

Recirculation

General.

Lurgi introduced recirculation for two main reasons, firstly, because it facilitates the removal of the heat of reaction, and, in particular, makes synthesis easier by preventing the formation of hot spots, and secondly because it distributes the synthesis more evenly over the catalyst bed by decreasing the change in partial pressure of carbon monoxide on passing from the top to the bottom of the catalyst. As a result, recirculation has the effect of increasing the proportion of olefines in the products, of allowing higher temperatures to be used without the occurrence of excessive methane formation, and of increasing the life of the catalyst.

Lurgi's original experiments were done in their own laboratory by enclosing a small compressor and its motor in a gas-tight container and using this as the recirculation pump. But the real tests of the process were done in conjunction with Hoesch-Benzin in one of the full-scale reactors of the Hoesch plant.

When the aim of the synthesis plants was to produce petrol more efficiently, interest centred on recirculation of synthesis gas and this field was developed by Lurgi. But when the aim changed to the production of olefines for the Oxo synthesis, interest changed to recirculation of water-gas. This field, started by Lurgi and Hoesch, was then developed by Hoesch and by Ruhrchemie independently, and at the end of the war the position was that Ruhrchemie had nearly installed all the plant necessary for converting their medium pressure section to work in this way, and Hoesch, who had installed everything necessary for synthesis gas recirculation as advocated by Lurgi, were on the point of starting up this plant for water-gas recirculation. Schaffgotsch were also preparing to change over to recirculation.

Water-Gas Recirculation, Medium Pressure.

Water-gas recirculation requires a higher temperature than synthesis gas recirculation. Lurgi say that the life of the catalyst is uncertain but is probably about the same as for synthesis with synthesis gas without recirculation. This is to be compared with a life of some 3 months for synthesis with water-gas without recirculation.

Both in the case of Hoesch and of Ruhrchemie, although the plant would involve 2 or 3 synthesis stages - 3 at Hoesch - the gas in Stages II and III is too dilute for recirculation in these stages to be sound economically, because the gain in olefines would not be sufficiently big. This recirculation would be confined to Stage I. At Hoesch, an active carbon plant was arranged in the recycle gas stream, and a 1:2 or 1:3 recirculation was to be used.

The gas between the stages is best adjusted by addition of water-gas converted by the water-gas-shift reaction. A proposal had been made to make the adjustment by submitting a part of the residual gas from Stage I to this reaction, because this would have the advantage that any water-gas shift that occurred in the synthesis would be utilized. It was rejected, however, since it would involve having an active carbon plant, under pressure, to remove all hydrocarbons from the gas which was to be treated by the water-gas-shift reaction, and it would also involve carrying this reaction out under pressure.

Ruhrchemie were going to aim at a conversion of $(CO + H_2)$ of 65% in Stage I and the Hoesch plant was to be worked so that some 60% of the total products were formed in Stage I. Details of the proposed method of running at Hoesch, based on pilot plant tests of all stages of the process are given in Table 37.

Table 37.

Proposed Water-Gas Recirculation, Hoesch-Benzin.

Water Gas	46,000 N. cu. m./h.
Recirculation Gas	115,000 N. cu. m./h.
Water-gas rate in Stage I	1,050 N. cu. m./reactor/h.
Contraction	50%
Temperature	200 - 225°C.
Reactors in Stage I	44
II	16
III	8
Olefines in Products	
Spirit	70%
Diesel Oil	50
Heavy Oil	40

It was calculated that the extra olefines made in this way would completely cover the cost of the recirculation - the olefines from Hoesch were to be sold to Ruhrchemie for RM. 380/t. This was not merely a war-time calculation because under peace-time economy the demand for olefines is still high. It should be noted that the olefines produced do not increase the octane number of the lighter products sufficiently to make them into a good petrol. In comparing costs of recirculation with those of straight-through running the power required for the recirculation pumps may be taken as 1/10th of the power required by the main compressors, for a plant working at 10 atm. Hoesch gave the following comparison, see Table 38, between their costs for synthesis without recirculation and the estimated costs for recirculation. The calculations were made in 1940.

Table 38.

Comparison of Costs for Recirculation
with those for Normal Synthesis

	With Recirculation	Without Recirculation
Production of Primary Products	55,000 t./year	55,000 t./year
Wages and Salaries	1.90 Rpfg./kg.	1.77 Rpfg./kg.
Power, from outside	1.31	0.67
Coke	8.20	8.20
Water	0.47	0.30
Catalyst	1.23	1.86
Capital Charges	8.50	8.50
Working Materials	1.10	1.10
Taxes	0.50	0.50
Total Cost	23.21	22.90

All the proposals and estimates considered up to now were for synthesis with the ordinary cobalt catalyst as now used, but some years ago Lurgi developed special diluted cobalt catalysts for use for medium pressure synthesis with recirculation.

they were found to be poor for straight-through running but were very good with recirculation, dilution of the catalyst resulting in the formation of little wax and a large proportion of benzine, and the recirculation increasing the olefine content of the benzine to 60% and allowing higher temperatures to be used without excessive methane formation.

Ruhrchemie tested one of these catalysts, supplied by Lurgi, in a large-scale reactor. It contained 400 parts kieselguhr per 100 parts cobalt, was in the form of threads and had a good mechanical strength. It was tested at medium pressure and 215 - 225°C., i.e., some 15° higher than the temperature used for a normal catalyst, and gave the same output of products per reactor per hour as a normal catalyst, the products containing 60 - 70% benzine. It was easier to start up and to run than ordinary catalysts, and in spite of the higher temperature it gave less deposition of carbon. It must be remembered, however, that this test, like all Ruhrchemie tests, was done at the standard space velocity, and since the diluted catalyst was a very light one, it corresponded to several litres/g. Co/h. The results therefore were extremely good when judged on this basis.

Lurgi gave the following results for a catalyst of the composition Co 100: ThO₂ 5: MgO 10; kieselguhr 600. For synthesis at 7 atm. pressure, 223°C., space velocity 100 vols./vol. catalyst/h. and recirculation ratio 4:1, the contraction was 76% and the yield of products, including gasol, 120g./N.cu.m. ideal Gas. The course of the synthesis is shown by the gas analyses in Table 39.

Table 39.

Synthesis with Lurgi Diluted Cobalt Catalyst

	Water-Gas	Water-Gas and recycle gas	Residual Gas
CO ₂	2.1	5.2	6.1
C _n H _m	-	0.2	0.3
CO	38.7	44.2	45.1
H ₂	51.0	26.4	21.3
CH ₄	0.3	4.7	5.8
N ₂	7.8	19.1	21.6

If two stages were added, worked without recirculation but with the addition of converted water-gas before each, the specific yield would be increased to 155 g., of which 135 g. would be liquid of the composition shown in Table 40.

Table 40.

Composition of Liquid Products from Water-gas
Recirculation with Lurgi Diluted Cobalt Catalyst

Boiling Range	Percentage of Total Liquid Product	Olefine Content %
- 200°C.	58	60
200 - 320°C.	30	45
320 - °C.	12	

Synthesis Gas Recirculation, Medium Pressure.

Hoesch gave the following particulars of a recirculation experiment conducted by them and Lurgi in a full-scale reactor: - A standard Ruhrchemie mixed catalyst was used with a gas rate of 1,000 cu.m./reactor/h., which was decreased to 800 cu.m. in 3 to 4 months, the temperature being increased from 200 to 215°C. during this period. A pressure of 7 atm. and a recirculation ratio of 2 was used. The best yield was 116 - 117 g./cu.m., including gasol, and this fell to 113 g. at the end of the experiment. There was no deposition of carbon and the reactor was discharged easily.

In another similar trial lasting 8 months with very little deterioration, the temperature was kept constant at 195°C. for 5 months, and then at about 200°C. for the next 3 months. It is estimated from this that the effective catalyst life would be about a year.

Earlier failure of Ruhrchemie to repeat the good results claimed by Lurgi was probably due to the fact that, at that time, Lurgi's catalyst was a more active one than Ruhrchemie's. The present position is that Ruhrchemie

consider that the extra cost involved in synthesis gas recirculation is not covered by the small improvement effected in the synthesis. Hoesch agree with this, but Lurgi do not, and they emphasize in particular the high yield per reactor obtained by recirculation, and the increase in the octane number of the primary motor spirit from 45 to 55.

Synthesis Gas Recirculation, Atmospheric Pressure.

This was investigated by Brabag both in single full-scale reactors and finally in a complete section of their plant, in both cases the recirculating gas being passed through an active carbon plant to remove hydrocarbon gases before it was passed back into the reactors. They first showed that the contraction is almost independent of the recirculation ratio, and also that it responds to changes in gas throughput in the same way as if no recirculation were being used. This is shown in Table 41.

Table 41.

Recirculation at Atmospheric Pressure

Gas Rate, N. cu. m./h.	Recirculation Ratio	Contraction %
1,000	3.21	43.4
	2.34	44.5
	1.45	45.3
500	3.50	61.4

A comparison of the performance of a full-scale reactor running with recirculation with that of another without recirculation was then made, and it showed that although recirculation did not diminish the production of methane it increased the conversion and hence the yield of liquid products for the same total gas throughput. Details are given in Table 42.

Table 42.

Recirculation at Atmospheric Pressure
in One Full-scale Reactor

	Without Recirculation	With Recirculation
Recirculation Ratio	-	0.41
Time, hours	2,684	2,679
Revivifications, Solvent	-	1
Hydrogen	4	4
Average Conditions and Performance		
Temperature, °C.	185.3	186.1
Gas-rate, N.cu.m./t.Co/h.	1,116	1,178
Conversion of CO, % U _{CO}	60.5	78.4
Methane, as % of CO converted	17.1	16.8
CO ₂ " " "	6.7	8.4
Yield of Liquid Products, t./day/t.Co	2.02	2.38

The whole of the plant Schwarzheide-I was then run with recirculation and the performance compared with that of Schwarzheide-II which was worked in the normal way without recirculation. Keeping the gas rate at the normal value, 900 N.cu.m./t.Co/h., the pumps available could only give a recirculation ratio of 0.27, but even with this the methane formation decreased from 12 to 10% of the CO reacting, the CO₂ formed remained the same, the conversion of CO, U_{CO} increased from 78 to 84% and the production of liquid CO₂ products increased from 2.19 to 2.36 t./day/t. cobalt. The gas throughput was then decreased to 700 - 760 N.cu.m./h. and the recirculation increased to 0.41. The yield and the CO conversion were bigger than before, the production/day/t. cobalt rather less, as would be expected, but the formation of CO₂ decreased from 7.5 to 4.5 - 5.5%. The specific yield was about the same as would have been obtained by 2-stage working, being some 124 - 126 g. liquid products/cu.m. ideal gas. On account of the smaller gas formation the residual gas was very suitable for use in a second stage.

Recirculation favours the production of products of lower molecular weight, the amounts of gasol and of C₆ - C₁₀ hydrocarbons being increased. The olefine content of the products is also increased. The amount of catalyst wax is decreased to a quarter of its normal value, and as a result, the number of reactivation treatments with hydrogen or solvent is correspondingly decreased. The saving effected by this and by the increased production of products must be weighed against the cost of the extra power required for the recirculation. No data for this are available.