

# Standard Oil Company (Indiana)

## INFORMATION DIVISION TRANSLATION T47-10

API-TOM Reel 40, Frames 51-56

Oberhausen-Holtzen, June 12, 1939

To: Prof. Martin, et al

Polymerization of Gasol (Trans.: L.P.G.) with Increasing Charge  
(Charge of Director Albert)

### Summary

(1) By the utilization of narrow reaction tubes it was possible to increase five-fold the charges of gasol in comparison to the amounts which the U.O.P.C. described but that the polymerization fell below 90%, farther to increase ten-fold whereupon the value of the polymerization, also by increase of the temperature to 240-250° declines only to 80-85%.

(2) The strongly exothermic reaction which proceeds caused no superheating; a good distribution of the temperature in the reaction tube occurs with the great rate of flow.

The apparatus utilized in these experiments is described in supplement I. It consists of a reaction tube (15 mm. i.d. 1300 mm. long, ca. 320 cc. capacity) which possesses an electric heater with 3 external temperature measuring positions. The feed of the gasol to the furnace occurs from a high pressure bomb by means of an iron tube which for the purpose of preheating of the gasol is wrapped about a small water-filled bomb, which is heated in an oil bath. (Wrapping ca. 6.8 m. long  $F = 0.17 \text{ m}^2$ ). The addition of water was carried out in such a manner that, by means of a submerged tube, a determined amount of nitrogen was led into the bottom of the small water-filled bomb where it took along a portion of the water vapor (the amount was previously determined at different temperatures and pressures). The nitrogen laden with water vapor was introduced into the gasol conduit before the oil bath in order to obtain an intimate mixture between gasol and water vapors which were heated jointly in the oil bath in order to prevent a condensation of the water on the upper portion of the catalyst. The furnace is filled with the Ipatieff catalyst (275 cc.).

The Americans used a reaction furnace of 50-80 mm. i.d. for the polymerization and give the following polymerization conditions:

Temperature - 190°-205°C.

Pressure - 50-70 atm.

Charge - 1 l. liquid gasol = 0.5 kg on 0.5 l. catalyst

Original olefin content of the gasol - 30-40 vol.%

H<sub>2</sub>O-addition - 1 mol.% calculated on gasol.

In the first experiments these conditions were accurately kept. Since there were 275 cc. of catalyst in the furnace, the previously-described amount of charge of gasol with 29.6% of C<sub>2</sub>H<sub>6</sub> + C<sub>4</sub>H<sub>8</sub> yielded 120 cc. of poly-napth/hr. in a 95-98% polymerization.

Since in the earlier experiments - without water addition - increasing charges have affected very favorably the boiling course of the products obtained, there should be established in these experiments how far the charge can be increased, in general, without sharply decreasing the polymerization, further how the reaction proceeding exothermally at high charges works out on the temperature of the several reaction zones in the narrow tube.

The following experiments were carried out with 200 cc., 400 cc. and 800 cc. of poly-naphtha formation per hour. At a rate of 200 cc./hr. the temperature of 200°C. suffices to get a 90-95% polymerization, at a 400 cc. hourly rate the temperature must be raised to 220-225°C. if a polymerization of 90-95% is to be obtained. Condensate of 400 cc/hr. corresponds to a charge of ca. 1.2 kg. of gasol or a space time yield of 1300 l. naphtha/m<sup>3</sup> reaction space per hour or 1450 l. naphtha/m<sup>3</sup> catalyst/hr.

In the further increase of the charge to 800 cc. condensate/hr., the polymerization decreased in spite of the increase of the temperature to 240-250°C. and reached an average value of 80-85%. About 2.4-2.6 kg. of gasol were necessary as charge. This corresponds approximately to ten-fold of the amount which the Americans stated for the charge.

The space-time yields in these experiments amount to 2600 l./m<sup>3</sup> reaction space/hr. or 2900 l. naphtha/m<sup>3</sup> catalyst/hr.

Since the polymerization decreased at a charge of 800 cc/hr. a further increase was omitted. These ratios all refer to a charge of utilized gasol of 29.6 vol.% C<sub>7</sub>H<sub>6</sub> + C<sub>8</sub>H<sub>8</sub>. The space-time yields could be correspondingly raised at higher olefin content. On account of the resulting reaction heat a superheating in the narrow reaction tube could not also be established at the high charge of 2.5 kg. gasol/hr.

According to the view of Dir. Albert this should have its basis in that the cooling zones of the external wall (on account of the small diameter) can be more effective and make impossible a resulting peak temperature of the reaction in the interior of the tube, which by application of tubes with large diameters even at high charge cannot be prevented (see supplement I, figure 2).

From the weight calculation of several experiments can be concluded that a C-deposition in the shape of higher polymerization hardly takes place, since the experiments do not exceed a value of 1-2%.

Whether a rapid fatigue of the catalyst enters at high loads, cannot be stated, since the duration experiments in this direction have not yet been carried out.

In conclusion a table follows with data of several poly naphthas at increasing charge.

T A B L E

	<u>I</u>		<u>II</u>		<u>III</u>	
	<u>Charge 200 cc/hr.</u>		<u>Charge 400 cc/hr.</u>		<u>Charge 800 cc/hr.</u>	
	<u>Crude</u>	<u>Distillate to 200° C.</u>	<u>Crude</u>	<u>Distillate to 200° C.</u>	<u>Crude</u>	<u>Distillate to 200° C.</u>
d <sub>20</sub>	0.725	0.735	0.723	0.735	0.718	0.727
n <sub>D</sub> <sub>20</sub>	1.4216	1.4226	1.4219	1.4225	1.4194	1.4172
Reid-pressure	0.47	0.24	0.71	0.24	0.46	0.15
Unsaturated % after Kettwinkel	90	92	86	90	89	76
Octans Number	CFR Mot. 79.5	Mot. 80.2 Res. 95.0	CFR Mot. 78	Mot. 78 Res. 93.7	Mot. 78.8 Res. 93.7	Mot. 80.2 Res. 95.2
Boiling Initial	50° C.	34° C.	32° C.	33° C.	34° C.	43° C.
Boiling End	232° C.	194° C.	224° C.	196° C.	198° C.	195° C.
10%	-	93°	39°	88°	45°	95°
50%	127°	121°	122°	117°	114°	113°
95%	210°	187°	205°	184°	190°	182°
S.K.Z. *	137.5	126	134	122	128	122

\* (Trans.: Boiling Characteristic Number?)

From the table is to be seen that the properties of the three naphthas are fairly equivalent. At greater charge (lesser polymerization) the boiling position (supplement 2) is most favorable and the specific gravity the lowest. Almost the whole fraction in all cases is to be used as motor naphtha. The portion of aviation naphtha ( $-165^{\circ}$  C.) lies very favorable with 80%. The octane numbers of all also lie in the same range according to CFR motor at 78-80 octane number and according to Research at 93-95 octane number.

/s/ Spiske

Translated by H. J. Cohen, Feb. 8, 1947  
Requested by R. F. Marschner  
Checked by C. C. Miller, Feb. 13, 1947  
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Attachments in Original

Supplement 2

Boiling point plot of volume per cent versus temperature  $^{\circ}$ C. for three investigations.

Supplement 1

Polymerization apparatus.

"Polymerisation von Gasol mit steigenden Durchsätzen"

Oberhausen-Holten  
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