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A CHRONOLOGICAL SUMMARY OF AND COMMENTS ON DR. MICHAEL'S  
ON THE LIQUID PHASE PROCESS (SCHAUMFAHRWEISE)

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The Schaumphase Process, or Liquid Phase Suspension Process, was investigated by Dr. Michael in 1940. Similar processes were tried early in 1935 by Ruhrchemie and Gewerkschaft Victor on cobalt catalyst. These tests, however, yielded poor results when compared with the dry phase atmospheric pressure cobalt synthesis in a fin-tube converter. A rectangular high tower was used as a converter. The reaction heat was removed by water-cooled tubes uniformly divided over the cross-section area of this converter in numerous layers. The flow of the synthesis gas was either concurrent or countercurrent to the flow of the suspension. The initial results, being fairly promising, could only be retained for a short time. The formation of  $\text{CH}_4$  increased to an amount prohibitive to economical application of such a process. This fact was found to be due to the settling of the catalyst on the cooling tubes. Thus, this procedure was abandoned.

Dr. Michael started his Schaumphase Process in a cylindrical converter with a stirrer. Besides experiencing difficulty with the stirrer-packing, sedimentation of the catalyst on different parts of the equipment, especially on the inner wall of the converter, was observed. The action of the stirrer on the gas and suspension distribution was designated as perfect. The application of a porous plate "Schaumstein" was apparently found to be satisfactory as well, though a better action of a stirrer, formerly claimed, has not been revoked. When using the porous plate, similar sedimentation of the catalyst on the wall of the converter was observed. A slowly rotating stirrer, scratching continuously the wall of the converter, was built in. Later, it is claimed, the

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deposit of the catalyst was not caused by the sedimentation but by an insoluble sticky material formed during the synthesis reaction in the sump of the converter.

The size of the pores in the porous plate is said to be of essential importance, as well as the size of the bubbles. When the bubbles are too small, the separation of the gas from the oil suspension is no longer perfect. The converter contains too much gas volume; thus, the capacity of the converter decreases. Large bubbles ascent faster.

The figures given by Dr. Michael in internal reports of the I.G. are chronologically, as follows:

May 20, 1940:

Schaumphase Synthesis for Production of Middle-Oil. Synthesis

Gas composition is apparently 1.0 H<sub>2</sub> to 1.2 CO. CO<sub>2</sub> content in the synthesis gas must be below 2%. The reaction is performed in three stages. The third stage has to be operated on high temperatures and will yield mainly gasoline.

Space-Time Yield: 600 kg./m<sup>3</sup> reaction volume/day

Specific Yield: 165 g.(C<sub>5</sub> and above)/m<sup>3</sup> of CO+H<sub>2</sub> present in the fresh synthesis gas and at 93% conversion.

Before the first stage, between the first and second stages, and between the second and third stages, a CO<sub>2</sub> removal plant is provided. For 100,000 m<sup>3</sup> of water gas/hr., 570 m<sup>3</sup> reactor volume is necessary:

1st Stage - 10 Units, each 32m <sup>3</sup>	= 320 m <sup>3</sup>	reactor volume.
2nd Stage - 4 " "	40m <sup>3</sup>	= 160 m <sup>3</sup> " "
3rd Stage - 3 " "	30m <sup>3</sup>	= 90 m <sup>3</sup> " "

The conversion rates of each stage are given as follows:

1st Stage - 50%  
 2nd Stage - 50%  
 3rd Stage - 72%

Neglecting the formation of noncondensable hydrocarbons, the space velocity (volumes of feed gas per volume of catalyst per hour) can be estimated roughly as:

1st Stage - 290 space velocity  
 2nd Stage - 209 " "  
 3rd Stage - 258 " "

The space-time yield in the first stage calculated from the specific yield given as 104 g. C<sub>3</sub>+ and the space velocity is 744 kg./m<sup>3</sup>/day.

The space-time yield of the second stage calculated from the specific yield of 52 g. C<sub>3</sub>+ and the space velocity is 724 kg./m<sup>3</sup>/day.

The space-time yield of the second stage calculated from the specific yield of 30 g. C<sub>3</sub>+ and the space velocity is 743 kg./m<sup>3</sup>/day.

The average space-time yield, according to the above figures, is about 740 kg./m<sup>3</sup>/day. This would be 25% more than the figure given previously by Michael with about 600 kg./m<sup>3</sup>/day.

The total specific yield is given as 186 g. C<sub>3</sub>+, including 13 g. of alcohols, which would reduce the figure to about 182 g. of pure hydrocarbons, C<sub>3</sub>+

Conversion rates are given as:

1st Stage - 50% - Specific yield = 104 g. (including 6 g. alcohols)  
 2nd Stage - 50% - Specific yield = 52 g. (including 4 g. alcohols)  
 3rd Stage - 72% - Specific yield = 30 g. (including 3 g. alcohols)

Total conversion 93%, total specific yield 186 g., including 30 g. of alcohols and including 21 g. of C<sub>3</sub>+C<sub>4</sub>. The CH<sub>4</sub>+C<sub>2</sub>H<sub>6</sub> formation is by calculation 2% in the first stage, 3% in the second stage, and 20% in the third stage.

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The above-mentioned results are proven only in the first stage. The second stage is said to have been calculated, and the third stage is said to be proven in a short test with a corresponding gas composition. When before each stage of synthesis the  $\text{CO}_2$  content is less than 2%, the following partial pressures of  $\text{CO}+\text{H}_2$  can be calculated, taking into account the small increase of volume by formation of 2 to 3%  $\text{CH}_4$  and some hydrocarbons, noncondensable;

1st Stage - about 96%  $\text{CH}_4$  - 2%  
 2nd Stage - about 91%  $\text{CH}_4$  - 3%  
 3rd Stage - about 86%  $\text{CH}_4$  - 20%

It is remarkable that with the synthesis gas containing 86%  $\text{CO}+\text{H}_2$  at 72% conversion, the formation of  $\text{CH}_4$  is as high as 20%. For the reported space velocities and conversion rates, the values for the formation of  $\text{CH}_4$  are presumably too optimistic in the first stage as particularly in the second stage. The value given for the third stage may be right for a short time in the reaction of a fresh catalyst, but it would certainly be much higher when operated for a longer time with such high space velocities. A conversion of 72% at 258 space velocity ( $\text{CO}+\text{H}_2$ ) might require temperatures at which the decomposition of the liquid occurs. The truth in this assumption may be proved by data given later by Michael when space-time yields are 350  $\text{kg.}/\text{m}^3/\text{day}$  and temperatures not higher than 260-270°C. Temperatures exceeding 270°C. are said to crack the oil so that oil from foreign sources would be necessary in order to maintain the oil balance.

It remains to be mentioned that at this time the consumption of catalyst, including regeneration, is 4.7 liters per ton of product; the cost of one liter of catalyst equals about RM 3.20, or \$1.30 per liter. The production per cubic meter of catalyst is, therefore, about 215 tons of hydrocarbons. This figure is far above the corresponding figures for

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the cobalt catalyst as used in German chemical plants. The cost of RM 3.20 per liter is almost identical with those of the cobalt catalyst based on equal production of hydrocarbons.

1941:

In 1941, results are reported for production of middle oil and of gasoline:

Middle Oil Process:

Reaction Temperature	240-250°C.
Conversion Rate	90%
Space-time yield	200 kg./m <sup>3</sup> /day
Specific Yield	170 g. l+s hydrocarbons/Nm <sup>3</sup> of CO+H <sub>2</sub> (including 7 g. alcohols in the reaction water)

Products:

Gasoline	30%
Oil (-350°C.)	30%
Paraffin	40%
C <sub>3</sub> +C <sub>4</sub>	4-5%
CH <sub>4</sub> +C <sub>2</sub>	3%

3 stages - 3 CO<sub>2</sub> removals.

Gasoline Process:

Reaction Temperature	300-310°C.
Conversion Rate	90%
Space-time Yield	400 kg./m <sup>3</sup> /day
Specific Yield	160 g. (including C <sub>3</sub> , C <sub>4</sub> , and alcohols)

Products:

Gasoline	60% Res. Octane No. 90
Oil (-350°C.)	30%
Paraffin	10%

3 stages - 3 CO<sub>2</sub> removals.

These results differ considerably from those given the year before regarding space-time yields. For almost identical specific yield (2nd and 3rd stages are calculated again) the space-time yield has dropped to almost 25% of that previously reported. The synthesis gas used had apparently H<sub>2</sub>:CO ratio equal to 0.8:1. Nothing is reported about the consumption ratio.

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June, 1942:

In June, 1942, Dr. Michael reported the following data:

CH <sub>4</sub> +C <sub>2</sub> formation	5%	10 g./Nm <sup>3</sup>	CO+H <sub>2</sub> at 90% conversion
C <sub>3</sub> +C <sub>4</sub> (80% olefins)	10%	19 " "	" " " "
Alcohols (C <sub>2</sub> , C <sub>3</sub> , C <sub>4</sub> )	6%	11 " "	" " " "
(in reaction water)			
Liq. + Solids, Hydrocarbons.	79%	150 " "	" " " "

Gasoline	-50° C.	2%	3 g./Nm <sup>3</sup>	CO+H <sub>2</sub> )
"	50-100°C.	22%	33 " "	" " )47% Gasoline
"	100-150°C.	16%	24 " "	" " )70 gms. refined
"	150-200°C.	10%	15 " "	" " )Res. O. No. 70

Middle Oil	200-350°C.	30%	45 g./Nm <sup>3</sup>	CO+H <sub>2</sub> Cetane No. 70
Paraffins	> 350°C.	20%	30 " "	" " " "

July, 1942:

In July, 1942, Dr. Michael reported that the recirculating oil-catalyst suspension is cooled by about 5°C. The achieved space-time yield of a converter with reaction volume of 1.5 m<sup>3</sup> is 350 kg./m<sup>3</sup>/day. Michael claims that for production of 80 metric tons/day of hydrocarbons a reactor volume of 50 m<sup>3</sup> is sufficient (this is evidently a mistake, because 50 x 350 = 17.5 tons per day). For 80 tons per day a reactor volume of 230 m<sup>3</sup> would be necessary or, in other words, 5-1/2 times as much.

A thousand standard m<sup>3</sup> CO+H<sub>2</sub> yield:

	Oxygenated Compounds	Olefins
240 m <sup>3</sup> CO <sub>2</sub> = 474.6 kg.		
44 kg. H <sub>2</sub> O		
10 kg. CH <sub>4</sub> +C <sub>2</sub> H <sub>6</sub>		
18 kg. C <sub>3</sub> +C <sub>4</sub>	-	80%
9 kg. Alcohols in reaction water	-	-
77 kg. Gasoline - 200°C.	4%	70%
47 kg. Oil - 200-350°C.	2%	56%
31 kg. Paraffin > 350°C.	1-2%	-
Total: 710.6 kg.)		
In-Gas: 733.7 kg.)	Conversion - about 97%	

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August, 1942:

Synthesis Gas: The most favorable synthesis gas is water gas produced by means of oxygen. The nitrogen as well as the CO<sub>2</sub> content should not exceed 1-2% each in order to achieve a high conversion of the gas. The H<sub>2</sub>:CO ratio should be 0.8:1 to 0.75:1. The total sulfur is not to exceed 2 mg./m<sup>3</sup>.

Catalyst: At present, the raw material for the catalyst is iron-carbonyl. It is either decomposed at 250°C. in oil or burned to hematite and reduced. 2% of potassium borate are added and the mixture is pulverized under oil. Nothing certain can be said about the life-time of the catalyst; it certainly might be several months or a year. No catalyst could be run over a period of more than 2-1/2 months. It is claimed that sulfur impurities in the synthesis gas, caused by war conditions, also contaminated the catalyst. The regeneration of the catalyst is simple. The catalyst is melted, reduced, and pulverized. The concentration of the catalyst is 0.35 to 0.40 kg. per liter of oil-catalyst suspension.

The reaction temperature is 250-275°C. 3 stages of operation and 3 CO<sub>2</sub> removal plants.

Gas recycle is employed (no figures are given about the rate of recirculation). The space-time yield is given for one 1-1/2 m<sup>3</sup> converter (that is, a single stage operation -- the other stages are still calculated) as 310 kg./m<sup>3</sup>/day at 250°C. and a space velocity of 80; as 470 kg./m<sup>3</sup>/day at 275°C. and a space velocity of 125.

Products:

Specific yield = 164 g. primary products (solid and liquids, including 9 g. valuable products (alcohols) from the reaction: water.

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18 g. C<sub>3</sub>+C<sub>4</sub> (80% olefins)Product Distribution:

	Weight (1+g)	Alcohols	Olefins	Paraffins	Esters, Acids, etc.
-50°C.	4	0	85	12	3
50-100°C.	20	5	83	7	5
100-150°C.	16	15	67	11	7
150-200°C.	10	12	62	20	6
200-250°C.	12	12	63	17	8
250-300°C.	10	10	54	25	11
300-350°C.	8	5	45	38	12
350°C.	20	-	-	-	-

Grade of branching 25-26%  
 " " C<sub>4</sub> " 15%

1943:

The following figures were given:

Reaction temperature 250°C.  
 Pressure 20 atm.  
 Reaction volume 1.5 m<sup>3</sup>  
 Space-time yield 350 kg./m<sup>3</sup>/day

Products:

Gasoline 45%  
 Oil 30%  
 Paraffin 12-15%  
 C<sub>3</sub>, C<sub>4</sub> 2%  
 Alcohols 4% (in the reaction water)

General Remarks:

Space-time yield in a converter of 8 meter height equals 300 kg./m<sup>3</sup>/day at 250°C.

Space-time yield in a converter of 3 meter height equals 500 kg./m<sup>3</sup>/day at 250°C.

Gas bubbles of uniform small size could only be produced by Schaumstein (porous ceramic); this was true only when the gas flow did not

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exceed 28 liters/cm<sup>2</sup>/hr. If this figure is taken as a limit, the number of converters is larger and the space velocity applicable is considerably less than, for instance, in the Duftschmidt process. The resulting increase of equipment investment might be found prohibitive for the process.