

ALIPHATIC DICARBOXYLIC ACIDS FROM OIL SHALE ORGANIC MATTER – HISTORIC REVIEW

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Abstract. *This paper gives a historic overview of the innovation activities in the former Soviet Union, including the Estonian SSR, in the direct chemical processing of organic matter concentrates of Estonian oil shale kukersite (kukersite) as well as other sapropelites. The overview sheds light on the laboratory experiments started in the 1950s and subsequent extensive, triple-shift work on a pilot scale on nitric acid, to produce individual dicarboxylic acids from succinic to sebacic acids, their dimethyl esters or mixtures in the 1980s.*

Keywords: *dicarboxylic acids, nitric acid oxidation, plant growth stimulator, Estonian oil shale kukersite, Krasava oil shale, Budagovo sapropelite.*

1. Introduction

According to the National Development Plan for the Use of Oil Shale 2016–2030 [1], the oil shale industry in Estonia will consume 28 or 9.1 million tons of oil shale in the years to come in a “rational manner”, which in today’s context means the production of power, oil and gas. This article discusses the reasonability to produce aliphatic dicarboxylic acids and plant growth stimulators from oil shale organic matter concentrates. The technology to produce said acids and plant growth stimulators was developed by Estonian researchers in the early 1950s, bearing in mind the economic interests and situation of the Soviet Union. The new technology was subjected to laboratory tests at the laboratory of high-molecular compounds of the Institute of Chemistry of the Estonian SSR Academy of Sciences (Institute of Chemistry), as well as to pilot tests at Kiviõli Oil Shale Chemical Integrated Plant (Kiviõli Plant) and, on a continuous basis, at the Experimental Works of the Estonian SSR Academy of Sciences (Experimental Works). There was a plan to build a commercial experimental plant

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in Kohtla-Järve, Estonia for production of dibasic acids, with a payback period less than a year, but, due to political changes in the Soviet Union in the early 1990s, it was never realized.

In Soviet times, the oil shale industry in Estonia was influenced by the development of the oil and gas industry in the other parts of the country, Siberia particularly. Earlier, before large-scale oil and natural gas extraction was launched, it was profitable to produce oil and gas from sapropelite fuels – oil shale and sapropelic coal. Later, starting from the 1960s, the techniques using said fuels were abandoned in the Soviet Union in favour of natural gas. For example, after taking into use Siberia's cheap natural gas, chamber ovens at V. I. Lenin Kohtla-Järve Oil Shale Processing Complex (Kohtla-Järve Complex), which had mainly produced oil shale gas for the city of Leningrad (St. Petersburg), were closed down.

In the USSR, there were five-year plans for the development of the national economy that all Soviet republics had to fulfill. While oil shale industries in free economies in the rest of the world were losing their importance, this was not the case in the planned economy of the Estonian SSR. So, it was mainly due to this that after restoring its independence in 1991, Estonia still remained a country with the most developed oil shale industry in the world. Today, due to the rise in oil prices, oil shale has not lost its attractiveness in the world. At the same time, the crises that have been caused by the drops in oil prices have repeatedly raised the question of the competitiveness of oil shale industry. The development of the partly state-owned oil shale industry in Estonia can be slowed down, if needed, or stimulated by taxation.

Low global oil prices triggered a crisis in the oil shale sphere and favoured the co-production of shale oil and power. In addition, new markets were searched for the products of oil shale thermal treatment products such as phenols, the most characteristic compounds of Estonian oil shale kukersite (kukersite) processing. Methylresorcinols, one of the representatives of phenols, have found application in the cosmetic industry, for example. Being all distinctive products of kukersite thermal processing, methylresorcinols as well as oil alkanes and alkenes provide important information about the nature and unique properties of its organic matter as a raw material for the chemical industry.

2. Thermal destruction vs oxidizing destruction

Preliminary data about the highly polymeric organic material of kukersite was obtained from its elemental analysis. Oil shale organic matter of sapropelic origin differs from that of humite coals in hydrogen and oxygen contents. After the determination of alkanes, alkenes and long-side-chain alkylresorcinols in semicoking oil, researchers, including Klesment [2], found that only small amounts of phenols were formed by thermal decom-

position of most sapropelites, except kukersite. When establishing the structural formula of kukersite organic matter, Lille [3] suggested that phenols in the retort oil resulted mainly from the thermal conversion of alkyl-1,3-benzenediol units originally present in kerogen. However, the established formula differed from that based on *n*-alkyl-1,3-benzenediols put forward earlier by Blokker et al. [4]. Sun et al. [5] found these phenols to be characteristic of most Ordovician petroleum source rocks formed by the marine colonial microorganism *Gloeocapsomorpha prisca* as kukersite.

It is to be mentioned that alkylresorcinols are relatively rare in nature, they are found in molluscs and some species of bacteria. *Gloeocapsomorpha prisca* microfossils belong, for example, to the phylum of cyanobacteria. Based on the chemical analysis conducted by Aarna and Lippmaa [6], kukersite organic carbon is composed of aromatic cycles (19%), naphthenic cycles (50–75%) and paraffinic chains (6–31%). Nuclear magnetic resonance spectroscopy (NMR) tests demonstrated the importance of the aromatic structural elements in kukersite organic matter [7]. Aromatic compounds could partly arise from aliphatic structural elements during semi-coking at temperatures of 500–550 °C.

There is another way to study the structure of high-polymer organic matter – low-temperature oxidizing destruction using potassium permanganate, nitric acid or any other oxidizing agent. Kogerman applied Bone's severe coal organic matter oxidation method when studying in 1919–1921 at the Royal College of Science and Technology, London, UK [8]. Oxidation of coals in the alkali aqueous solution of potassium permanganate gave benzene carboxylic acids from benzoic to mellitic acids with six carboxylic groups, all being characteristic of humites, while the more coal was metamorphosed, the more carboxylic groups per molecule were obtained. In addition, oxalic (HOOC–COOH, C₂) and formic (HCOOH, C₁) acids, and oxidation end products such as carbon dioxide and water were formed. However, oxalic acid with some portion of short-chain aliphatic monocarboxylic acids formed during Bone's permanganate oxidation from kukersite provided yet little information about the structure of its organic matter. At the same time, under severe conditions of the Bone oxidation, no benzene carboxylic acids characteristic of humites were obtained from kukersite.

After his death, Kogerman's research work on kukersite structure was continued by Aleksandra Fomina, Linda Pobul and Zinaida Degterjova at the Institute of Chemistry. On Pobul's initiative, the researchers modified conditions of Bone's oxidation and improved analytical methods, which allowed determination of aliphatic dicarboxylic acids, from succinic (HOOC–(CH₂)₂–COOH, C₄) to sebacic (HOOC–(CH₂)₈–COOH, C₁₀) acids, while no benzene carboxylic acids were identified [9, 10]. The 33-stage RuO₄ oxidation affords more than 40% aliphatic acids from kukersite organic material [4].

When heating kukersite, we should reach the temperature at which the aromatic structural elements of organic matter become stable to the oxidative decomposition and benzene carboxylic acids are formed. Such experiments were not performed. An indirect answer, however, exists as in addition to aliphatic acids, mainly benzene carboxylic acids with three to five acid groups per molecule were obtained as oxidation products of solid residues of autoclaving under pressure at 250 and 300 °C, while upon oxidizing semi-coke, mellitic acid was also formed [11].

The absence of benzene carboxylic acid in the oxidation products of organic matter of natural kukersite suggested the possibility of producing aliphatic dicarboxylic acids with no benzene carboxylic admixtures, to replace the adipic and sebacic acids commonly used in the chemical industry.

3. The situation in the 1950s

After World War II, women's nylon hosiery made from adipic acid and parachutes made from nylon fibre began to appear in the black market in the USSR. Nylon technology was developed by the Du Pont Company in the 1940s. The post-war world production of capron (nylon-6, $[-CO(CH_2)_5NH-]_n$) from adipic acid was up to 30,000–35,000 tons per year and that of nylon 6.6 ($[-OC(CH_2)_4CO-NH(CH_2)_6NH-]_n$) made from hexamethylenediamine ($H_2N(CH_2)_6NH_2$) and adipic acid ($HOOC(CH_2)_4COOH$) was five times as high.

In a secret factory in Dzerzhinsk, only 14,000 t of caprolactam $[(CH_2)_5C(O)NH]$ was produced in 1958, but it was planned to increase production to 22,000 tons. As a by-product, 1000 t of adipic acid was formed annually. A tonne of the suitable raw material – phenol – cost more than 4,500 roubles, and there was a shortage of it. In order to improve the situation, the Council of Ministers of the USSR (USSR Government) and the Communist Party adopted a regulation in 1958 to increase the production of polymeric materials, including synthetic fibres, during the following years. Special attention was paid to polyamides.

At the same time, preconditions for issuing such a regulation were favourable. The State Nitrogen Industry Institute had been investigating the possibility of producing caprolactam from benzene, over cyclohexane and nitrocyclohexane, since the 1950s already. In Lisichansk Chemical Combine in Severodensk established in 1951, there was designed a plant with an annual capacity of 10,700 tons of caprolactam and 16,000 tons of adipic acid. The price of adipic acid produced over cyclohexane was estimated at 3,750 roubles/t. The USSR Government took a decision to boost the production of caprolactam, but there was also concern about the exhaustion of cyclohexane and benzene as raw materials, so, other source materials were searched for. One of the materials that would have suited for the

production of adipic acid was kukersite, but about which Soviet decision-makers knew next to nothing. At the same time, research workers at the Institute of Chemistry were, of course, not informed of the plans of the Communist Party and the Government, they read about the high demand for adipic acid in the world from foreign newspapers.

4. Pilot experiments at Kiviõli Oil Shale Chemical Integrated Plant

In order to implement the dicarboxylic acids technology, an experimental unit with a periodic working cycle was launched at Kiviõli Plant, as a follow-up to lab tests. Rein Veski, a foreman of the lime producing shop at Männiku Building Materials Works, was employed as a junior researcher and also mechanics and laboratory assistants were hired to work on the new device at Kiviõli Plant (Figs. 1, 2). Aleksandra Fomina, head of the laboratory of high-molecular compounds of the Institute of Chemistry, was responsible for the organizational issues of implementation. But as her doctoral defence and the work of the Research Council section “New Methods for Complex Processing of Coals” in Tbilisi in April 1962



Fig. 1. A historic moment at Kiviõli Oil Shale Chemical Integrated Plant – the first launch of the oil shale oxidation reactor. Back row: junior researcher Rein Veski (left), mechanic Ragnar Palmre and junior researcher Aleksandr Iljin; front row: assistant chemist Esta Nuutre (left) and senior researchers Linda Pobul and Zinaida Degterjova.



Fig. 2. Periodical-cycle dicarboxylic acids units at Kiviõli Oil Shale Chemical Integrated Plant: a 74-litre oxidation reactor and the nitric acid “storage” (on the left), a vacuum distillation device and a dichloroethane “storage” for extraction of raw dicarboxylic acids (on the right). Junior researcher Rein Veski recording the data, Aleksandra Fomina, head of the laboratory of high-molecular compounds of the Institute of Chemistry, Estonian SSR Academy of Sciences, watching the progress of the oxidation experiment and junior researcher Aleksandr Iljin holding manually the pressure in the reactor at the required level.

overlapped, Rein Veski was assigned a task to present, in her place, an application to Soviet coal scientists in Tbilisi for funds for the designing of a large-scale unit for production of dicarboxylic acids at the Experimental Works. The authors of the application were, in addition to Rein Veski himself, also Aleksandra Fomina, Silvia Kivirähk, Zinaida Degterjova and Aleksandr Iljin, all from the Institute of Chemistry, and Ilmar Tänav and Arno Hannus from Kiviõli Plant.

The successful pilot tests performed on periodical-cycle units at Kiviõli Plant, as well as positive feedback from specialised research institutes from other Soviet republics that had carried out tests on purified dicarboxylic acids mixtures spoke strongly in favour of the new, larger device. The start funds were allocated by Soviet decision-makers and later, it was easier to get additional finances thanks to the support from the interested organizations from all over the Soviet Union.

5. Experiments on dicarboxylic acids experimental plant

The experimental plant for production of dicarboxylic acids was designed by a team led by Anton Onton at the projection institute Eesti Tööstusprojekt on the basis of data obtained from the Institute of Chemistry. In parallel to the installation of equipment, engineers and equipment maintainers were trained. Primarily on Viktor Ahelik's instructions, the flotation beneficiation device was built and put into operation at the Enrichment Processes Department of the Institute of Chemistry, to supply the new oxidation unit with kukersite organic matter concentrate called kerogen-90. For this, Aleksander Kitsnik had worked out the kukersite jet grinding technology.

Late in 1964, a bottleneck was resolved: the reconstructed acid-proof plunger pumps were adapted to a continuous dose of the nitric acid suspension of kerogen-90 under pressure to oxidation reactors. In the early 1965, oxidation experiments were commenced. Rein Veski of the laboratory of high-molecular compounds of the Institute of Chemistry was appointed a scientific supervisor of operation of the dicarboxylic acids experimental plant. Linda Pobul and Zinaida Degterjova from the same laboratory were responsible for the purification of crude acids through vacuum distillation and crystallization, later Avo Männik supervised the carrying out of experiments on the purification of crude acids via dicarboxylic acid dimethyl esters.

As is known, nitric acid reacts exothermically with almost any organic matter and the reaction can easily go out of control. Namely this happened on a periodical-cycle reactor at Kiviõli Plant when the first experiment was carried out. However, no such problems occurred on the oxidation unit of the experimental plant of continuous flow reactors, which was essential for the further development of the technology.

Another issue the researchers and engineers had to deal with was the resistance of 1X18H9T stainless steel reactors working in the media of nitric acid and oxides at 140 °C. Occasionally, rewelding of joints was necessary, for which argon welding suited most. Vambola Kallast from Tallinn Polytechnical Institute (now Tallinn University of Technology) and the dicarboxylic acids experimental plant engineer Artur Laaman tested various metals, to find the most suitable material for reactors and other devices. Titanium appeared to be of highest durability.

The residual nitric acid was removed from the reaction mixture in a vacuum evaporator equipped with a gate stirrer and the regenerated nitric acid was directed to the oxidation unit. The highly toxic dichloroethane was used for extraction of crude dicarboxylic acids at Kiviõli Plant but not at the Experimental Works. The abandonment of the extraction step significantly simplified the technology. Crude dicarboxylic acids were fed to a high-vacuum distiller. A prototype of the distiller was a laboratory glass distilling apparatus, which was made by Pobul using the trial and error method. The construction of the high-vacuum distiller differed from those of industrial

devices. There was some concern about the reliability of the new distiller, which was twenty times as large as the laboratory device, but it worked without failure.

6. Road to large-scale production. Step 1: Production of dicarboxylic acids

The continuous oxidation of the 87–90% concentrate of kukersite organic matter was carried out in a cascade of four reactors, using 30% nitric acid in the presence of air oxygen at 140 °C at 10 atm, the ratio of the 100% nitric acid to kukersite organic matter was 3.38:1 [12, 13]. Each reactor was equipped with a steam jacket, a cooling worm and an aeration nozzle to allow compressed air to pass through the entire cascade of reactors (Figs. 3, 4).

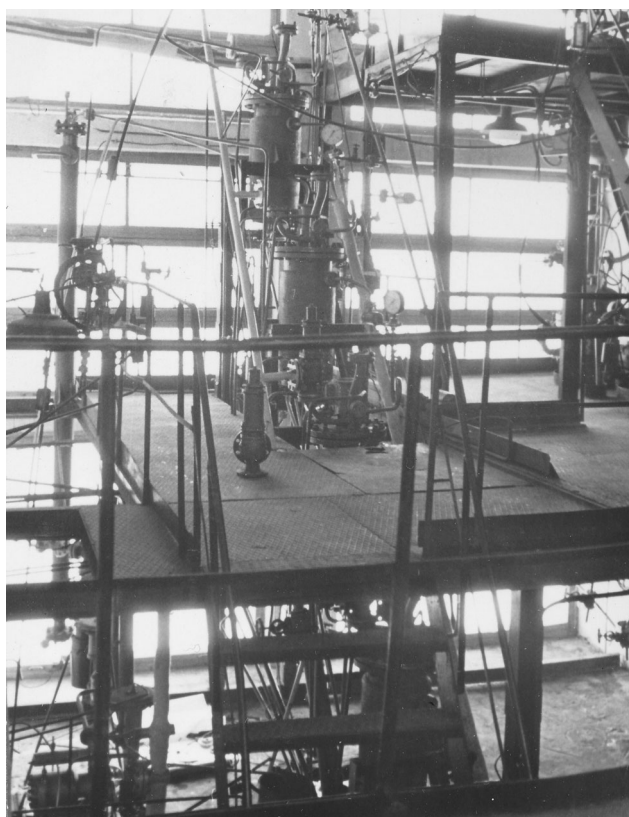


Fig. 3. A cascade of reactors at the Experimental Works of the Estonian SSR Academy of Sciences for a continuous flow oxidation of organic matter of oil shale into dicarboxylic acids.



Fig. 4. Head of the dicarboxylic acids experimental plant Avo Poom (left) and scientific supervisor Rein Veski in the oxidation unit control board room.

The reaction mixture was throttled to setting tanks and separated into the reaction solution and insoluble oxidation products. Nitric acid was removed from the reaction mixture in a vacuum evaporator equipped with a gate stirrer. At the end of evaporation, crude dicarboxylic acids were blown through with live steam to remove excess nitric acid. The total amount of the recovered nitric acid was 62.3% and the consumption of nitric acid was 1.32 kg per kg of organic matter. As a result of the chemical processing, the products were obtained (calculated with reference to dry organic matter of concentrate) as follows: 76.5% crude dicarboxylic acids (containing 65.6% dicarboxylic acids C₄–C₁₀), 15.2% oxidation intermediate – insoluble polyfunctional acids, and 11.5% mineral residue. When oxidation was carried out in severe conditions (at higher temperature and with longer time), no polyfunctional acids were formed. Aqueous solutions of potassium, sodium or ammonium hydroxides may be used for the neutralisation of polyfunctional acids to produce plant growth stimulators. The process is exothermic [13, 14].

Crude dicarboxylic acids which melted at a temperature of 85–95 °C were metered into a batch vacuum distiller at a residual pressure of 3–10 mm Hg, and distilled in the temperature range from 150 to 250 °C. At the end of the process, the temperature was raised to 330 °C to make the coke-like

distillation residue porous and brittle for its easier removal from the distiller (Fig. 5).

The sublimate and the fractions of the distillate were trapped in the condensation system. Succinic acid and glutaric acid admixtures as sublimate were collected into the sublimate collector during the whole process. Chemically pure succinic acid was separated by double recrystallization from water and by activated carbon at the second step of purification. The distilled acids C_4 – C_{10} or their fractions were pure enough for direct use, but the fraction distilled at 170–230 °C needed purification in a two-step recrystallization in water if more valuable end products were kept in mind.

Using the simplified dibasic acids technology, the yield of crystalline succinic acid was 2.2% and that of redistillate 24.1%, accounting for 26.3% of total diacids. In addition, 18.4% plant growth stimulators were obtained, forming 43.5% of kukersite organic matter. Upon preparation of the mixture of crystalline acids, the yield of crystalline succinic acid was 2.2%, that of

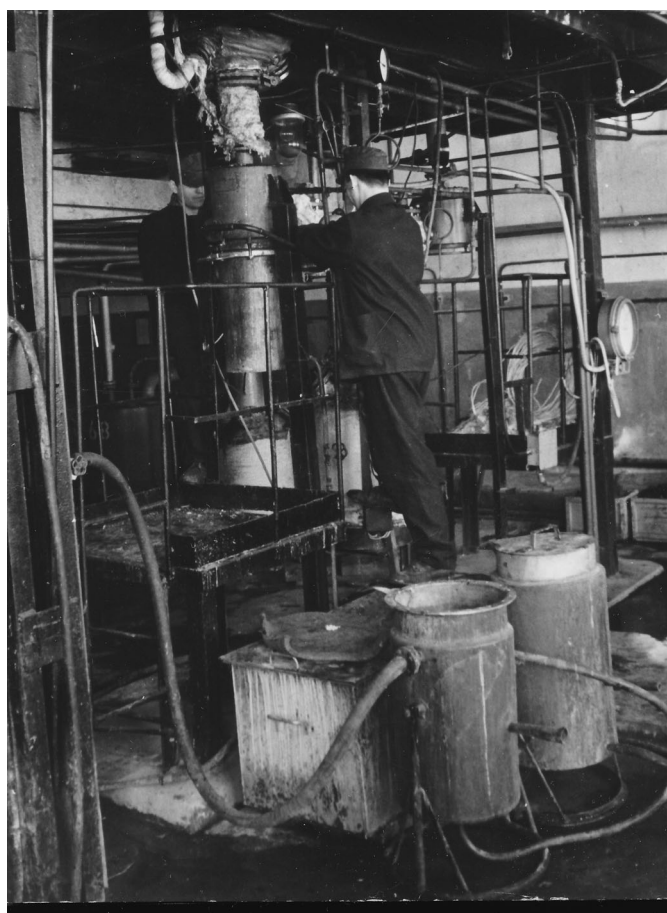


Fig. 5. An operator servicing a high-vacuum dicarboxylic acids distillation unit.

the concentrate of crystalline acids C_6-C_8 was 6.2% and redistillate 16.7%, which totalled 25.1% of the diacids obtained.

Table 1 presents the composition of distilled, redistilled and crystalline dicarboxylic acids.

In the 1970s, the need for the chemically pure succinic acid in the USSR was 3000–5000 t/a, the acid was mostly imported as its domestic production did not satisfy the demand. Several research institutes in the Soviet Union were engaged in the working out of the most suitable method for production of sebacic acid. For example, at the All-Union Scientific Research and Design Institute in Tula, longer diacids were electro-synthesised from kukersite succinic acid. The concentrate of C_6-C_8 acids was tested for production of frost-resistant plasticisers and diacids at the All-Union Plastics Scientific Research Institute of the USSR Ministry of Chemical Industry. For the purpose of saving on sebacic acid, for the manufacture of frost-resistant ($-60\text{ }^\circ\text{C}$) plasticisers, pure sebacic acid was replaced by the concentrate of diacids C_6-C_8 . Experiments for production of frost-resistant plasticisers were also carried out at the Leatherette Plant in Plunge, Lithuanian SSR. The Soviet military industry was interested in frost-resistant aviation lubricants made from the concentrate of C_6-C_8 acids. At Vladimir Scientific Research Institute for Synthetic Resins, redistilled acids were successfully tested for production of polyurethane foams.

In 1968, there were performed successful pilot-scale tests on a 70 kg batch of the concentrate of C_6-C_8 acids as frost-resistant plasticisers at the All-Union Plastics Scientific Research Institute. In 1974, a 250 kg batch of

Table 1. Composition of distilled, redistilled and crystalline dicarboxylic acids [13]

Dicarboxylic acid	Example 1		Example 2		
	Succinic acid*	Redistilled acid***	Succinic acid*	Concentrate of crystalline C_6-C_8 acids**	Redistilled acid***
Succinic acid	99	9	99	traces	11
Glutaric acid	–	31	–	2	30
Adipic acid	0.9	26	0.9	56	26
Pimelic acid	–	13	–	20	14
Suberic acid	–	9	–	18	8
Azelaic acid	–	4	–	2	4
Sebacic acid	–	4	–	2	3
Total	99.9	96	99.9	100	96
Yield from kukersite organic matter, %	2.2	24.1	2.2	6.2	16.7

* White, lustrous and odourless

** Pale creamy solid substances

*** 100 kg batch of white crystalline powder, melting point $110-130\text{ }^\circ\text{C}$, iron content up to 0.0019%, ash content 0.03%

the redistillate was produced for Vladimir Scientific Research Institute for Synthetic Resins, to train the pilot plant staff to produce polyurethane foams, for example DUDEG 2.

The kukersite-based plant growth stimulator has proved its efficacy in numerous successful tests carried out since 1964. The first biological tests were conducted at the Estonian Agricultural Academy under the guidance of Helmut Raig who used the methods of coleoptile length and seeds moistening [15, 16]. Later the stimulator was subjected to tests in various climate and soil conditions across the USSR under the supervision of the Moscow Timiryazev Agricultural Academy, the Central Institute for Supervising and Testing in Agriculture, etc. The largest batch of the stimulator produced on the dicarboxylic acids experimental plant was 300 kg. Carried out with permission of the USSR chief health officer, agricultural production tests proved to be successful, according to feedback from the experimenters. The stimulating doses were very small, about 1 kg/ha, the risk of overdose was almost non-existent, which occurred, for example, with succinic acid. The use of stimulators via spraying plants and soaking seeds or tubers increased crop yield by 15–20%. The stimulating effect was especially noticeable in dormant buds in strawberry, cucumber and tomato [14].

Based mostly on the experimental data obtained on the experimental plant in the first half of 1967, the Russian-language “Instruction for designing industrial experimental plant for production of succinic acid, fractions of dicarboxylic acids, ПИУ-3 type polyurethane foams, plasticisers and plant growth stimulators from kukersite kerogen” was prepared at the Institute of Chemistry, according to the design standards of the projection institute Lengiprogaz, Leningrad. The documentation concerning the technology of pilot production of adipic acid provided by Lisichansk Chemical Combine, the State Nitrogen Industry Institute and other specialized institutes was helpful.

A significant contribution to the development of the technological process was made by Ilmar Nikopensius (then Eduard Talder), head of the dicarboxylic acids experimental plant. The abovementioned instruction was approved by the Head Office of Oil Shale Processing of the USSR Ministry of Oil Industry. By order of Kiviõli Plant, Lengiprogaz wrote the pertaining technical economic feasibility report. Representatives of Kohtla-Järve Complex watched the balance experiments during which batches of dicarboxylic acids and kukersite-based plant growth stimulators were produced to be tested by specialised institutes all over the Soviet Union.

7. Road to large-scale production. Step 2: Production of dimethyl esters of dicarboxylic acids

In 1966, candidates of sciences Rein Veski and Avo Männik, junior researcher Jevgenia Bondar, mechanic Aare Pärn, and seasonally also senior

researchers Linda Pobul and Zinaida Degterjova from the laboratory of high-molecular compounds of the Institute of Chemistry, started working at the Experimental Works to deal with the production of dimethyl esters of dicarboxylic acids. Emilia Männik, Sibille Müller and Olga Ikonopistseva worked in the research group led by Avo Männik.

In 1969, on Avo Männik's initiative, a rectifying column was constructed in the Special Construction Bureau of the Estonian SSR Academy of Sciences, which was mounted at the Experimental Works. The column enabled production of 32% diacids, instead of the former 26.3%, and 38% as their methyl esters (Table 2, Fig. 6). The mixture of trimethyl esters of aliphatic tricarboxylic acids was also obtained. Dimethyl esters were separated from high-boiling admixtures by fractionation (the efficiency of the column was 10–20 plates) under vacuum at 10 mm Hg at a temperature of up to 190 °C.

According to the specialised institutes of the USSR that had carried out tests on dicarboxylic acids and kukersite-based plant growth stimulators, mixtures of di- and trimethyl esters as well as individual esters could be used instead of dicarboxylic acids for production of the same products as from diacids. For example, the final distillate of DME C₄–C₅ could be used for synthesis of polyurethane foams, DME C₆–C₁₀ for the manufacture of frost-proof plasticisers (–60 °C), etc. In addition, esters could be easily re-esterified with higher alcohols to produce plasticizers or lubricants. According to the USSR Ministry of Chemical Industry, the production of a dimethyl ester of sebacic acid with a yield of 2% at a cost of 6,000 roubles/t would have been a substantial gain, reflecting the extremely tense situation in the field of frost-resistant plasticisers and aviation lubricants. The experimental plant was already able to produce more than 6% diacids to replace sebacic acid. Calculations showed that replacing sebacic acid with the concentrate of C₆–C₈ acids or their methyl esters in the manufacture of plasticisers produced an economic effect to the amount of 500–1500 roubles/t.

Table 2. Production of aliphatic dimethyl esters (DME) and trimethyl esters (TME) of aliphatic tricarboxylic acids from kukersite organic matter, %

Esters and stimulator	Variation 1	Variation 2
DME of succinic acid	8.4	–
DME of glutaric acid	9.2	–
DME of C ₄ –C ₅	–	16.0
DME of C ₆ –C ₁₀	21.2	18.8
TME of tricarboxylic acids C ₆ –C ₁₅	–	3.5
Total	38.8	38.3
Plant growth stimulator	18.9	18.9
Grand total	57.7	57.2

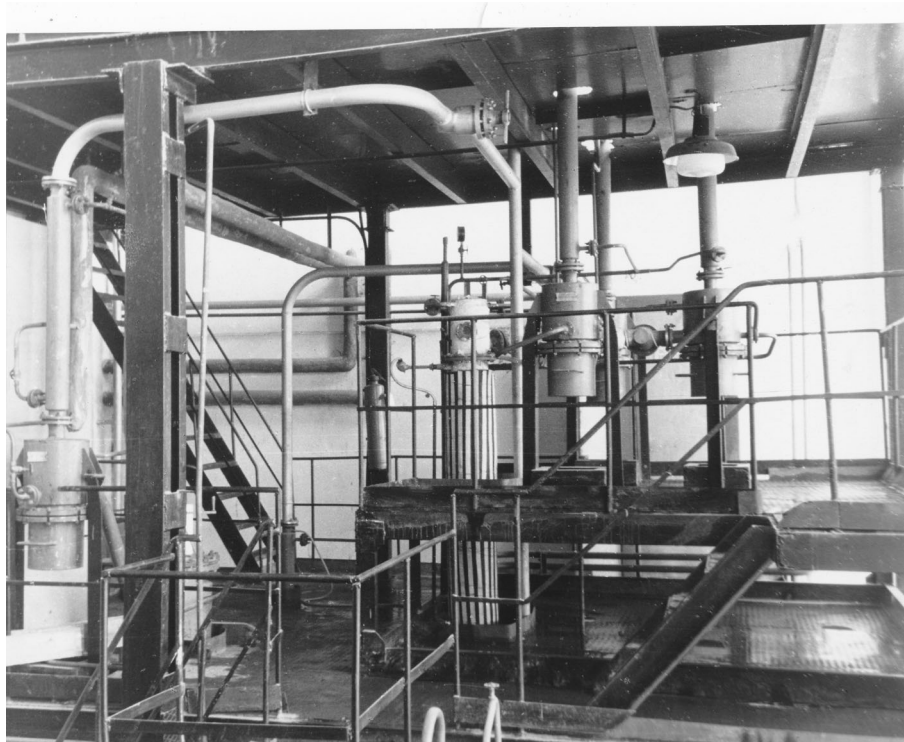


Fig. 6. A rectification column for dicarboxylic acid dimethyl esters with receivers.

Today those interested in the diacids/diesters technology should, of course, make all calculations of costs in dollars or euros, considering current prices.

In the USSR badly needing hard currency to boost its economy, there was made a decision before the collapse of its economy to build an experimental plant in Kohtla-Järve. The plant with a capacity of 100,000 tons of kukersite organic matter per year was to produce 25,100 tons of diacids and their mixtures and 18,400 tons of plant growth stimulators. The annual economic effect of acids production alone would have been 28 million roubles and the payback period less than a year, while investments in equipment would have been lower than those in adipic and sebacic acids production [17]. At the same time, the Government Regulation concerning the production of individual pure diesters and their mixtures was under preparation. The pertinent technology would have enabled production of diesters 32,400 t/a, thereby almost doubling the economic effect. Calculations were based on an assumption that the plant for production of diacids, esters and nitric acid would have been established in Estonia as a complex to allow the pipeline transport of nitric acid.

At the beginning of the 1970s, the wholesale price of fine-grained oil shale was 4.0, tailings 3.17 roubles/t. At the same time, Slantsy Oil Shale Chemical Integrated Plant (now Zavod Slantsy) sold kerogen-70 at 60 roubles/t (net cost 47 roubles/t), while the net cost of the concentrate to be produced at a planned 30,000 t flotation mill was then calculated 33.6 roubles/t or, at an even greater capacity, 25 roubles/t and kerogen-90 32.4 roubles/t.

8. Patents and dissertations

The technology of dicarboxylic acids was protected by the Author's Certificates of the USSR which had been prepared by the workers of the Institute of Chemistry of the Estonian SSR Academy of Sciences, the Experimental Works of the Estonian SSR Academy of Sciences and Kiviõli Oil Shale Chemical Integrated Plant, while some of them were prerequisites for patenting the respective innovations in foreign countries [18–23].

There were defended a number of candidate's or doctor's dissertations on related subjects by the researchers of the Institute of Chemistry. The following will list the dissertations and authors, as well as supervisors and the year of defence: "Oxidation of Estonian kukersite oil shale kerogen with alkaline permanganate" by Linda Pobul (supervisor A. Fomina, 1958), "Nitric acid oxidative destruction of kukersite kerogen" by Zinaida Degterjova (supervisor A. Fomina, 1962), "Genesis and chemical nature of kukersite" by Aleksandra Fomina (doctor's dissertation, 1962), "The development of chemical technology of aliphatic dicarboxylic acids and plant growth promoters from kukersite kerogen" by Rein Veski (supervisor A. Fomina, 1969), "Investigation of transesterification and hydrolysis reactions of dimethyl esters of saturated aliphatic dicarboxylic acids" by Sibille Müller (supervisors A. Fomina and A. Männik, 1970), "Chemical nature and action of oil shale plant growth stimulator" by Vera Punga (supervisors A. Fomina and Z. Degterjova, 1973), "Study on the synthesis of mixtures of saturated α,ω -dicarboxylic acids in the synthesis of polyesters and polyester urethanes" by Silvia Kivirähk (supervisors G. Kolesnikov and A. Fomina, 1975), "Investigation of deep enrichment technology for kukersite oil shale and exploration of enrichment technology" by Aleksander Kitsnik (supervisor R. Koch, 1978), "Study of the organic matter structure of sapropelite oil shale by the method of nitric acid oxidation" by Jevgenia Bondar (supervisors A. Fomina and R. Veski, 1982). In addition, a doctoral dissertation "Analysis of the possibility of separating the saturated aliphatic dicarboxylic acid mixtures" was defended by Jüri Kann at Tallinn Polytechnical Institute (supervisor A. Aarna, 1967). At the same time, there were carried out tests in 1967–1971 by Aili Kogerman at the Institute of Chemistry on the mixtures of diacids for the synthesis of polyamides and wool modifiers.

9. Situation in the production of adipic and sebacic acids

Internet access to an overview of production of individual dicarboxylic acids will cost private users about \$ 5,000 and corporations about \$ 10,000. However, some of the related materials can be viewed for free. Today the cost of production of succinic acid is from 16,000 to 30,000 t/a, increasing 10% a year. The acid is mostly obtained as glutaric acid, a by-product of adipic acid production.

In 2012, the global demand for adipic acid was up to 2.3 million tons and has increased since then by 3–5% a year. In 2016, the global adipic acid market size was valued at \$ 7.1 billion (revenue) and 3.74 million tons (volume), increasing respectively by 6.0% and 4.1% per annum in 2017–2025 [24]. 85% of the high-purity adipic acid goes to the production of nylon-66, while adipic acid of lower purity is suitable for making polyurethanes (5%), and for producing adipic acid esters (4%) and other products (6%), also in the food industry that uses dicarboxylic acids in its manufacturing processes.

Approximately 95% adipic acid is produced from cyclohexane. In the first stage, cyclohexane is oxidized with air oxygen (125–165 °C, 8–15 atm, 4–11% conversion and about 85% selectivity) to KA oil (the mixture of cyclohexanol and cyclohexanone). In the second stage, the mixture is further oxidized to adipic acid by 40–60% HNO₃ (KA oil:nitric acid 40:1, the selectivity for adipic acid is 93–95% with some portion of succinic and glutaric acids as side products) in the presence of copper and vanadium catalysts, the total selectivity under optimal conditions thus being about 80%.

Adipic acid is mostly produced in China, the United States, Japan and Germany, but also in South Korea, Taiwan, Canada, South America and elsewhere. The average selling price of the acid in 2012 was 1,600 \$/t and has not significantly changed since then, according to public offering. The main manufacturers are Invista, Ascend, Honeywell, BASF, Radici, China Shenma and PetroChina. Azot in the city of Severodonetsk, Ukraine produces 50,000 tons of crystalline adipic acid and 60,000 tons of liquid caprolactam per year. Rivneazot in Rivne (formerly Rovno), Ukraine produces adipic acid 25,000 tons per year to the domestic market at about 25000 Ukrainian Hryvnia/t, and the mixture of succinic and glutaric acids as a by-product. Lisichansk Chemical Combine, today Severodonetsk Azot Association, was an important know-how centre for the diacids pilot plant design and assembly.

Considering that the market quantities of pimelic acid (C₇) rarely exceed 600 tons (with a price of 600–5000 \$/t), its market price is usually given as 1–99 \$/kg. This acid is suited for the production of a deficient amino acid lysine. Suberic acid C₈ is a minor by-product of sebacic acid production. Azelaic acid C₉ is not available in large quantities, it is produced from oleic acid.

Sebacic acid is mainly produced by heating castor oil with alkali to high temperatures, to about 250 °C. The resulting ricinoleic acid $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ is cleaved to capryl alcohol $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_3$ and sebacic acid. Although the sebacic acid yields are low, this route has proved to be cost-competitive. In 2009, the production capacity was 150,000 t/a, while the need was 140,000 t/a. In 2001, larger batches of sebacic acid cost 5,600 \$/t, in 2009, 3,600 \$/t and today the price is 2,500–3,500 \$/t [25]. China with 100,000 tons per year is the largest exporter of sebacic acid.

13. Concluding remarks

The technology of production of dicarboxylic acids, their methyl esters and plant growth stimulators was also applied on the experimental plant to the heavily enriched oil shale of Krasava occurrence, Bulgaria, above the order of the USSR foreign trade organisation V/O Vneshtehnika [26, 27], and, in cooperation with Irkutsk Polytechnical Institute, to the difficultly grinded Budagovo boghead with an organic content of as high as 86.7%, which needed no enrichment [28]. The grinded Estonian dictyonema oil shale of very low organic content was processed self-initiatively on the experimental plant, to gain experience to oxidize raw materials of very high mineral content. The acids obtained from Krasava oil shale and Budagovo sapropelite contained a small amount of benzenecarboxylic acids as additions, but despite that were still suitable for production of the same products as diacids from kukersite.

Laboratory experiments evidenced that there are many suitable sapropelites for production of aliphatic dicarboxylic acids with some portion of benzene carboxylic acids [29], but kukersite may be the only oil shale to yield merely aliphatic acids, with no additions.

Pilot-plant experiments on dicarboxylic acids production lasted for tens of years. Today there is solid know-how to further develop the technology of production of these acids from sapropelites. However, only time will tell whether the application feasibility of the dicarboxylic acids technology pays off in the modern market economy*.

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