having a low content of olefins. The right side of the picture illustrates the influence of the aromatics content on the tolerance to water. Again, a cat cracker and a reformate gasoline, though this type of premium quality with approx. the same olefin contents, were contrasted with each other. The performance of the cat cracker gasoline with its low aromatics content is clearly poorer than that of the high-aromatics reformate gasoline.

5. **The OCTAMIX EPA Waiver**

For legal reasons methanol cannot legally be blended into gasoline without the addition of higher cosolvent alcohols. In a methanol/gasoline mix, the higher cosolvents such as ethanol, propanols and butanols are deemed necessary to prevent fuel system and engine corrosion, to protect against phase separation and to reduce the extreme vapor pressure increases. Moreover, the processes of producing and then blending these individual higher alcohols with methanol are difficult, time-consuming and expensive, making the methanol-higher alcohol mixes too expensive for gasoline blending.

Any manufacturer of a fuel or fuel additive in the USA must either show that the fuel is substantially similar to fuels used in certification of vehicles beginning in 1975 and thereafter, or obtain a waiver showing that the manufacturer's fuel does not contribute to the failure of any emission control device or the emission control system.

On August 7, 1987, the Texas Methanol Corporation submitted a waiver application to the Environmental Protection Agency (EPA) for the introduction into commerce of a gasoline-alcohol fuel, referred to as OCTAMIX. Texas Methanol Corporation maintains a licence agreement with Lurgi GmbH for the OCTAMIX process.

This waiver was granted on February 1, 1988 provided the following conditions are met:

- The final fuel consists of a maximum of 5 vol.% methanol, a minimum of 2.5 vol.% cosolvent in unleased gasoline. The cosolvents are any one or a mixture of ethanol, propanols, butanols, pentanols, hexanols, heptanols and octanols within the following constraints: the ethanol, propanols and butanols or mixtures thereof must compose a minimum of 60 percent by weight of the cosolvent mix, whereas a maximum limit of 40 percent by weight of the cosolvent mix is placed on the pentanols, hexanols, heptanols and octanols or mixtures thereof. Furthermore, the heptanols and octanols are limited to a maximum 5 percent by weight of the higher molecular weight alcohol mix (pentanols, hexanols, heptanols and octanols).
- A maximum concentration of up to 3.7 percent by weight oxygen in the final fuel is observed.

- Petrolite's proprietary corrosion inhibitor formulation TOLAD MA-10, is blended in the final fuel at 42.7 milligrams/liter.

- The final fuel must meet ASTM D439--84a Standard Specifications for Automotive Gasoline with the qualification that Test Method D 323 for RVP be replaced by the "dry" test method described in ASTM D-2 Proposal P-176, Proposed Specification for Automotive Spark Igniton Fuel, Annex A.3 or by automatic appartus described in Annex A.4 of the D-2 Proposal 176.

- The final fuel must meet the maximum temperature for phase separation as specified in ASTM D-2 Proposal P-176. Table 4 using the test method for water tolerance contained in Annex A.5.

- The fuel manufacturer must take all reasonable precautions, including identification and description of the product on shipping manifests, to ensure that the finished fuel is not used as a base gasoline to which other oxygenated materials are added, provided, however, that up to two percent by volume of methyl teriary butyl ether (MTBE) will be allowed in the base stock to which the alcohols are added if the MTBE is present only as a result of commingling in transport and storage, not purposefully added as an additional component to the alcohol blend.

- Specifiations for alcohol purity attached to the decision document as Appendix D are met.

The OCTAMIX waiver test fuel additive composition is listed in Figure 14.

Conclusions

The test results discussed above show clearly that OCTAMIX blended gasoline behaves almost in all respects like already commercially used oxygenates. OCTAMIX as neat alcohol fuel may increase its perspective. We are confident therefore that OCTAMIX will find a worldwide market within a foreseeable future, once it has been extensively tested in vehicles after more product for this purpose becomes available i.e. from the demonstration plant currently being started up.

To conclude, it may be said that Lurgi can today offer a process for the production of alcohol mixes which does not include any absolutely new or unproven elements under the aspect of either catalysts or technology.

PUBLICATIONS:

Heinz Hiller, Emil Supp, LURGI:
"OCTAMIX-Verfahren - eine moderne Variante der LURGI Methanoltechnologie",
Erdoel und Kohle Bd 38, Heft 1, Januar 1985

Emil Supp, LURGI:
OCTAMIX A Fuel Methanol that needs no Cosolvent" presented to the London Conference on the European Fuel Oxagenates Market, July 1986.

Wayne Kreis, Texas Methanol Corp.: "Understanding EPA's New Motor Fuel aiver: "OCTAMIX" presented to the 1988 National Conference on Octane and Oxygenated Fuels, March 1988, San Antonio, Texas.

Wayne Kreis, Texas Methanol Corp.: "The Development of OCTAMIX in the USA" presented to the 1988 World Methanol Conference, Frankfurt, December 1988.

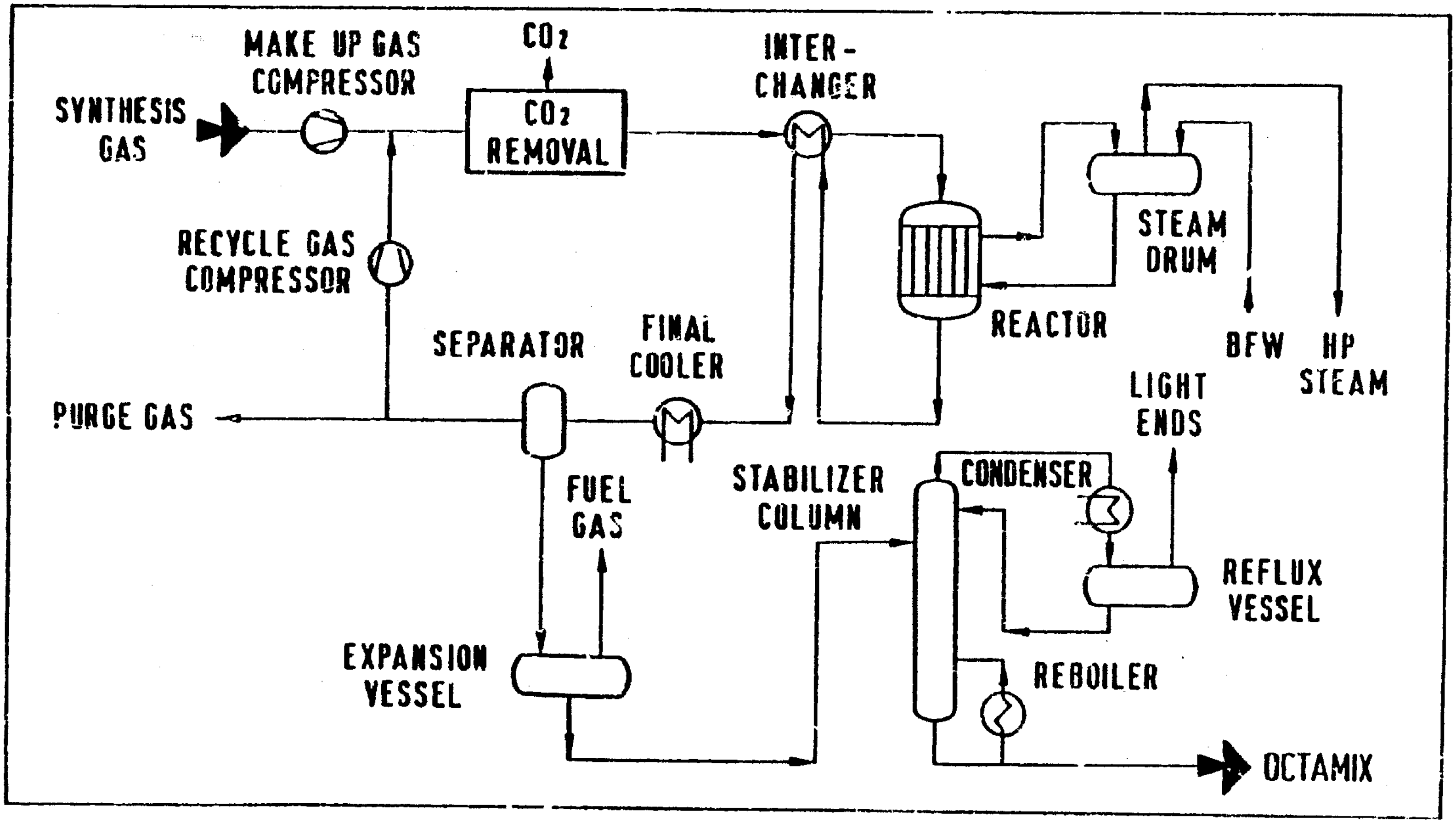

Fig. 1 OCTAMIX Synthesis

Octamix Compositions (wt %)

	Octamix 40 a			Octamix 40 b			Octamix 50		
	Total	Alcohols	Esters Ketones	Total	Alcohols	Esters Ketones	Total	Alcohols	Esters Ketones
C_1-Oxygenates	59,7	59,7	–	59,6	59,6	–	49,8	49,8	–
C_2-Oxygenates	7,4	7,4	–	15,1	15,1	–	9,3	9,3	–
C_3-Oxygenates	3,7	3,7	–	6,0	6,0	–	4,7	4,7	–
C_4-Oxygenates	9,3	8,2	0,1	6,6	6,6	–	10,3	10,2	0,1
C_5-Oxygenates	5,1	3,6	1,5	3,8	3,2	0,6	6,4	4,5	1,9
C_6-Oxygenates	7,7	3,3	4,4	4,1	2,8	1,3	9,6	4,1	5,5
C_7-Oxygenates	4,9	3,[illegible]	1,9	3,1	1,8	1,3	6,1	3,7	2,4
C_8+ -Oxygenates	2,8	0,5	2,3	1,2	0,3	0,9	3,4	0,6	2,8
Hydrocarbons	0,1	–	–	0,1	–	–	0,1	–	–
Water	0,3	–	–	0,4	–	–	0,3	–	–
	100,0	83,4	10,2	100,0	95,4	4,1	100,0	86,9	12,7
H_2/CO Syngas		1,0			1,0			0,95	
$P_{Reaction}$ (bar)		70,0			70,0			100,0	
$T_{Reaction}$ (°C)		270,0			270,0			275,0	
Recycle C_1+ Light Ends (kg/kg)		–			0,3			–	

Fig. 2

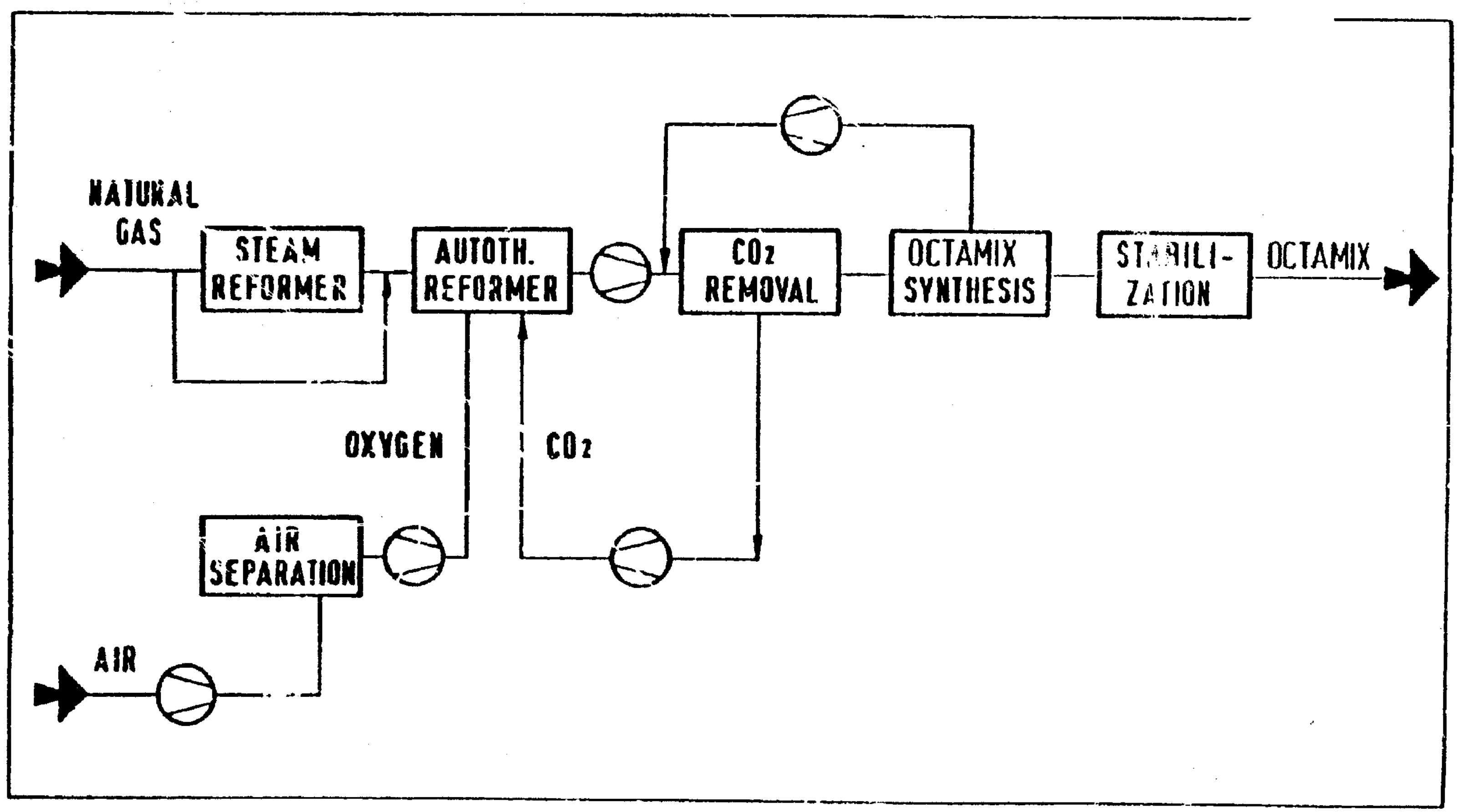

Fig. 3 Production of OCTAMIX from Natural Gas using Combined Reforming

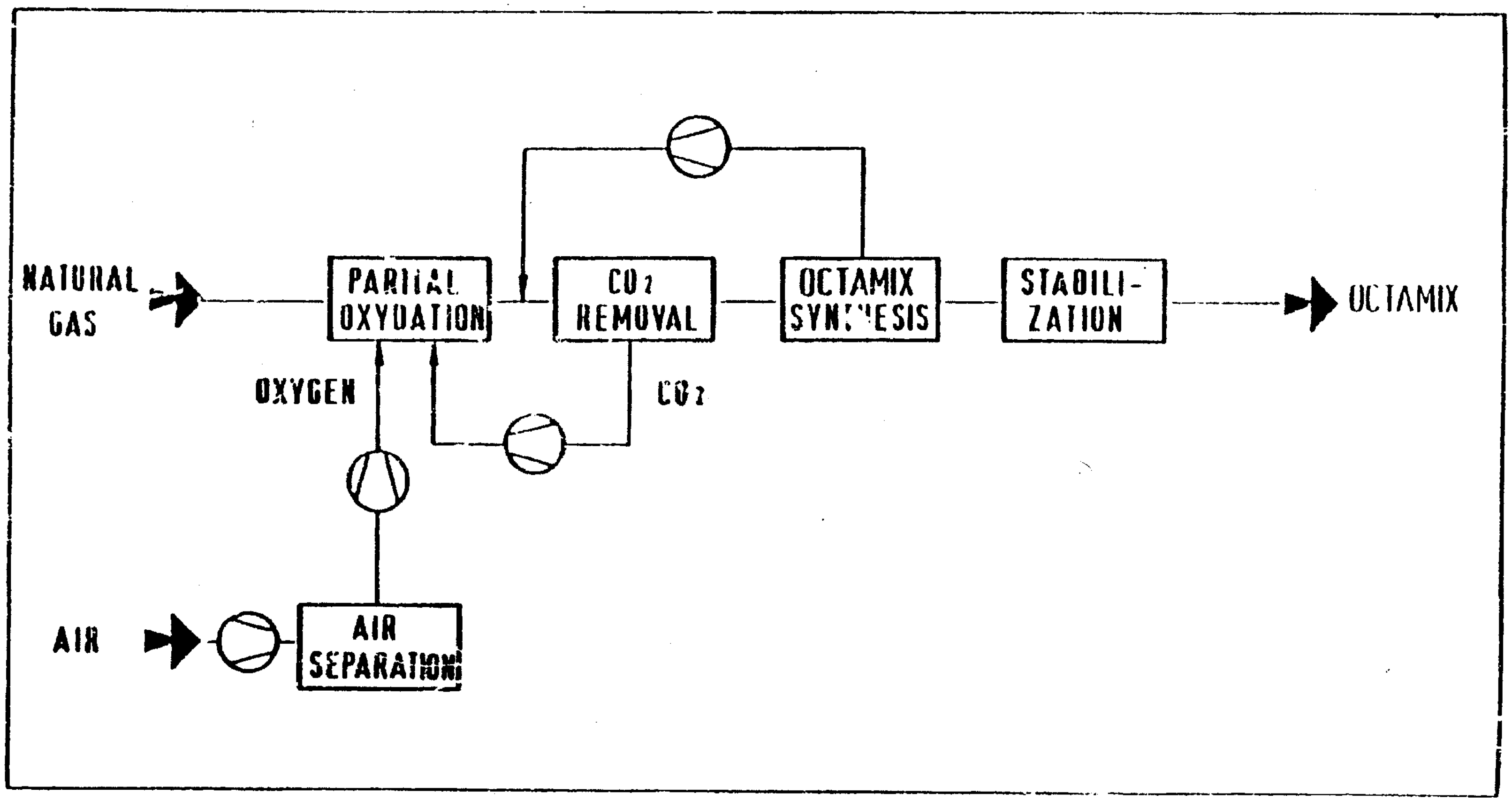

Fig. 4 Production of OCTAMIX from Natural Gas using Partial Oxydation

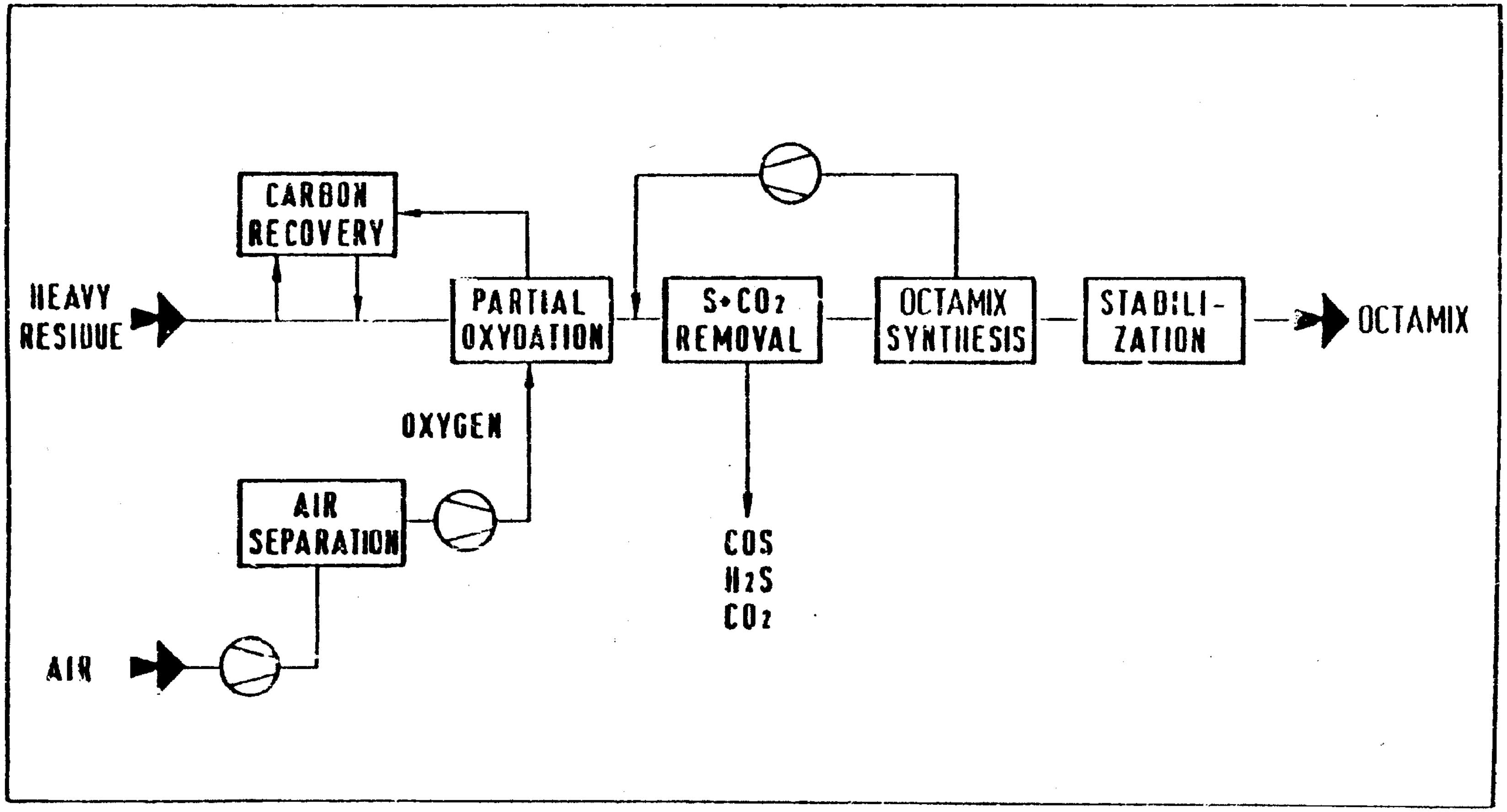

Fig. 5 Production of OCTAMIX from Heavy Residue

Thermal Efficiency of Octamix Production

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Feedstock	Thermal Efficiency
Natural Gas	
Combined Reforming	60.0 %
Partial Oxidation	61.1 %
Propane - Asphalt	56.3 %
Coal	55.6 %

Fig. 6

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Properties of Base Gasoline

	Regular			Premium		
	Type I Cat. Cracker	Type II Reformate	Type III Blended	Type I Cat. Cracker	Type II Reformate	Type III Blended
Density (UG/L)	0.747	0.750	0.734	0.756	0.776	0.761
RVP (bar)	0.465	0.420	0.560	0.465	0.420	0.560
RON	91.3	90.7	91.3	98.3	99.3	98.2
MON	82.4	82.9	82.9	88.1	88.3	88.1
Composition (% p. Vol.)						
Sat. Hydrocarbons	37.0	56.0	48.0	45.0	34.5	33.5
Olefines	26.0	10.0	27.0	16.0	11.0	20.0
Aromatics	37.0	34.0	25.0	39.0	54.5	46.5

Fig. 7

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Blending Densities of Octamix

	Density (kg/l) at 15 °C	
	Pure Component	Blending Density
Octamix 40 a	0.8078	0.8253
Octamix 40 b	0.8065	0.8242
Octamix 50	0.8017	0.8162
Meth. 60 % TBA 40 %	0.793	0.8037

Fig. 8

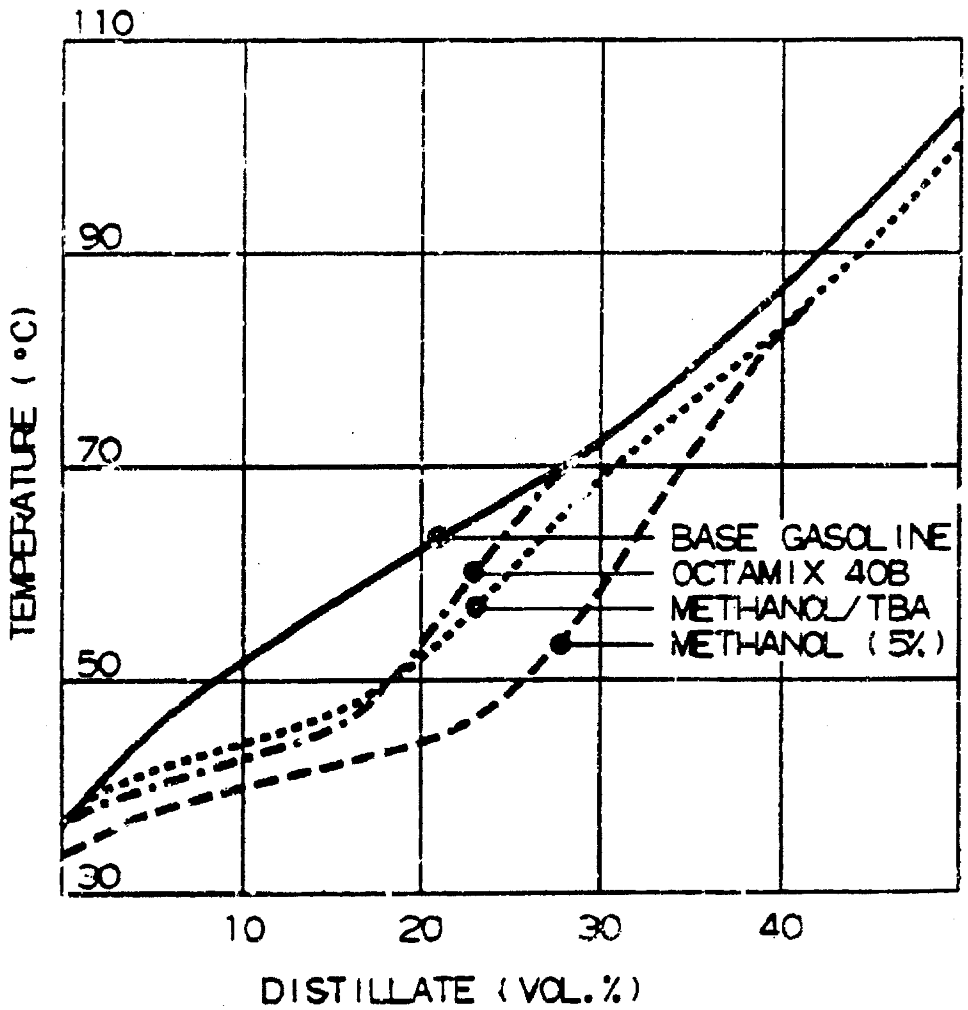

FIG. 9 BOILING CHARACTERISTICS
OF GASOLINE/ALCOHOL MIXTURES

Influence of Alcohol Blending on Reidt Vapor Pressure

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Regular Gasoline	Base Gasoline	Octamix 40 a	Octamix 40 b	Octamix 50	Methanol TBA
Type I	0 465	0.585	0.590	0.570	0.580
Type II	0.425	0.585	0.585	0.560	0.580
Type III	0.560	0.670	0.680	0.660	0.675

Premium Gasoline	Base Gasoline	Octamix 40 a	Octamix 40 b	Octamix 50	Methanol TBA
Type I	0.510	0.585	0.585	0.570	0.570
Type II	0.515	0.590	0.595	0.600	0.575
Type III	0.520	0.655	0.615	0.645	0.650

Fig. 10

Octane Improvement by Octamix Blending

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	Research Octan Number			Motor Octan Number		
	Base Gasoline	Base Gasoline + 5 Vol % Octamix 40 *	Blending Octan Number	Base Gasoline	Base Gasoline + 5 Vol % Octamix 40 *	Blending Octan Number
Regular Gasoline						
Cracker - Typ	91.3	92.9	123.3	82.4	83.1	96.9
Reformate-Typ	90.7	92.3	122.7	82.9	83.7 *	98.9
Blended-Typ	91.3	92.8	121.3	82.9	83.6 *	96.9
			Av. 122.4			Av. 97.6
Premium Gasoline						
Cracker-Typ	98.3	99.1	114.3	88.1	88.2 *	90.1
Reformate-Typ	99.3	99.8	109.3	88.3	88.3 *	88.3
Blended-Typ	98.2	98.9	112.2	88.1	88.2 *	90.1
			Av. 111.9			Av. 89.5

Fig. 11

Octane Improvement by Alcohol Blending

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Regular Gasoline

Base Gasoline Ron = 91
Mon = 83

	Blending Ron	Blending Mon
Octamix 40 a	118	97
Octamix 40 b	120	98
Octamix 50	123	98
Meth. / TBA	122	99

Premium Gasoline

Base Gasoline Ron = 99
Mon = 88

	Blending Ron	Blending Mon
Octamix 40 a	108	88
Octamix 40 b	111	89
Octamix 50	113	89
Meth. / TBA	113	90

Fig. 12

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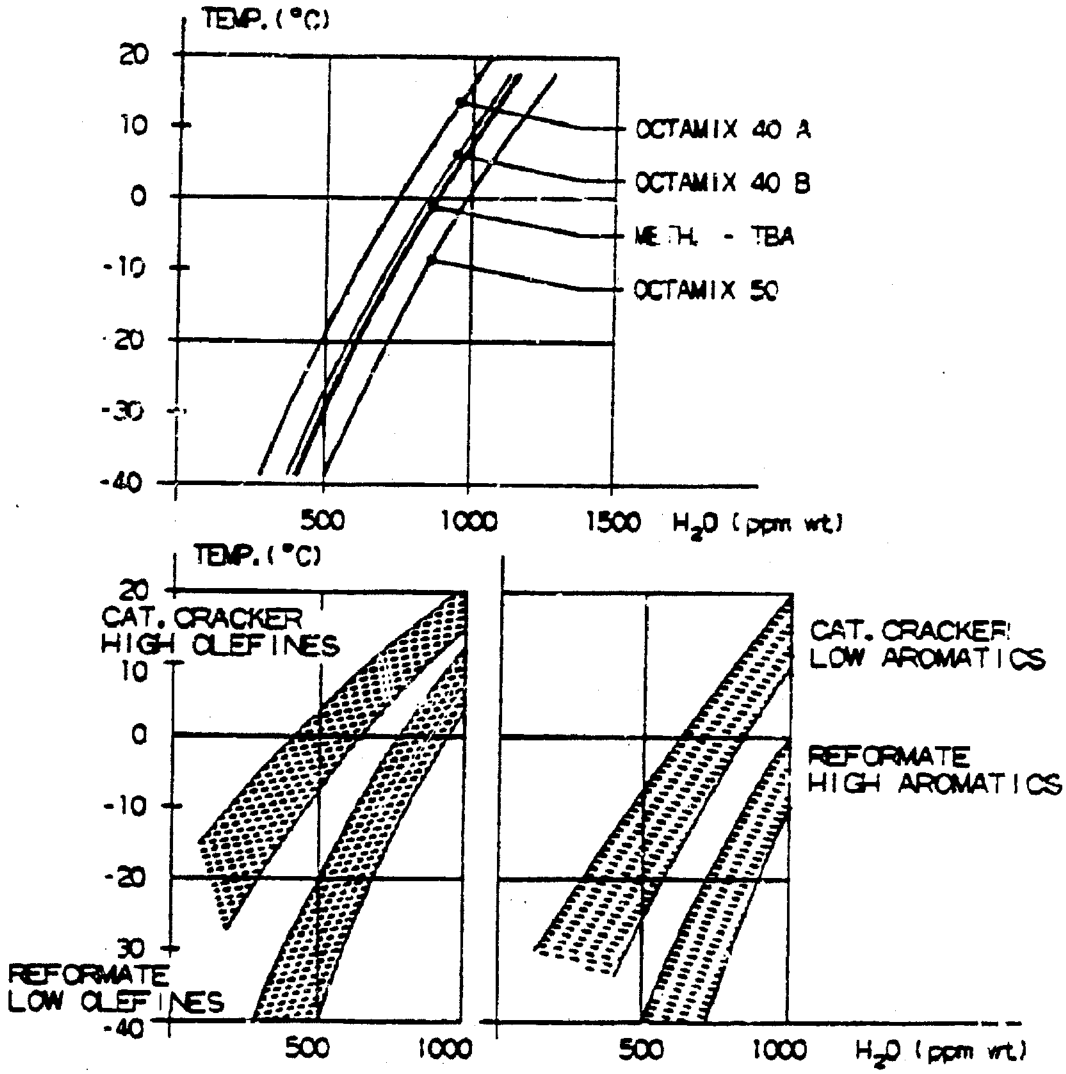

WATER TOLERANCE OF DIFF. GASOLINES

FIG. 13 WATER TOLERANCE OF GASOLINE/ALCOHOL-MIXTURE

Fig. 14 LURGI

Octamix-Analysis

Composition (according GC-Analysis)			
Methanol		64.5	wt%
Ethanol		11.5	wt%
Propanoles		5.2	wt%
Butanoles		7.4	wt%
Pentanoles		3.4	wt%
Hexanoles		2.6	wt%
Heptanoles		1.2	wt%
Octanoles		0.2	wt%
Ketones	(C_5 - C_8)	1.8	wt%
Esters	(C_5 - C_8)	0.8	wt%
Water + Hydrocarbons (0.08 wt% H_2O)		0.1	wt%
Total component identified		98.7	wt%
+ Unidentified Components plus analytical errors		1.3	wt%
Total		100.0	wt%

Ultimate Analysis (Analysis on Elements)		
Carbon	46.30	wt%
Hydrogen	12.77	wt%
Oxygen	40.93	wt%
Total	100.00	wt%