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High Pressure Experiments
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THE PRESENT STAND OF THE SYNTHETIC OIL EXPERIMENTS

The principal work in recent times consisted in adapting the foam synthesis method involving the use of foam plates to industrial production. For this purpose, a reactor of 1.5 m^3 capacity was designed in the spring of 1941, and has since been completed and put in operation.

Promising results have been obtained during the recent months with a smaller reactor of 25 l capacity. It is still at present in operation.

A third reactor of 300 liters capacity is being equipped with means for violent stirring, instead of a foam plate. Great technical difficulties have been met in the stuffing boxes of the mixer shaft. Tests have at present been interrupted, and the reactor changed over to the foam plate method. It has been used for a short time, and then removed from the stall, to make place for the 1.5 cbm reactor which had in the meantime been completed. It is being reerected in the stall 304.

The Construction of the Experimental Reactors

All experimental reactors contain essentially the same structural parts as the large industrial units. A foam plate is installed near the bottom of the reactor space for the distribution of the gas, a degasifier top at the head of the reactor, in which the rising foam will give up its gas, and the liquid is then returned by an outside line to the bottom of the reactor by means of a pump. The liquid rises again in the reactor, counteracting the tendency of the catalyst to settle. The rate of circulation is, however, not determined merely by the settling of the catalyst, but also by the need of removing the heat of the reaction

in the liquid phase by a cooler which forms part of the outside circuit. Were one to limit the temperature rise of the liquid to 10°C, the liquid would have to circulate at a synthesis temperature of 250°C at the rate of once every three minutes. Cooling will then lower the temperature of the liquid by the required number of degrees.

The cooling of all our experimental reactors, including the 1.5 cbm reactor, was done in the reactor jacket. The change is insignificant but offers constructional advantages in experimental work. Oil will be used as an intermediate cooling agent, and it will surround the reactor and be pumped in a circuit through a cooler. When starting, the oil will be heated in a preheater, and will in this way gradually bring the reactor up to the required temperature.

Several technical difficulties had to be overcome at the start, chiefly with the stuffing boxes of the liquid phase circulation pumps. The suspended catalyst, containing iron oxide and carbonate, acts as a polishing substance and cuts grooves in the shafts. We have succeeded in eliminating this and other difficulties by a number of suitable measures, and the original few days of continuous operations have been lengthened to months. A reserve pump is added to the 1.5 cbm reactor, and one may expect no interruptions of production for mechanical causes.

Catalyst

Iron from iron oxide obtained on burning iron carbonyl has been used as the catalyst. The iron oxide was pasted with a solution of potassium borate, dried in small lumps, reduced in an excess of hydrogen at 450°C, and the iron produced ground in heavy oil. The particle size is 1 - 5 microns.

The catalyst is used in a proportion of 300 - 400 kg per cbm of the liquid phase. The dispersion medium consists of the high boiling fraction obtained in the synthesis. The activity of the catalyst show no marked decrease after one month of operation . Whenever we had previously observed a dying off of the activity, it had been caused by sulfur in the gas, and became apparent very quickly. This source of difficulties could be completely eliminated by a more perfect purification of the gas.

If the catalyst had deteriorated because of the poor quality of the gas, it can be readily reactivated. This is done by roasting it, re-reducing and re-grinding in oil. In case of need, the process can be repeated many times. This keeps the catalyst costs of the foam process extraordinarily low.

Operations

20 atm pressure was used in all the cases. The gas was used in a proportion of CO : H_2 = 55 : 45. The low N_2 water gas of Oppau, the same as delivered to the butyl plant, was used, with the composition adjusted by the addition of CO. The gas contains only 1 - 2% N_2 and less than 1% CH_4.

Operations were tried at 250, 280 and 300°C. Preliminary experiments have also been run at other temperatures, e.g. 210°C. This latter temperature was condemned because of an insufficient time-space yield.

The amount of the liquid phase increases in amounts in operations below 250°C, and produces a continuous excess, is kept constant at 280°C, and at 280°C it decreases because of a continuous vaporization. In such a case, it must be regularly replenished from the high boiling fraction of the products.

Foam Plates

Foam plates with a sulfate content must be avoided. Plates have heretofore been used of quartz with sintered powdered glass and of width of pores of 0.1 - 0.2 mm. The small sizes have so far been found satisfactory, but large pieces have been found sensitive to thermal shocks. In the future chamotte plates will be used.

Results obtained in the 25 l1 Reactors

Operations have been continued in the 25 l1 reactors over long periods of many weeks with no difficulties. Any interruptions in the production were the results of outside causes, such as leaks in the stuffing boxes, occasional sulfur content of the gas, etc. All these causes are avoidable. No trouble of fundamental nature have been experienced. One may readily realize it, when remembering that the difficulties with iron catalysts are principally the result of the local excess temperatures produced in the gas phase, and their extremely serious consequences, but which can never

happen in the liquid phase. The low gasification and ethane and methane formation, is based on the same grounds. It amounts to less than 5%.

The time-space yield has been found to be better in the liquid phase operations than in the vapor phase, calculated to the compression space. One day yields of 0.2 - 0.3 kg per liter reactor volume have been obtained at 250°C, at 300°C as much as 0.7 - 0.8. With gas circulation a space time yield of 0.8 was obtained at 325°C, calculated to the space occupied by the catalyst, which corresponded to 0.4 kg for the total reactor space.

An industrial unit should be built of about the following dimensions: a vertical cylinder 2.5 m in diameter and 10 m high, which would produce about 4000 te/year at 250°C, and about 10,000 te/year at 300°C.

Over eighty five percent of the gas was converted in the 25 li reactors. It was therefore higher than in the gas circulation, where it remained below 80%. The gas conversion can, however, be made to reach 90, and even 95% by removing the CO_2 from the gas as it leaves the reactor, and where it is present in an amount of 50 - 60%, and returning the purified gas to the reactor. As a result of the low gasification, this gas would contain but little other inert constituents.

Composition and Quality of the Products.

The composition of the raw products can be seen in the table below.

The low gasification and great reduction in the gasol formation in comparison with the gas circulation method for the production of gasoline, are to be noted. The alcohols in the reaction water form about the same proportion of the total production as in the vapor phase operations, and have a similar composition, i.e. they are composed principally of ethanol, with less propanol, a slight amount of butanol, acetone and acetaldehyde.

About 25% of the middle oil produced at 250°C is composed of iso compounds. The hydrogenation number indicates a 60% unsaturated concentration of the middle oil. It is 70% in the 200°C cut, but in the fraction above 300°C it drops to 50% and less. There are in addition some 10% alcohols, and about the same amount of esters, aldehydes and ketones.

The oxygen content of the products obtained at 250°C forms 6% in the gasoline and 4% in the middle oil and paraffin. The so-called paraffin consists principally of oxygenated products, probably waxes.

Uses of the Products

The middle oils may have the following applications:

1) sulfonation to sulfones (detergents)
2) conversion to fatty acids, by Rappe's method (soaps)
3) oxidation to leather acids. (Pfirrmann)

Small scale sulfonation tests of the new middle oils produced fully water soluble products, as if no saturated compounds were at all present in the middle oil. Dr. Haussmann will leave the final decision on this problem until full scale production, and will work on it as soon as our new large reactor is ready. Dr. Bueren has reached the same conclusions working with the synthesis products with a different purpose.

Dr. Jahrstorfer has worked recently on the production of emulsifying wax from paraffin. The paraffin lends itself readily to cracking to a middle oil of a high olefin content.

The gasolines can be readily oxidized to lacquer alcohols and solvents, and practically the whole production can be used for subsequent chemical conversion.

/s/ Michael.

Comparative Data on the Foam Method and of the Products Obtained at Different Temperatures (pressure = 20 atm)

Temperature:	250°C	280°C	300°C
Space-time yield, kg/l catalyst space, per day	0.2 - 0.3	0.5 - 0.6	0.7 - 0.8
Changes in the amount of the liquid phase	Amount increases	Amount remains unchanged	Amount decreases, and must be replenished
Composition of the Products			
% gasol	4 - 6	6	8
%gasoline - 200°C	30 - 40	35 - 50	50 - 55
% middle oil -350°C	32 - 37	28 - 33	30 - 35
% paraffin, +350°C	20 - 30	15 - 20	5 - 10
% alcohols in reaction water	6	6	3
Octane number (research) of the crude gasoline	50	68	78
% olefins in middle oil	abt. 60	abt. 60	as yet unknown
% gasification	5	5	5