REVIEW

HYDROGENATION OF OIL SHALE AND POLYMERS

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Hydrogenation represents a universal method for producing liquid products from solid fossil fuels. Due to the specific structure of shale organic matter (SOM), shales may be hydrogenated under low hydrogen pressure (<10 MPa). When performing such hydrogenation of enriched Baltic oil shale, 98 % conversion of SOM into liquid and gas products was achieved. A principal route for producing gasoline, diesel and jet fuels as well as chemicals (60 %, on SOM basis) has been developed. Hydrogenation of polymers, which model structural elements of SOM, has been studied as well. The problems of processing and utilizing high-ash solid fuels have been examined.

Introduction

The potential for using hydrogenation for high conversion of Baltic oil shale organic matter to produce liquid products was shown almost seventy years ago. That was done by an outstanding chemist P. Kogerman, a specialist in oil shales [1]. Analogous studies were made using Gdov [2] and Volga-Basin [3] shales from Russia.

High-ash shales were processed under pressures of up to 30 MPa. High pressures are not used for technical and economical reasons (equipment erosion, high product prices). In the 50s, a method for high enrichment of shales using the methods of flotation and centrifugation was elaborated [4]. The yield of enriched shale was 30–35 %, where its concentration of organic matter was 80–90 %. Hydrogenation of concentrates for producing motor fuel was studied at the Fossil Fuel Institute and *VNIINeftekhim* (the former *LenNII*) [5, 6]. The annotations to some of these studies were published recently [7].

The organic matter of the shale self-associated polymers is probably represented by weakly bound (due to EDA-interactions) associations that are analogous to the multimers of low-metamorphose coals [8, 9]. Up to 80 % of these associations easily transform into low-molecular weight soluble

products when subjected to short-time action at temperatures 350–380 °C [10, 11]. Destruction of these soluble products into distillate products under hydrogen pressure and in the presence of a catalyst has to occur very fast since oxygen-containing and saturated hydrocarbon bonds are the main bonds present in shale associations.

A. Aarna (Tallinn Technical University) has shown that the carbon in shale occurs mainly in cyclic naphthenes (50–75 %) and paraffin chains (6–31 %), with 18–19 % being cyclic aromatic compounds. Oxygen present in SOM occurs mainly (up to 55 %) in phenolic ethers, up to 30 % in carboxyl groups of a phenolic nature and up to 16 % in carbonyl groups. The hydrogen content of shale organic matter is higher than that of coal (over 9 % and 5–6 %, respectively). Due to these characteristics, shale hydrogenation consumes less hydrogen and that makes processing economically favorable. Hydrogenation of polymeric materials, whose structure may be considered similar to that of structural elements of SOM, has given results [12–14] that confirm the main characteristics for SOM hydrogenation, i.e. yield and chemical composition of liquid products [5, 6].

Polymeric materials – wastes from processing and utilizing polymers – may be used as additives for coal hydrogenation. They initiate the process due to their higher reactivity [15]. SOM added to coal organic matter (in amounts of 10–20 %) has the same effect on the coal hydrogenation process. This method is now of interest for researchers in Germany, Russia, U.S.A., Japan, and other countries [16–18].

In Germany (in the town of Bottrop) polymeric and other wastes, as well as synthetic oil, are being processed. This processing takes place at the Kohleöl Pilot Plant. This plant has a capacity of 250 t/day. It was erected for hydrogenating coal and oil residues. In Russia (in the town of Tula) the same approach is planned at the No. 5 Pilot Plant, used earlier for hydrogenation of coal and oil tar.

Experimental data on hydrogenation of shale, polymers and coal, plus the present state of hydrogenation processes and prospects for their use are discussed below.

Hydrogenation of Shale

Samples of enriched shale were used as raw material. Flotation and centrifugal separation in heavy liquids, the method elaborated at Leningrad Institute of Technology and at All-Union Research Institute (VNIIPS), was used for enrichment.

Shale concentrates had the following characteristics: particle dimension <0.1–0.2 mm; moisture content W^a 1.2–1.3 %; ash content A^d 15–18 %; $CO_{2\,min}$ 2.4–2.5 %; S^d 1.7–1.8 %. The elemental composition was as follows (%, daf basis): C 74.2–74.7, H 8.9–9.0, S 1.2–1.4, N 0.4–0.5, O 14.5–15.0. The heat of combustion Q^{daf} equals 7500–8000 kcal/kg.

The mixture (paste) subjected to hydrogenation consisted of 40–45 % shale and 55–60 % of a shale liquid product with a boiling point over 300–320 °C. This liquid was obtained from gasification, hydrogenation, or pyrolysis of liquefaction residues. 0.5–3.0 % of a catalyst was added to the mixture. The salts and oxides of iron, nickel, molybdenum and tungsten, their mixtures, as well as the residues from alumina processing, nickel, chromium and iron ores were used as catalysts.

Hydrogenation experiments were carried out at the Institute of Fossil Fuels using a rotary autoclave (2 l) and a flow bench-scale unit (0.8 l). Sludge (shale liquefaction residue) was processed (pyrolized) in a flow unit with a mobile downflow layer of a solid heat carrier. The throughput rate of the unit was 3–10 kg of raw material per hour. In the autoclave, 90–95 % of SOM was converted into liquid products and gas within 15 min when the following reaction conditions were used: 410 °C, 8–8.5 MPa, in the presence of an iron-containing catalyst. The degree of SOM liquefaction and yield of products were affected by the reaction temperature (Fig. 1).
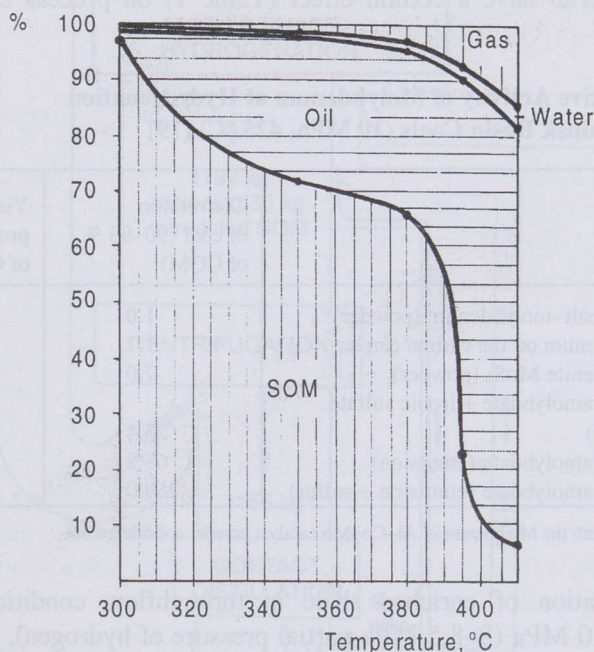

Fig. 1. Distribution of shale organic matter during hydro-genation in autoclave (initial pressure of hydrogen 40 at)

At temperatures over 420–430 °C an increase in both gas yield (from 10–12 to 20 %) and in hydrogen consumption (from 0.6–0.8 to 1.5–1.7 %) took place resulting from the destruction of the fraction that has a boiling point over 325 °C. The share of this fraction in the hydrogenates decreased from 50 to 30 % and correspondingly increased the content of gasoline and diesel fuel

fractions. Prolonging the reaction time up to 30–45 min has an analogous effect on the process. Elevation of the hydrogen pressure over 8 MPa showed no significant impact on process characteristics. The presence of active catalysts (0.5 %) containing Mo, W or Sn reduces the asphaltene content of the fractions boiling over 325 °C (from 38–40 to 18–19 %), hence simplifying their further processing. Nickel-containing catalysts are of a medium activity, and natural compounds (ores) of nickel and iron (2 %, on a SOM weight basis) have an analogous positive effect. A mixture of the salts of bi- and tri-valent Fe, Ni, or corresponding polymetal ores, represent effective catalysts for hydrogenation of SOM and even of COM.

Further studies were made for elaborating catalytic systems for coal low-pressure hydrogenation (6–10 MPa) based on the results of shale hydrogenation tests. The coal hydrogenation was performed with highly-effective, recoverable Mo- and Ni-containing emulsion catalysts. The presence of these catalysts (0.05–0.1 % of metal) during hydrogenation has given good results. The size of catalyst particles and the way in which they are introduced into the raw material have a certain effect (Table 1) on process characteristics [19, 20].

Table 1. **Relative Activity of Molybdenum at Hydrogenation of Kansk-Achinsk Basin Coals (10 MPa, 425 °C) [19]**

Catalyst	Conversion of coal (90–93 % of COM)	Yield of liquid products (82-85 % of COM)
Aluminium–cobalt–molybdenum (powder)*	1.0	1.0
Cobalt–molybdenum on the carbon carrier	1.7	0.9
Natural molybdenite MoS$_2$ (powder)	7.0	1.7
Ammonium paramolybdate + ironic sulfate (impregnation)	25.4	16.6
Ammonium paramolybdate (emulsion)	63.8	34.1
Ammonium paramolybdate (emulsion + sulfur)	259.0	168.0

* In comparison with the Mo content of Al–Co–Mo catalyst powder considered one.

Hydrogenation of enriched shale in throughflow conditions, under a pressure of 10 MPa (8–8.5 MPa partial pressure of hydrogen), demonstrated that the process has to be carried out at 440 °C when Ni-catalysts are used and a temperature of 460 °C is needed when iron-containing catalysts are used. Reaction times of less than 10 min corresponded to space velocities of 2.5–3.0 kg SOM/l · h. With these velocities, the hydrogenation rate exceeds that for brown coal from Kansk-Achinsk Basin (Russia) by almost six times. Since space velocity determines process efficiency, the data demonstrated higher reactivity of SOM compared with COM.

The SOM degree of liquefaction was 96–98 %, with a hydrogen consumption of 1.5–2.0 %. The yield of liquid products was 76–78 %,

including 40–45 % of compounds boiling below 325 °C. The gas yield was 18–20 %, and water was 8–9 %. Practically all of the added hydrogen (1.5–2.0 %) was consumed for formation of hydrocarbon gases C_1–C_4, whose yield was 8–10 %. These gases could be recycled into the process after conversion with steam. SOM contains about 15 % oxygen, of which about 4 % is emitted as CO_2 and 7 % as water. Due to hydration reactions, liquid products contain 9.55 % of hydrogen, compared to 9.03 % in shale and 9.20 % in the feed paste forming agent.
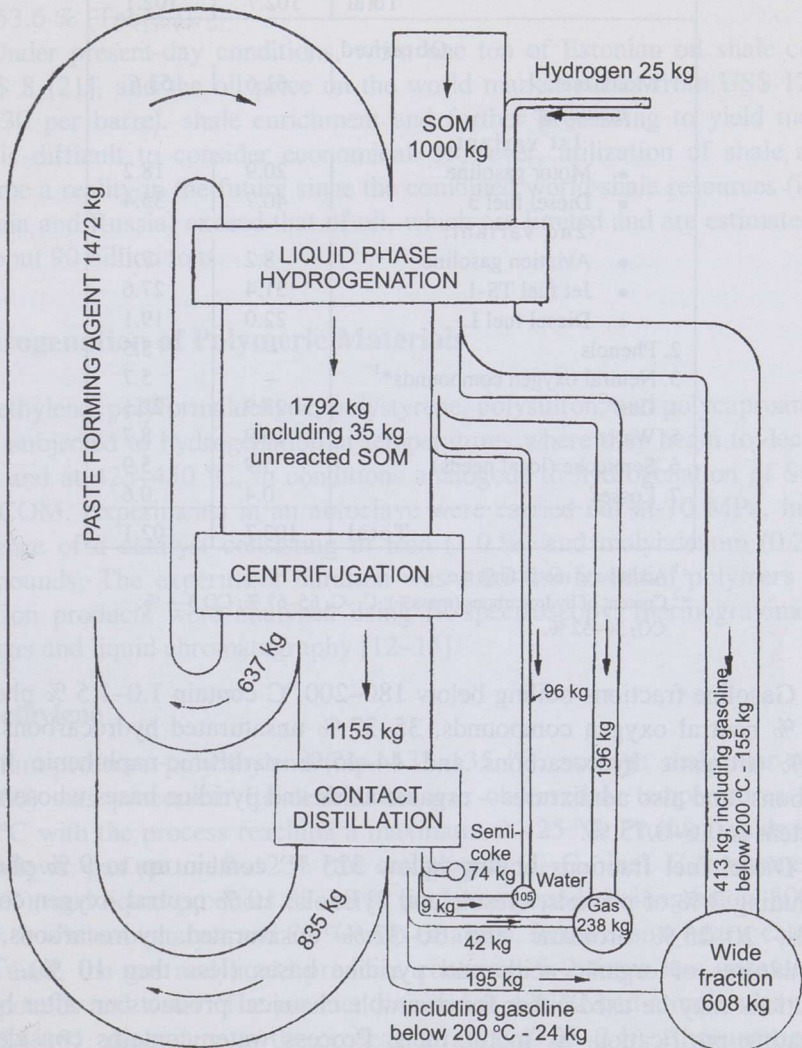
Figure labels:

- Hydrogen 25 kg
- SOM 1000 kg
- PASTE FORMING AGENT 1472 kg
- LIQUID PHASE HYDROGENATION
- 1792 kg including 35 kg unreacted SOM
- 637 kg
- CENTRIFUGATION
- 1155 kg
- 96 kg
- 196 kg
- 413 kg, including gasoline below 200 °C - 155 kg
- CONTACT DISTILLATION
- 835 kg
- Semi-coke 74 kg
- Water
- 9 kg
- 105
- Gas 238 kg
- 42 kg
- 195 kg
- including gasoline below 200 °C - 24 kg
- Wide fraction 608 kg

Fig. 2. Material flows of the liquid-phase hydrogenation process of enriched Estonian oil shale

Table 2. **The Yield of Products (mass%)**
at Processing Enriched Baltic Oil Shale
into Motor Fuel (Scheme I) and Chemical Products
(Scheme II)

	Scheme I	Scheme II
Taken		
1. Shale organic matter	100.0	100.0
2. Hydrogen for reaction	2.7	2.1
Total	102.7	102.1
Obtained		
1. Motor fuel	61.6	53.6
Including:		
1st variant:		
• Motor gasoline	20.9	18.2
• Diesel fuel 3	40.7	35.4
2nd variant:		
• Aviation gasoline	8.2	7.1
• Jet fuel TS-1	31.4	27.6
• Diesel fuel L	22.0	19.1
2. Phenols	–	5.5
3. Neutral oxygen compounds[1]	–	5.7
4. Gas[2]	23.9	22.1
5. Water	10.9	8.7
6. Semicoke (local needs)	5.9	5.9
7. Losses	0.4	0.6
Total	102.7	102.1

[1] Additive to motor fuels a.o.
[2] Content of hydrocarbons (mass%): C_1-C_4 65–67 %; CO 3–4 %;
     CO_2 30–32 %.

Gasoline fractions boiling below 180–200 °C contain 1.0–1.5 % phenols, 3.5 % neutral oxygen compounds, 35–37 % unsaturated hydrocarbons, 15–16 % aromatic hydrocarbons and 44–45 % paraffinic-naphthenic hydrocarbons, and also admixtures – organic acids and pyridine bases whose sulfur content is 0.6–0.75 %.

Diesel fuel fractions boiling below 325 °C contain up to 9 % phenols, including 3 % of phenols, cresols and xylenols; 10 % neutral oxygen compounds; 20–25 % aromatic and 30–32 % unsaturated hydrocarbons, and admixtures of organic acids and pyridine bases (less then 10 %). These fractions may be used either for desirable chemical products or, after hydrogenating purification, as motor fuels. Process water contains considerable water-soluble (incl. di- and tri-atomic) phenols and represents a good raw material for their extraction.

Since shale liquefaction products contain mineral components of ash and catalyst, the residue, after separation in a centrifuge of a part of the liquid

products, was pyrolized at 460 °C on a moving solid heat carrier. The coke formed was used for heating up the heat carrier. The yield of liquid products was 91–93 %, with gas, water and coke making up the balance.

The flow sheet for SOM hydrogenation and processing of high-boiling residues is given in Fig. 2. One can see that the yield of distillate products (the total wide fraction) was 60.8 % of SOM. The gasoline fraction was 18 %. Hydrofining (10 MPa, 380 °C) of the total fraction yielded up to 90 % fuel fractions (motor gasoline A-76, diesel fuels L and Z, jet fuel TS-1). The yield of motor fuels was 61.6 %, on a SOM basis, but separating chemical products using the methods of liquid-liquid extraction, the yield of motor fuels was 53.6 % (Table 2).

Under present-day conditions, when one ton of Estonian oil shale costs ~US$ 8 [21], and the oil price on the world market varies from US$ 12 to US$ 30 per barrel, shale enrichment and further processing to yield motor fuel is difficult to consider economical. However, utilization of shale may become a reality in the future since the combined world shale resources (incl. Estonia and Russia) exceed that of oil, which are limited and are estimated to be about 90 billion tons.

Hydrogenation of Polymeric Materials

Polyethylene, polyformaldehyde, polystyrene, polysulfon, and polycaproamide were subjected to hydrogenation at temperatures where they begin to decompose and at 425–450 °C, in conditions analogous to hydrogenation of SOM and COM. Experiments in an autoclave were carried out at 10 MPa, in the presence of a catalyst consisting of iron (1.0 %) and molybdenum (0.2 %) compounds. The experiment duration was 0.25–2.0 h. Initial polymers and reaction products were analyzed using IR-spectroscopy, thermogravimetry, and gas and liquid chromatography [12–14].

Polyethylene

Medium-pressure polyethylene (mp. 132–135 °C, average molecular mass 72,000) was processed. Its destruction was observed at temperatures over 375 °C with the process reaching a maximum at 425 °C. Product yields were as follows: gas up to 10–12 % (the compounds C_1–C_4, incl. C_2 monomers – 2–4 %); and liquid products 88–90 % (incl. compounds boiling below 300 °C – 70 % without catalyst and 80 % with catalyst). In the case where a catalyst was used, the gas and liquid products contain 1.5–2 times less unsaturated compounds and water. The product obtained at 425 °C had a molecular mass of 124–181, depending on the process duration (0.25–2 h). Consumption of hydrogen did not exceed 1.2 %. In the composition of fractions boiling below 300 °C, hydrocarbons C_5–C_{20} were identified. These were mainly normal

paraffins and olefins (25–30 %) but also mono- and di-substituted *iso*-paraffins occurred as admixtures.

The hydrogenation experiments, made by adding 1–5 % of inhibitors of radical polymerization reactions (anthraquinone, isobutylene, ionol), proved that destruction of polyethylene occurs according to the free-radical mechanism (not chain) through "occasional" breaking of carbon-carbon bonds due to intramolecular migration of hydrogen atoms. Formation of secondary products like tar, asphaltenes, and aromatic hydrocarbons was not observed. Consequently, structural elements of SOM that are analogous to polyethylene easily transform into low-molecular fractions of motor fuels under hydrogenation.

Polystyrene

So-called "unit-form" polystyrene (mp. 150–160 °C, average molecular mass 290,000) was used in experiments. Polystyrene began to decompose at temperatures over 300 °C. The yield of the fractions boiling below 140 °C was 21.5 % at 325 °C and increased to 65–70 % at 425 °C. Average molecular mass decreased from 265 to 112–124 depending on process duration. The gas formed (1.5–2.0 %) consisted of methane, ethane and propane. In the presence of catalyst and at reaction conditions of 10 MPa, 425 °C, and 1 h, polystyrene gave the following liquid products (mass%): benzene 1.2; toluene 17.6; ethylbenzene 41.1; isopropylbenzene 10.9; *n*-propylbenzene 1.6; aromatic hydrocarbons C_{10}–C_{17} 2.9; C_{18} and more 24.4 (not identified).

Since further experiments showed that 1.5 % of toluene, ethylbenzene, and isopropylbenzene were hydrodealkylated under these conditions, hydrogenation of polystyrene mainly yields products that are monomeric in nature.

Addition of anthraquinone (1.0 %), anthracene (5.0 %), ionol (1.0 %), and isobutylene (7.0 %) into the reaction mixture inhibits polystyrene destruction, but isobutylene, in an amount of 1.0–2.7 %, intensifies the process. Based on the experimental data the conclusion was drawn that polystyrene hydro-genation proceeds according to a radical-chain mechanism. Addition of polystyrene (5–10 %) to coal intensifies destruction of COM and increases the yield of distillate fractions.
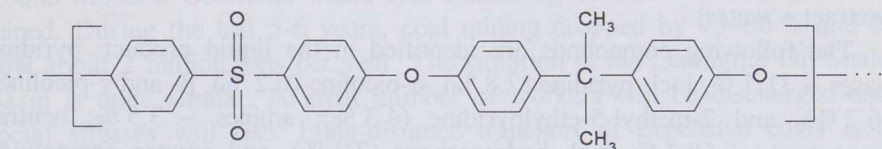
Polyformaldehyde

The initial polyformaldehyde was a typical linear polymer composed of simple polyethers, as determined by IR spectroscopy. The elemental composition was as follows (mass%): C 40.0; H 6.7; O 53.3. Decomposition of the polymer began at a low temperature – 230 °C. An increase in temperature leads to the formation of more gas that consists mainly of CO and CO_2 (maximum yield 58 % at 425 °C), and also more water (34 %) and hydrocarbon gases (14 %). At the same time, the yield of liquid products decreases from 23 to 7 % and that of solid residue from 17 to 4 %. The chemical composition of hydrogenation products is quite complicated. The water

contains methanol, formaldehyde and other oxygen compounds. Liquid products are represented also with the same compounds and admixtures (5 %) – paraffin-naphthenic and aromatic hydrocarbons, and asphaltenes.

The solid residue consists mainly of aromatic structures. Hence, SOM elements of polyformaldehyde structure may represent the main source of formation of carbon oxides, water and aromatic hydrocarbons, and highly condensed hydrocarbons among them. The latter may even be synthesized from SOM elements of a nonaromatic structure when processed under hydrogen pressure. Under SOM pyrolysis the reactions are accompanied by the formation of large quantities of aromatic structures in the shale oil.

Polysulfon

Polysulfon (molecular mass 46,000) having the following structure:

$$\cdots - \left[- \left\langle \bigcirc \right\rangle - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - \left\langle \bigcirc \right\rangle - O - \left\langle \bigcirc \right\rangle - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - \left\langle \bigcirc \right\rangle - O - \right] - \cdots$$

was subjected to hydrogenation.

Thermal decomposition of polysulfon begins at about 445 °C, but with hydrogenation it undergoes high transformation (over 40 %) into gaseous and liquid products at 400 °C. Elevation of process temperature to 425 °C increases the yield of liquid products up to 70 % and of gas up to 9 %. The yield of solid residue diminishes to 20 % and consumption of hydrogen is 3 %. The formed gas consists of hydrogen sulfide (over 50 %), hydrocarbons C_1–C_3 (~35 %), and carbon oxides (15 %). The main part of the benzene-soluble liquid products is represented by hydrocarbons, mainly diphenyl, diphenylmethane (ethylene-, ethane-, propane-), but also contains phenols (their yield is 7 %). Among the phenols the share of individual compounds is the following: phenol (58 %), o- and p-cresols (9 %), 3,5-xylenol (4 %), and phenols boiling over 230 °C (29 %). The asphaltene content of the liquid products is 18 %.

The characteristics of the solid residue differ sharply from the properties of the initial polymer providing indirect evidence of secondary reactions of condensation having taken place. IR-spectroscopy of the residue registered the structures close to carbenes and carboids usually forming at hydrogenation, pyrolysis and other processing of SOM and COM. The data on chemical composition of hydrogenisates obtained at different temperatures and reaction times allows one to rank the reactivity of atom groupings present in the polymer in the following order:

$$C_{ar} - S > C_{ar} - O > C_{alk} - C_{alk} > C_{ar} - C_{alk} > C_{ar} - C_{ar}$$
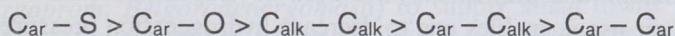
This order is in good agreement with thermodynamic calculations of bond strengths. Hydrogenation of thiokol (10 MPa, 425 °C), a polyalkylene compound in which methyl and ethyl linkages are separated by heteroatoms S–S and S–O, yields 97 % gas, incl. 47 % hydrocarbons, 35 % hydrogen sulfide and 28 % carbon oxides.

Polycaproamide

A sample of polyamide-6 (molecular mass about 10,000) with elemental linkages

$$\approx CO–NH–(CH_2)_5–$$
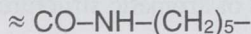
was used in experiments.

Destruction of this polymer begins at temperatures over 360 °C, and at 425 °C it is totally decomposed yielding gas (7.8 %) and liquid products (extract + water).

The following compounds are identified in the liquid product: pyridine bases – 31.7 %, incl. pyridine (2.8 %), α-picoline (6.2 %), β- and γ-picolines (6.2 %), and 2-methyl-5-ethylpyridine (4.3 %); amines – 3.5 %; neutral compounds – 68.3 %, incl. hydrocarbons (7.4 %), and oxygen compounds (13.0 %)

Heating of the polymer (425 °C, initial hydrogen pressure 5.0 MPa) in a helium medium yielded 54.3 % gas, 39 % liquid and 6 % solid compounds. The gas contains hydrocarbons $C_1–C_4$ (64.4 %), carbon monoxide (23.1 %), carbon dioxide (2.3 %), hydrogen (1.8 %) and ammonia (0.24 %).

An analysis of liquid products has shown that hydrogenation of the polymer occurs through breakage of N–C bonds and formation of highly reactive C–N radicals. These radicals are inclined to recombination reactions forming condensation products, including aromatic compounds.

So, once more the experiments have shown that cyclic (aromatic) compounds are formed from linear structures after thermal treatment. Discussion of the "aromatic" structure of solid fossil fuels, based on an analysis of liquid products of hydrogenation, pyrolysis, etc., is not well grounded. It is proposed to avoid (inhibit) the condensation process by adding inhibitors of radical polymerization mentioned above [22, 23].

The results of polymer hydrogenation prove the idea of high reactivity of organic matter of solid fossil fuels as well as their tendency to transform into low-molecular hydrocarbons and O–S–N-containing compounds. The conditions needed for the process may be created without using high pressures of hydrogen – a method largely used in industrial practice in times past. Economic characteristics of new methods are very likely more fruitful.

During recent years new micro-catalytic systems, including conditions for their formation and utilization, have been developed at the Institute of Fossil Fuels. Their usage enables one to decrease hydrogenation pressure to 6 MPa, i.e. significantly improving the processing efficiency as a result of a sharp

decrease in operational demands, especially power consumption. It also enables one to exploit equipment widely used in the oil-refining industry [20, 24]. All that means that the hydrogenation method may successfully be utilized for processing coal, enriched shale, and residues of polymers and rubber production at the beginning of this millennium, especially, as oil resources will be exhausted in the near future.

Conclusion

Finally, one needs to deal with quite a complicated problem – utilization of high-ash solid fuels. In Russia, the reorganization of the coal industry is happening along similar lines to the Estonian oil shale industry [21]. In several coal basins, mining will be sharply reduced. This also applies to the Round Moscow Coalfield, where coal containing 45–50 % mineral matter is mined. During the last 5-6 years, coal mining dropped by 75–80 % and is now about 2 million tons per year. The situation in the Leningrad Oil Shale Basin is quite similar. A great number of workers will be discharged and social stresses will rise. Long-distance transport of expensive coals is a serious economic task for communal and domestic consumers.

To solve the problems mentioned above scientists and producers try to control the impact of the coal industry reorganization by forcing the use of elaborate and new complex technologies to process high-ash coals. Small-scale boilers can be presented as an example. They are designed for fluidized-bed combustion of coal fines with subsequent capture of sulfur compounds. A method for production of granulated fuel for communal consumers has been developed [25].

The power industry is the largest consumer of coal. However, high-ash coals, when fired at power plants, emit large amounts of harmful sulfur and nitrogen compounds into the atmosphere. Their quantities exceed present emissions by a factor of three and future limits by a factor of eight. Because of that, the fluidized-bed technique with subsequent capture of sulfur compounds with limestone is the only effective way to burn coals. In this case, the content of sulfur oxides in flue gases will not exceed 400 mg/m^3 and that of nitrogen oxides – 200 mg/m^3.

New boilers operating as circulating fluidized beds have been designed by several Russian organizations (*Sibenergomash, VTI, Polzunov CKTI*). Boilers, with a production capacity 500 t of steam per hour, were designed for the New-Moscow Water-Power Plant but the project has not been built due to its very high investment requirement.

Low-capacity fluidized-bed boilers (steam production 25 t/h, efficiency 80 %, steam pressure 1.4 MPa at 225 °C) have been designed (*Tulaprojekt, VNIPIenergoprom, Belgorodenergomash*) to supply small towns with heat. 85 % of the sulfur and 99.6 % of the ash must be captured to fulfill environmental requirements applicable to combustion of coals containing up to 3 %

sulfur and 35 % ash. A boilerhouse with three boilers of total capacity $102 \cdot 10^3$ Gcal per year is to be designed, and it will provide the town of Venyov (Tula Region) with heat. A boiler will be erected near the *Progress* mine and its capital cost will be about US $9 million (in 1997 dollars). Ash-slag wastes are proposed to be utilized for producing building blocks using high-pressure casting, which is a non-kiln technology.

The other prospective trend to utilize the Round Moscow Coalfield coals is to use them for producing communal granulated fuel. The corresponding technology is already developed and patented (RF No. 2103328, priority from May 25, 1997). Burning of Round Moscow Coalfield high-ash brown coal (incl. sorted and granulated fines) in domestic furnaces is not efficient since the COM will not be completely burned. The process efficiency is below 40–45 % when coal is burned in boilers with a 10–25 t/h capacity and about 20–25 % in domestic furnaces. The organic matter of this coal is only partially burned (up to 0.3–0.5 of the lump depth) since coal has a low porosity and specific area. Large amounts of argillaceous components also agglomerate during combustion.

A new process for thermal preparation (drying, grinding) of small-size fractions of coal (ash content of 50 %) has been developed on an experimental-industrial scale. The inner pores of the coal will be increased by 8–10 times and the specific surface by 5–8 times. Coal fines (dust) with particle size below 0.2 mm are granulated using a simple method (plate granulation) and the resultant granules (15–25 mm) resist mechanical degradation. 98–99 % of their organic matter will burn up, and the burning process efficiency in domestic furnaces reaches 70 %. The total volume of the granules is consumed preserving the shape even after the organic matter is burned up. Almost no smoke is emitted and only minimum amounts of soot and dust are discharged with the ash residue.

A feasibility study has been carried out by the *Tulaproject*, the Institute of Fossil Fuels and the *Tulainzhneftegaz* to establish an industrial enterprise for producing 500,000 t/y. The capital outlay is calculated to be US$12 million and the pay-back will be within two or three years, depending on coal price and mineral component content of the coal (35–45 %).

Developed technology enables one to prepare granules from coal mixtures. The addition of Kuznetsk Basin coal (30 %) to Round Moscow Coalfield coal increases the heating value of the granules from 2500–2800 to 3800–4000 kcal/kg.

Now a plant for producing 150,000 t/y of granulated fuel is to be designed. Coal fines from the Obidimsk Deposit will be used as raw material. This deposit will be put into production in the near future and the goal of this project is to help eliminate the short supply of Tula Region domestic fuel and limit the importation of expensive coals from other coal regions of Russia.

The organic and mineral portions of Round Moscow Coalfield coals represent a prospective raw material for producing valuable chemical

products and materials since they contain considerable quantities of volatile compounds, humic acids, alumina compounds and even several rare and dispersed elements. Experiments carried out at the *Tulaugol* experimental plant have demonstrated that the Round Moscow Coalfield coal, and even iron pyrite from this basin, may successfully be used as additives (10–30 %) for processing low-ash brown coals of the Kansk-Achinsk Basin and coals from the other basins of Russia.

Liquid fuels are produced from these coals by hydrogenation under low hydrogen pressure. Coals are added to the coal liquefaction process instead of expensive Mo-catalyst. The regeneration of such catalysts is a very complicated process and elimination of that step makes the technology much simpler. If the Round Moscow Coalfield coals will be utilized to produce liquid fuels on an industrial scale many millions of tons are available for this purpose.

Large amounts of mined rock remain after mining and coal preparation and large areas are needed for their disposal. These dumps represent a potential for harm to the environment. Coal wastes of Round Moscow Coalfield are not well suited for making building materials since they contain much sulfur. However, the wastes contain organic matter (up to 20 %) and even remarkable amounts of Al (30–35 % Al_2O_3 in the mineral matter) and Fe (3–8 %, on an oxide basis). A new technology has been developed at *Tulaugol* for utilization of spoil piles. It foresees the production of fillers for manufacture of rubber goods (instead of talcum, chalk, alumina), pigments for the paint and varnish industry, and abrasives for cleaning agents.

Several products can be prepared from coal wastes due to their high Al_2O_3 content – alumina, coagulants, and fireproof and acid-proof materials. At the Institute of Fossil Fuels, *VNIIstrom* and other institutions a so-called "mild combustion" technology is being developed. The process temperature is relatively low (maximum 700 °C). Sulfur will be emitted in the flue gases, and iron compounds (siderite, pyrite a.o.) are transformed into magnetic compounds (magnetite, meggamite, mixture of pyrrhotites)

The magnetic susceptibility of the products increases several orders of magnitude and iron compounds may therefore be separated in a standard magnetic separator with low magnetic intensity. So, a low-ferrous concentrate (1 % or less Fe) is obtained. This is usable for production of fireproof and acid-proof materials as well as iron-containing (30 % or more Fe) raw material for metallurgical purposes. This will provide the prospective foundation for an industrial enterprise in the Round Moscow Coalfield since the current practice is to use large amounts of sub-standard, imported fireproof clays (US$ 25/t). As a result, the boilers of the coal industry will not have to be closed down and suitable raw materials need not lay in rock spoil heaps. Capital costs are US$ 35/t and product cost is US$ 11/t. In long-range plans, the manufacture of alumina, silicon carbide, silicon and aluminium alloys can be discussed.

Consequently, the implementation of new methods for combustion and utilization of solid fossil fuels in the power industry, public services, building-material industry and in other industries represent very essential elements in the reorganization of the coal and shale industries. This will support the maintenance of mining and make these branches of industry competitive.

Acknowledgements

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