

RESEARCH ON THE UTILIZATION OF THE BY-PRODUCTS OF HUNGARIAN ETHYLENE PRODUCTION

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The pyrolysis of naphtha was subject of some research at the Department of Chemical Technology as early as in the fifties. By that time, laboratory work on catalytic pyrolysis was focused on yields and properties of the liquid aromatic hydrocarbons, yields of ethylene were of secondary importance [1].

When the implementation of the commercial manufacture of ethylene in Hungary was proposed, the problems of by-products utilization demanded attention. Since then this Department has been at work on the technology of ethylene production, and since the pyrolysis operation plant of the Tisza Chemical Combine (TVK) started, it has been busy with given problems emerging at the processing plant.

Our research work took two principal directions. 1. Laboratory pyrolysis experiments aimed at determining the effect of experimental conditions on the amount of liquid hydrocarbons, i. e. of the so-called pyrolysis oil. Plotted as a function of temperature, and of space velocity, the yields of pyrolysis oil gave minimum curves; this finding has been duly explained [2]. 2. Samples of pyrolysis gasolines from pilot plants, and from processing plants, in Hungary and abroad, were collected: their composition, and possibilities of their use have been studied. Results on samples from Most (Czechoslovakia), Burgas (Bulgaria), and the MAFKI pilot plant (Hungary) showed high percentages of valuable aromatics, and also substantial amounts of unsaturated hydrocarbons, viz. mono-, and di-olefins, in conformity with literature data. These tend to form resinous substances, making the pyrolysis oils unsuitable for direct use. After pyrolysis of naphtha had been started at TVK in Hungary, we studied the pyrolysis gasolines there produced.

Utilization of pyrolysis gasoline

Among liquid products of pyrolysis, the pyrolysis gasoline can be used in several ways. Either it can be refined, and then added to motor fuels, or it can be used to the manufacture of resins, but this involves further unsolved

problems. Best economic results are achieved by the separation of the valuable aromatics, i. e. benzene, toluene, xylenes, from pyrolysis gasoline, though this way of utilization demands the greatest investments [3, 4].

Pyrolysis gasoline can be refined in several ways. Our previous experiments with sulphuric acid, and with vapour-phase clay treatment were in fair agreement both technologically and economically with data published in the literature, thus we concluded that at TVK no plant either for the sulphuric acid method or for clay treatment should be built [5].

Refining of pyrolysis gasoline by hydrogenation

Hydrogenation, a method likely to be superior to those mentioned above, can be carried out either in one step or in two steps. In a protracted series of laboratory experiments hydrogenation in one step was found to be the simplest solution. In this process only compounds which tend to form polymers, viz. the di-olefins, get saturated, while aromatics and mono-olefins remain unaffected. The product of this one-step liquid-phase hydrogenation is a very valuable component in motor gasolines. Hydrogenation optimization studies involved the effect of temperature, pressure, space-velocity, change of liquid to vapour ratio, on palladium and on nickel-containing catalysts. Further calculations concerned the process economics of this hydrogenation because it was thought likely that the yearly 25 000 metric tons of pyrolysis gasoline produced by TVK might be advantageously utilized in this way. Following our proposals, TVK invited tenders for this hydrogenation process, from several firms, without tangible results.

Resin -manufacture, the other way to utilize pyrolysis gasolines

This must be preceded by distillation, the di-olefin contents of the so-called resin cut, i. e. the part distilling between 120 and 190°C, being polymerizable. This problem has been more intensively studied by the research institutes MAFKI, and MÜKI. Our department studied the possible utilization of the polymerization residue, and of other unutilized fractions.

The polymerization residue, the so-called monomer-free solvent naphtha, is, after appropriate refining, a good solvent for varnishes. Various methods of refining have been tested, such as refining with sulphuric acid, clay treatment, and hydrogenation: the best products were obtained by two-step hydrogenation. Experts in, e. g. the varnish plant of the TVK found these refined monomer-free solvent naphthas quite suitable for use.

The first distillate, i. e. that obtained up to 120°C is also a problem as far as its utilization is concerned. This so-called light aromatic cut, or BT-

fraction, is composed mainly of benzene and toluene; thus it might furnish the raw material for an aromatics extraction process, further it might be used as an additive to motor fuel in order to improve octane ratings. Of course, preliminary refining is needed in both cases: di-olefins, and, in the case of aromatic extraction, also mono-olefins must be removed or hydrogenated. Laboratory experiments on refining by sulphuric acid treatment covered one-step, and two-step hydrogenation. Hydrogenation proved to be best; the light aromatic fraction was found to be a very good feedstock for the production of benzene and toluene. Also tests on octane-ratings furnished good results. After the saturation of di-olefins by one-step hydrogenation, the octane-number of the product was 98, thus, this raffinate was suitable for improving octane-numbers.

Since these possibilities could not yet be realized commercially, as an interim solution we suggested this pyrolysis gasoline to be transported to the Nyírbogdány Petroleum Co. where the cuts up to 140 or 150°C are recovered by normal-pressure distillation; the residue is used as fuel. The distillate is first refined by sulphuric acid treatment, then it is neutralized, clarified, and admixed with an inhibitor. Due to its high aromatics content, the product thus obtained is a very good motor fuel additive. Recently, the refining with sulphuric acid has been substituted by clay treatment. These ways of utilization could be realized without capital investment because they did not require special distillation plant nor refinery equipment. This is, however, not to consider the problem of the utilization of pyrolysis gasoline as definitively solved, perspectively hydrogenation is certainly more profitable.

Treatment of pyrolysis process waste waters

Another serious problem of the TVK pyrolysis process plant is the disposal of waste waters. Already at project and design level, as we got to study the technology adopted, we have directed attention to the danger of emulsification. In this we have been proved right: in trial runs a rather stable oil-in-water waste was produced. The formation of this phase was due to direct cooling in counter-current with water in the "foam column." In consultation with works staff the common view emerged that a modification of the flow-pattern in the column, and addition of an active substance to the water in the circulation coolers would reduce emulsification without changing the technology. It would, however, be preferable to establish a two-grade cooling system, cooling first the pyro-gas to about 100°C with wash-oil, followed by indirect cooling. Thus the separation of heavy and light tars would have been accomplished, and the formation of an emulsion prevented. As our suggestions could not be adopted, our further task consisted in studying the

effluents and in devising some method to break the emulsion. Three directions of study were followed, viz.

1. testing the effects of pH, soluble additives, and demulsifying agents;
2. clarification (flocculation) by chemical treatment of the emulsion;
3. breaking the emulsion in a column with a special packing.

The emulsion in question proved to be quite sensitive to mineral acid, to alkali, and to salts; much of the emulsified pyrolysis gasoline separated in the form of a flaky precipitate; higher temperatures accelerated this precipitation. Among the various water-treatment demulsifiers a Hungarian product, Demulkorr-3170, proved to be suitable; process experiments with it were proposed.

Concerning clarification by chemical treatment we found that iron(III)-, and aluminium(III)-salts producing in a hydrolysis at pH 8 flaky precipitates of great specific surface are efficient in adsorbing tars from water. 200 mg per litre of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at 20°C and pH 8, proved sufficient to clarify the waste water samples collected in the TVK-plant. Following our suggestions and report, a clarification pilot plant is being designed for the TVK site.

Several series of experiments were devoted to the possibility of breaking the emulsion in question in a packed column. The packing used consisted of a uniform 1 : 1 mixture of two substances, of the same particle size, with different electrode potentials. First, breaking of a synthetic model emulsion on a packing made up from iron — charcoal grains of 2 to 3 mm diameters was tested at various temperatures, pH-values, and residence times. In our laboratory apparatus, treatment on this packing proved suitable with waste water samples from the circulation loop. Further experiments are in progress, preparations for pilot tests in the process plant have been started.

Drying of pyrolysis gas

This also was one of the problems posed by the ethylene production at TVK. Early 1967, we suggested to the constructors Petrolber Co. that, instead of drying as originally designed, the removal of water should be effected by molecular sieves. At present, one of the two drying-adsorbers is packed with active alumina (made by Péchiney), the other half with alumogel and half with a Soviet zeolite-type molecular sieve. The drying effect is good, adjustment to the prescribed dew point is satisfactory. There is one drawback, however, namely that the adsorbers need frequent regeneration since the water-adsorbing capacity of the packings is not sufficiently known. In our experimental pyrogas-drying apparatus water-adsorbing capacity, useful life, load, lowest possible dew point for several kinds of aluminas and zeolites are being studied. Our design served as basis for the establishment of a three-

column adsorption battery in the TVK pyrogas separation plant. The first trial runs have been accomplished; in order to compare the adsorbents available, further experiments are in progress, as scheduled.

The problem of drying the pyrolysis gas raised that of the mechanical strength of the drying adsorbents. Abrasion studies have shown French alumina to be the most suitable, followed by zeolites from the USSR. Alumina from Almásfüzitő showed the highest abrasion loss.

It is known that the fourth Five-Year Plan involves establishment and launching of an olefin works ten times the present pyrolysis plant. Perhaps it is partly due to the work of this Department that the necessity of the hydrogenation of by-product pyrolysis gasolines has been recognized: a single-step hydrogenation unit will integrate the ethylene production plant.

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Summary

Problems of the utilization of Hungarian ethylene by-products are discussed. It has been established that the most simple way to utilize the gasoline resulting from the pyrolysis is to use it, after a single-step liquid phase hydrogenation, as high-quality motor fuel blending component. Refining and utilization of the distillata obtained by pyrolysis and suitable to resin production have also been studied. Several methods have been used for testing the treatment of waste water from the pyrolysis unit and at using ferrous-sulphate heptahydrate has been found to be the most advantageous.

Finally, some results concerning the drying of pyrolysis gas by means of molecular sieves are discussed.

References

1. SIKLÓS, P.: *Acta Chimica Hung.* **36**, 197 (1963).
2. VAJTA, L.—SIKLÓS, P.—POZSGAI, T.: *Periodica Polytechnica. Chem. Eng.* **9**, 145 (1965).
3. VAJTA, L.—SIKLÓS, P.: *Magyar Kémikusok Lapja* **21**, 395 (1966).
4. VAJTA, L.—SIKLÓS, P.: *Magyar Kémikusok Lapja* **21**, 441 (1966).
5. VAJTA, L.—KÁROLYI, J.—SIKLÓS, P.—SZEKENYI, I.—NEUMANN, E.: *Periodica Polytechnica, Chem. Eng.* **9**, 161 (1965).

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