

FILM STUDY GROUP

REPORT

T.O.M. REEL NO. 28

Prepared by

STANDARD OIL DEVELOPMENT COMPANY

Comments on Reel 28

Page 270 (From the beginning of the reel to Item 29)

A list of flow sheets which are given in the index to this reel covering preparation of butanediol, butadiene fractionation, and the production of iso-octane from isobutyl alcohol.

Item 24

Gives a flow sheet for the polymerization of isobutylene and fractionation of the polymers.

Items 25-29

Include flow sheets for the hydrogenation of di-isobutylene.

Items 50-58

These items include flow sheets and material balances for the production of butadiene from butane by chlorination and dehydrochlorination. These flow sheets are only of minor interest to the oil industry but are included for those who might be interested.

Items 59-62

These items give flow sheets for the polymerization of butadiene to make buna-D which is a polymer of butadiene alone.

Items 63-69

These items give flow sheets for the preparation of oppanol (Vistanex). The titles of the flow sheets involved are as follows:

- Flowsheet of Oppanol plant
- Details of polymerization reactors
- Flowsheet for ethylene drying
- Piping for polymerization reactors
- Flowsheet for ethylene refrigeration system
- Preparation of oppanol emulsion
- Preparation of oppanol emulsion

Items 70-75

Flow sheets on the recovery of chlorine from HCL by oxidation.

Items 92-96

~~Six flow sheets on the preparation of polymer oils from ethylene.~~
The titles of the flow sheets are as follows:

- a. Detail flowsheet, Part I (polymerization, catalyst separation)
- b. Detail flowsheet, Part II ($AlCl_3$ complex decomposition)
- c. Detail flowsheet, Part III (final oil refining and methanol recovery)
- d. Detail flowsheet, Part IV (gas recovery)
- e. Detail flowsheet, Part V (blending of ester oils and final clay treating)

Items 97-102

These items give the material balances and flow sheets on the manufacture of iso-octane from normal butane involving the isomerization of 1/2 of the butane to isobutane and the conversion of the other 1/2 of butane to normal butenes by chlorination and dehydrochlorination and the alkylation of the two to make iso-octane. The titles of the various items are as follows:

- a. Material balance
- b. Material balance
- c. Butane isomerization
- d. Proposed flowsheet for dehydrochlorination
- e. Proposed flowsheet for alkylation of Blechhammer stock.
- f. Alternate proposal for alkylation of Blechhammer stock.

Item 107

General chlorination schemes at Heyderbrack for preparation of propylene, isobutylene and butadiene.

Items 108-111

These items give general flow sheets for the manufacture of 20,000 tons per year of iso-octane from butane by isomerization of part of the butane to make isobutane and by chlorination-dehydrochlorination of the rest of the butane to make butene and the alkylation of the C_4 hydrocarbons to make iso-octane; there follows three flow sheets giving details of this process.

Items 120-121

Material balance flow sheets for the manufacture of BF_3 from (a) fused boric acid and (b) metaboric acid followed by a detailed flow sheet for process.

Item 2

1943 report on the removal of CO with ammoniacal copper carbonate solution in which the cuprous content is 1.4 mols per liter and in which the cupric content is 0.2 mols per liter and the extraction is carried out at 20-25°C.

Pages 21-223

Pages 21-223 are a series of reports by the I.G. at conferences held during the period 1940-1942. Beginning page 21-72 there is a June 24-25, 1940 report on the following subjects:

- a. Isomerization
- b. Dehydrogenation
- c. Alkylation
- d. Neohexane
- e. Aromatization
- f. Poly benzines

A four page review of this topic, prepared by California Research Corporation follows page 6 of these comments.

The index of the subject matter covered in this section is given on page 22. On pages 28-33 in this section there is given some interesting information on the preparation of neohexane. For example, it is stated that by thermal alkylation of isobutane with ethylene at 175 atmospheres pressure, a yield of 80% of gasoline having an octane number of 78 (mm) is produced which fraction consists of 40% neohexane and the balance of which has an octane number of 72 (mm).

Beginning on page 73-97 there is a March 16-17, 1942 report on butane dehydrogenation, butylene concentration, isomerization, alkylation, and polymer gasoline. The contents of this report are given in the index on page 75.

Beginning on page 98, January 4-1941, there is a report on the following subjects:

- a. Alkylation with sulfuric acid.
- b. Isomerization of normal butane with aluminum chloride.
- c. Alkylation of isobutane with propylene in the presence of $\text{BF}_3\text{-HF}$ or $\text{BF}_3\text{-H}_2\text{O}$.
- d. Alkylation of isobutane with ethylene using $\text{BF}_3\text{-H}_2\text{O}$ or $\text{BF}_3\text{-HF}$ as a catalyst.
- e. Aromatization of normal paraffins.
- f. Polymer gasoline
- g. Dehydrogenation of butane and propane.

In this section there is included on pages 107-108 the effect of various promoters on the BF_3 catalyst involved.

Page 110

Gives a table showing the results on aromatization of low octane number gasolines in which the octane number is increased from 12 and 26 to approximately 74 and 70 over aluminum oxide-chloric oxide catalyst with the aromatic content of the product around 60%.

Pages 116-170

Beginning on this page there is a January 29-30, 1941 report on the following subjects:

- a. Catalytic dehydrogenation
- b. Alkylation
- c. Acid polymerization.
- d. Isomerization
- e. Polymer gasoline.

The contents of this report are given on pages 117-118. On page 169 of this report some information is given on the concentration of olefins using the 50% solution of silver nitrate which is discussed in greater details in other films.

Pages 171-223

These pages are a repeat of pages 116-169 and are to be ignored.

Pages 226-249

(April, 1941) Report on the analysis of the product obtained from the alkylation of the isobutane with butenes or propylene. In the summary of this report on pages 15-16 the authors state 1) the alkylation of isobutane with propylene using sulfuric acid does not produce triptane, 2) the alkylation of isobutane with normal butenes does not give the expected iso-octane but instead the unexpected trimethyl pentanes. In the alkylation of isobutane with butenes, the highest octane number is obtained with butenes-2 (MM96), a medium one with butene-1 (MM93.5) and the lowest with isobutene (MM91), 5) Increase of the reaction temperature (to 220°C.) when working with n-butene-2 effects not only considerably lowering of yields but also octane number, 6) isobutylene is considerably superior to normal butylene in yield, gasoline fraction, and octane number.

Pages 250-266

July 28, 1943 report on the isomerization of normal butane with aluminum chloride and an aluminum chloride containing catalyst. A summary of the results obtained is given on pages 254- and 265-266. Among the conclusions drawn are 1) that the aluminum chloride supported on a catalyst (aluminum oxide is used in this work) gives higher yields but has a shorter life and also results in more cracking reactions, 2) sublimed aluminum chloride is preferable to technical aluminum chloride.

Pages 274-284

This gives a discussion of the methods of preparation of the catalyst and methods for the analysis of its constituents.

Patent Memoranda

Page 290

1. Separation of straight and branched chain high molecular weight fatty acids from each other by extraction of the iso acids with methyl formate and butanone.

Page 292

2. Selective hydrogenation of acetylene in its mixtures with ethylene and hydrogen containing gases by catalytic hydrogenation with nickel catalyst in the presence of small amounts of metal carbonyls. If CO is present the latter is not necessary.

Page 299

3. Recovery of osmium from reaction processes in which osmium tetroxide is used, e.g., for the reaction of peroxides with allyl alcohols and for the addition of hydroxyl groups to double bonds.

Page 301

4. Use of condensation product of mixture of alcohols that result from Oxo synthesis with ethylene oxide in the form of a water emulsion as a water soluble textile oil.

Page 307

5. Pretreatment of gel (used as a carrier for cobalt catalyst in synthesis process) at 700-1100°.

Page 309

6. Preparation of active titanium oxide gels.

Pages 317-319

7. Preparation of highly dispersed aluminum oxide.

Page 323

8. Preparation of propylene chlorhydrin by the hydration of allyl chloride in the presence of 84% sulfuric acid at a temperature of 25°C.

Pages 331-334

9. Use of pure magnesium biphosphoric as a catalyst in place of UOP catalyst. The composition of this catalyst is given on pages 333 and 334.

Page 339

10. Use of olefins containing a tertiary or quaternary carbon atom in Oxo reaction to produce aldehydes.

Page 341

11. Chlorbutanes from normal butylene and HCL without catalyst at room temperature and 30 atmospheres of HCL.

Page 343

12. Preparation of zirconium oxide gels (pH6-8).

Page 345

13. Promotion of catalysts that contain metals that form carbonyls (used for converting lower olefins to higher alcohols by the Oxo process, with heavy metals from groups 1 and 5 or 6.

Page 347

14. Dehydrogenation of propylene to allene.

Page 349

15. Preparation of solid polymers from ethylene using aluminum chloride containing small amounts of aluminum powder.

Page 352

16. Addition of calcium chloride to fused iron catalyst to obtain a catalyst having reduced temperature sensitivity.

Page 354

17. Preparation of water soluble zirconium oxide catalyst. This list of patent memoranda has been selected from those given in the reel as being of possible interest to the industry. It is to be emphasized that these are merely patent memoranda and not patent applications.

Pages 358-360

Removal of diolefins from olefin gases by selective hydrogenation of the former to the corresponding olefins after the gases have been passed through a filter to remove impurities.

Pages 362-373

A series of reports which deal with the production of iso-octane from butane by a process involving isomerization of the normal butane to make isobutane, chlorination and dechlorination of the isobutane to make isobutylene, polymerization of the latter to make dimer and ~~hydrogenation of the dimer to iso-octane.~~ Pages 362-368 describe the whole process and include flow sheets thereof. Pages 371-373 list the equipment required to produce isobutylene from 5,000 tons per year of isobutane by chlorination and dehydrochlorination.

Pages 374-380

~~Costs, steel requirements and utilities for iso-octane process described above.~~

Pages 381-416

Comparative costs of preparation of isobutylene by catalytic dehydrogenation of isobutane and by chlorination and dehydrochlorination of isobutane.

I.

Isomerization of Gaseous Hydrocarbons

Summarized Report: Dr. Pohl

In Leuna the isomerization of n-butane is carried out in two directions:

A. Isomerization of n-butane under hydrogen pressure with tungsten catalysts

B. Isomerization with aluminum chloride under lower pressures

A. Isomerization of n-butane with tungsten sulphide

Further attempts were made in systematic catalyst research and development of the operating conditions.

Catalyst research has definitely showed that WS_2 produces the best isomerization. On the basis of this discovery the operating conditions alone remained to be improved. By limiting the temperature range to $400-415^\circ$ and increasing the partial pressure of the H_2 (to about 40 atm. for a total pressure of 200 atm.), in contrast to previous operation, an average conversion of 30-40% with an i-butane yield of 85-90% could be obtained without any noticeable drop for periods exceeding 5 months. Experiments were made on a 100 cc scale. Operation on a large scale should not present any unsurmountable difficulties.

The isomerization experiments at 700 atm. were less favorable than those at 200 atm.

Experiments at 100 and 50 atm. total pressure have given the same satisfactory results as those carried out at 200 atm. Experiments are conducted at present with respect to the life of the catalyst, when these pressures are applied.

The experiments seem to disclose in a general direction that it is better to operate at a lower total pressure and to select the partial pressure of the hydrogen as high as possible.

B. Isomerization of n-butane with $AlCl_3$

Isomerization with $AlCl_3$ was thoroughly studied in the liquid and in the gaseous phase. In order to establish the most favorable operating conditions the influence of temperature, partial pressure of HCl, duration, olefin and H_2O content in the initial material were studied. From a technical point of view a substantial improvement was obtained by placing the $AlCl_3$ in a contact zone filled with glass beads (Raschig Rings) and heating with steam. The $AlCl_3$ -double compounds formed in the isomerization reaction and having a high catalytic action coat the glass beads with a thin film, and after losing their activity through gum formation may be withdrawn from below. By this arrangement an $AlCl_3$ consumption of 1% could be obtained, referred to the i-butane formed. By introducing fresh $AlCl_3$ this method of operation can be rendered continuous. Experiments were made both in the liquid and in the gaseous phase. The optimum operating temperature is 100° . The experiments, which are not yet completed, essentially deal with the establishment of the optimum partial pressure of HCl, the charging capacity, and the best dimension of the catalyst chamber with respect to the $AlCl_3$ consumption. The gas phase equipment in Leuna has operated for months without trouble, while operation in liquid phase still requires the elimination of certain deficiencies in the apparatus. For initiating the reaction it is of advantage to start with an olefin-containing gas in order to accelerate the formation of the aluminum chloride double compound. The crude butane was at first entirely dried by treatment with sulfuric acid, but later it was found that the presence of a trace of water was of advantage, presumably due to the formation of HCl; the partial pressure of HCl is about 10-20%.

Operation in the gaseous phase is conducted at 7-15 atm. at about $100^\circ C$. The space velocity is 0.25, the conversion is 40-50% and the yield of i-butane reaches 90-95%. The charging capacity is better at higher pressure. The reaction tube consisted of iron; no corrosion was observed. Length of the tube 2m, diameter 45 mm. The dimension of the catalyst chamber is still being investigated since the catalyst was not yet entirely exhausted (the catalytic sludge was still active).

A semi-industrial apparatus designed for a throughput of 40 kg of butane per hour is being constructed in Leuna.

In contrast to the isomerization with tungsten sulfide, no hydrocarbons with 0-2 C-atoms are formed in the operation with $AlCl_3$. The quantities of propane formed by cracking of the iso-butene amount to 5% of the input; high boiling isomeric hydrocarbons are also formed (about 3% of the input).

Hantge reports on isomerization experiments conducted in Oppau. Tests were only made in autoclaves and the results do not exceed those obtained in Leuna. The $AlCl_3$ consumption in these experiments was not below 5%.

Ringer asks if other hydrocarbons have been selected for isomerization, in addition to butane. Above all, the molecular size of the n-paraffins should be established at which a limit is set for their isomerization. American workers are investigating this field with respect to aviation gasoline. The isomerization of pentane, hexane, and heptane should also be investigated by us because this problem may become of importance, should our interest be directed toward the lube oil range. The problem of isomerizing the lower boiling fractions of Fischer gasoline is also important.

Bahr reports on experiments in this connection which were carried out on Fischer fractions with tungsten sulfide at $400^\circ C$ under high pressure for the purpose of improving the octane number. Cracking increases for higher hydrocarbons and the most difficult fractions to treat were the Fischer fractions boiling from $150-180^\circ$.

Pohl points out that the activity of the $AlCl_3$ can be increased by small quantities of additives (e.g. $SiCl_4$).

In summary Ringer states that isomerization with tungsten sulfide has reached the point of maturity from a technical point of view, but that experiments must be continued in the direction of using lower pressures which, on the basis of previous work, may be considered promising. 85% yields may be counted upon.

The isomerization experiments with $AlCl_3$ on a small scale have yielded good results with butane and the yields are apparently somewhat higher than with tungsten sulfide. The losses in $AlCl_3$ sludge, which are now as low as about 1%, can not be considered to be a deciding factor in the calculation of the process. Since this process is to be tried on a semi-industrial scale in Leuna, the two processes will soon become comparable. Oppau is continuing their autoclave experiments so that their work is no duplication.

A secondary problem is the isomerization of pentane and hexane. The patent situation is being investigated for Germany as well as for Europe.