ECOLOGICALLY CLEAN HYDROGEN PRODUCTION FROM COALS

Stepanov A.V., **Polunkin E.V., Matusevich G.G.***
Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine,
Kharkov highway 50 (2nd corps of the Institute), Kiev, 02160, Ukraine
Fax: 8 (044) 559 7181 E-mail: matusgala@rambler.ru

Presently the most economical method of hydrogen production is the steam conversion of methane (natural gas) with subsequent conversion of CO. But the cost of gas is high, it reaches \$450/1000 m^3 at the European market. It is therefore necessary to use up other sources of hydrocarbon raw material for hydrogen production.

Ukraine possesses limited reserves of oil and gas, which at the present level of output will come to an end in 25-30 years. The basic power resource of Ukraine is coal, with its supplies of more than 300 milliard tons, and its output can last a few centuries. Therefore coals must be viewed not only as a power fuel but also as a raw material for production of hydrogen, motor-car fuels, high-calorie gases and chemical products.

For the use of brown and pit coals with large maintenance of volatiles the complex procession of these fuels is the most effective approach for production of synthetic liquid products, synthetic gas, power generating.

Therefore the most rational way is to create coal converting power-chemical complexes in the areas of coal output. These complexes may include enriching of coals, semicoking or hydrogenization, production of liquid products, gasification of semicoke and other rests, extraction of hydrogen, combined (gas and steam) power plant, installations for rejects and tails retreatment.

The effective method of hydrogen and ecologically clean fuel production for power plant is gasification of solid fuels with subsequent cleaning of synthetic gas. About 70 % of chemical energy of fuel transform into the synthesis-gas. In combination with the use of physical heat of gas the energy-material coefficient reaches 90 %. Therefore combined power plants with fuel gasification are ecologically clean and gain more acknowledgement. Hydrogen is selected from synthetic-gas by adsorption or diaphragm technologies.

The technology of hydrogen production with concomitant generation of electric power has the following stages. Coal or semicoke and tailings are gasified by steam-oxygen mixture. During gasification the temperature reaches 1500˚C in the direct-flow reactor, and practically all of hydrocarbons are converted. The gas consists mainly of H_2, CO, CO_2, H_2 S and negligible quantity of other components.

According to the technology developed the combined plant work is carried out as follows. Raw material (pulverized coal) and the water is fed in the mixer, equipped with mechanical or cavitational agitator. The suspension (pulp) is pumped by the special pump in the burner device of the gasificator. Oxygen is fed in the gasificator to pulverize emulsion or suspension.

The pressure in the gasificator is conditioned by the pressure in the combustion chamber of gas turbine and fluctuates from 1,4 MPa to 2,2 MPa. The maximal temperature in the reactionary area peaks at 1500˚C, and at the exit from the gasificator it equals 1100-1200˚C. The synthesis-gas from the gasificator enters the waste-heat boiler, and then the scrubber, where it is cooled down and washed by water. The washwater with the particles of ash and black flows down in the sump, from where it is partly recirculated in the mixer, and partly, is directed to sewage treatment. The synthesis-gas is purged from sulphureous compounds in the absorber. Combustion heat of the purified synthesis-gas depending on the composition of raw material, process parameters and other factors equals 9300-9500 kJ/m^3. The synthesis-gas is mixed up with nitrogen, that goes out from the adsorber. This mixture is a good fuel for turbo-engines that provides very small exhaust of nitrogen oxides. This mixture enters the combustion chamber of the turbo-engine, and the products of combustion generate steam in the waste-heat boiler.

Substantial factor of the hydrogen production expenses increase and efficiency reduction of plants with steam-oxygen fuel gasification is the heavy expenditures on the oxygen manufacture by the cryogenic methods of air separation, when energy consumption comprises 0,45-0,5 kWhr/m^3 for 95-98 % oxygen at low pressure. On the basis of air separation analysis it was determined that substantial decline of energy consumption is secured by the adsorption recovery of oxygen following the changed technology.

The air separation by sort cycle adsorption at variable pressure is carried out on carbon or alumosilicate molecular sieves. O_2 is far more quickly adsorbed by the carbon molecular sieves, while N_2 – by the alumosilicate sieves. These properties of sorbents are considered during the air separation process. Adsorption-oxygen installations produce technical oxygen at sufficiently high pressure with maintenance of O_2 equal to 87-93 %. Nitrogen is desorbed at low pressure and usually is not utilized.

We consider that the substantial decline of energy consumption can be attained by diversification of air separation adsorption, when oxygen is adsorbed on carbon molecular sieves, and the nonabsorbed nitrogen at high pressure is utilized as an additional working body in the gas turbine. Oxygen is desorbed at low pressure and then compressed to pressure in the gasificator. It secures reduction of energy consumption for oxygen recovery.

The reduction of energy consumption is achieved as follows. In adsorbers oxygen is adsorbed in amount of 16-19 % of the given air. The rest of O_2 and nitrogen is removed. Energy for the oxygen compression to pressure in the gasificator (taking into account losses) is 20-22 % of air compression energy. Total energy for air and oxygen compression to 2,5 MPa is approximately equal to 0,2 kWhr/m^3 O_2. Nitrogen compounds with cleared synthetic-gas, and the mixture is supplied in the combustion chamber of gas turbine. As a result of working body amount increase the turbine power increases at stable power of the air compressor. Additional power compensates energy consumption for oxygen separation for approximately 55-60 %. Thus expenses on own needs decrease and efficiency of the combined plant increases.

For production of clean hydrogen the process of short cycle adsorption with desorbtion by depressurization has been applied. All of the components, except for hydrogen, have been adsorbed on the ceolites. The nonadsorbed H_2 has been leaded away under pressure of 2-2,5 MPa. The desorbtion products consisting of CO, CO_2 and remaining H_2 have been directed as an additional fuel in the waste-heat boiler. The use of this gas and steam, obtained in the waste-heat boiler, has provided considerable increase in power of the steam-turbine plant as compared to power of ordinary plant.

For the production of 1 kg of H_2 we need 8-10 kg of organic mass of coal depending on its composition. But from the same fuel the electric power has been generated. It fully satisfies the own needs of the plant and is simultaneously a commodity product. For gasification of the Donetsk anthracite with maintenance of organic mass equal to 75 % for production of 1 kg of H_2 about 12 kg of this fuel are required.

Conclusions

For the case when it is necessary to get the maximal amount of hydrogen on the unit of raw material and to generate electric power only for own needs, it has been developed the flowsheet of installation in which practically all of CO is converted and the output of hydrogen is increased. The production of clean hydrogen is fulfilled by diaphragm technology. In this case the expense of coal is about 7 kg per 1 kg of hydrogen, but its prime price is slightly higher because of electric power generation decrease. The described technologies of hydrogen production are low rejects**.** In the gas turbine the cleared fuel is burned at low temperature that provides the minimum output of NO_x, all of sulphurous ingredients are processed in commodity sulphur or sulphuric acid.