International Meeting on Chemical Engineering and Biotechnology

Extracts of Research and Development Lectures

ACHEMASIA '89

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Industrial Coal Chemistry - State of the art and perspectives

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After an introduction to modern coal chemistry covering e.g., coal structures and properties, the most important technologies of coal conversion to chemical raw materials are discussed in detail. Processes delt with include carbonisation, gasification, hydrogenation, plasma pyrolysis as well as hydro pyrolysis of coal.

High-temperature carbonisation (coking) of coal leads to metallurgical coke, coke-oven gas, crude benzene, and coal tar. It is presently the most important technical coal conversion process. The liquid products of coal cracking serve as raw materials for the production of dyestuffs, synthetic polymers, pharmaceuticals, pesticides, carbon black, carbon electrodes and technical graphite.

Ammonia, methanol, oxo-alcohols, acetanhydride, aliphatics (via the Fischer-Tropsch synthesis) are important chemicals made from synthesis gas (CO/H_2), obtained by coal gasification. During the last decade the traditional processes of coal gasification have been further developed. The new "second generation" processes are characterised among other things by the application of higher pressures and temperatures during gasification. For reduction of costs coals covering a wide range of quality are used with the more recently developed processes.

New developments in coal hydrogenation include improvement of the Bergius-Pier process as well as the introduction of "co-processing" techniques. The materials obtained by coal hydrogenation can be used as e.g., motor fuels.

Plasma pyrolysis converts coal to acetylene while hydro pyrolysis leads to aromatic tars. Both types of coal conversion are promising, but they are still in the stage of research projects.

Development of coal conversion technologies in China with special reference to the future of coal liquefaction

Prof.Dr.Gao Jin-sheng; East China Univesity of Chemical Technology

1)Situation of energy supply in China:It is well known that the major energy resource of China is coal, making up 75% of total energy consumption. The other primary resources are crude oil (18%) natural gas (2,5%) and hydro power(4,5%).At present and for times to come there are sensitive problem areas to be considered:

- uneven distribution leading to an overload of the transport system
- coal is rich in ash and about 3o% of coal reserves are rich in sufur (above 2%) thereby leading to severe environmental pollution.
-China has low natural gas reserves and the crude oil tends to become heavier.

This has led to a shortage in energy supply especially in town gas, gasoline and diesel fuel.

2)Status of development in coal conversion technologies:The significant coal concersion technologies in China are combustion followed by coking and gasification.

2a)Combustion of coal makes up 72% of industrial fuel and 92% of domestic fuel.One of the key problems is that thermal effiency is very low for industrial boilers, 5o-6o%, and power generation consumes 4oo -45o g/kWh. However China achieved striking improvements in fluidized bed boilers of which more than 5ooo units of 6 t/h to 13o t/h steam are in operation.

2b)The capacity of coke ovens is about 4o mio t/a but many of the facilities are rather out of date with chamber heights ranging from 2,5 to 4,3 m. The latest development goes for 6,o m ovens with 35,4 m^3 in volume. However, in the countryside a large number of bee-hive ovens are still in operation. Altcgether this results to a rather questionable coke quality.

2c)In 1ooo small scale fertilizer works about 25 mio. t/a anthracite or coke is converted into synthesis gas in old mode water gas generators. The production of low BTU industrial gas and town gas using coal is still very popular. However, a new generation of gasifiers is now under development.

3)Development and perspective of coal liquefaction in China: In the 195os there was in north east China a refinery making lubricants and transport fuels from low temperature carbonisation tar and a F-T synthesis plant.

Since 1979 the national Commission of Science & Technology and other related ministries undertook new projects for the development of coal

liquefaction. The main institutions participating in these projects are: Research Inst. of Coal Chemistry, Beijing ; Reserach Inst of Coal Chemistry of the Academy Sinica, Taiyuan ; Research Inst of Heat & Energy, Anshan ; East China University of Chemical Technology,Shanghai ; Technical University, Taiyuan. Three small pilot units (o,1 t/d) are now operating. Results obtained so far from these units and laboratory scale tests are as follows

-In Comparison with Illinois No.6 coal/USA and Westerholt coal/FRG the conversion and oil yield of Yanzhou coal/China is apparently better.

-Yanzhou coal in continous experiments on o,1 t/d unit yielded a conversion of 92,7% and an oil yield of 66,1 %.

-In cooperation with H.C.Itoh Corp./Japan and HRI/USA the Beijing Coal Chemistry Inst. in 1984 conducted a prefeasibility study based on the H-coal process. The design capacity is 3,73 mio. t/a Yanzhou coal.

Expected products are:

1,3 mio t/a	syncrude
118 ooo t/a	LPG
84 ooo t/a	Sulfur
29 ooo t/a	Ammonia

Based on 1982 prices the investment would have been 2,417 bill. Yuan at a price of 5oo Yuan per ton of syncrude.

And there are further perspectives for coal liquefaction. A so far untapped potential for direct coal liquefaction are the large resources of suitable lignites in the provinces of Nei Mongol and Yunnan. An output of 6o mio. t/a of vacuum refinery residue from petroleum could be the base for large scale coprocessing. Both routes would help to satisfy Chinas growing demand especially for transport fuels.

xperimental Screening for the liquefaction potential of Chinese coals.

rof.Dr. H.H. Oelert, TU-Clausthal

:hina is rich in coal resources and highly dependend on coal as the)utstanding source of energy. Out of a total ROM-production of about bill. t in 1989 more than 9o% is transformed into heat and power.Only ı certain percentage is used for coking and metallurgy or gasification ınd fertilizers. Other technologies might be needed in future for sub- ;tituting other supplies and for chemicals. Transformation of coal in- :o liquids is the most obvious choice.

)ased on cooperative research since 198o this report summarizes some)f the results from screening Chinese coals for their liquefaction)otentials. Coals in China vary from soft brown coal to anthracite)ut only a selected number in the range of 7o - 85 % C(dmf) could so :ar be tested in our project concentrating on lignites from Yunnan and Nei Mongol and some hard coals from different locations in East- to :entral-China.

'or four lignites controlled autoclave experiments were undertaken ınder different conditions and in comparison with lignites from other :ountries. Based on a method developed from a large number of interna- :ional lignites the conversion of Chinese lignites at 41o°C and to some legree 435°C can be precalculated from analytical coal data, and the)il yield from these lignites can be assessed from the H/C-ratio of :he feed coals. Variations of experimental conditions, catalysts and H-transfer reveal different response of Chinese lignites as presented .n detail. Lignites Shengli and Xundian are suitable for liquefaction ıt conversion of 8o% and oil yields up to 6o%. A method is presented :o characterize each lignite in its specific sensitivity versus the ıain process parameters in direct liquefaction.

'or hard coals Yanzhou coal is chosen by Chinese authorities as a kind)f standard for liquefaction. Coordinated experiments at Shanghai- and :lausthal universities are directed to an intensive testing of Yanzhou :oal in liquefaction not only varying process parameters in liquefaction :xperiments but also the nature of slurry oil and catalysts. With pre- ıydrogenated anthracene oil the oil yield from this coal is 59,6% only ;lightly above 57,7% from a process derived light recyle oil but both ;uperior to experiments with the model compound tetralin yielding only 14,4 %. Under set conditions further experiments are directed to the :omparison of 9 different one-way and standard catalysts. Even at only 135°C addition of an optimized mixture of red mud and sulfur compound .eads to an oil yield of more than 5o%. This is also presented in com-)arison with Hainan iron ore taking into account the sensitivity versus

temperature and the transformation of asphaltenes into oils.
The last section of the report is devoted to coprocessing, the combined once-through processing of coal and petroleum refinery residue. This is concentrated on hard coals from Anhui province and vacuum residues from Anqing and Snanghai refineries. In comparison with international standard coals a combination of Pangi coal and vacuum residue from Daqing crude oil gave encouraging results and were chosen for studying the coprocessing potential of Chinese coals and petroleum residues and are presented in detail discussing various influences and options.
In a limited survey based on selected Chinese coals and laboratory experiments the potentials of Chinese resources are demonstrated to be good to excellent in direct coal liquefaction as well as Coprocessing for future technological developments.

D. Behrens, Frankfurt am Main

Hydrogen technology: New Concepts and Research Requirements

A particular challenge on the chemical industry is to supply mankind in the long term with sufficient energy, available anywhere in the world. The generation and storage of energy are closely linked to chemical processes.

The burning of primary fossil energy sources like coal and oil, the desulphurization and denitrification of waste gases where fossil energy sources are burned, the enriching of nuclear fuels and their reprocessing after burn-up in the reactor, the production of photovoltaic solar cells, the storage of energy in electrochemical batteries - ultimately all these are chemical processes which make high demands on chemists in research, development and industry. There is certainly good reason to speak of a "chemistry of energy".

The paper deals with one section of the "chemistry of energy": that of hydrogen technology. The opinion generally held by many experts is that the introduction of a hydrogen economy is no longer a question of principle, but simply one of time and of technological and economic scale. An obvious next step, therefore, is to use practically based pilot projects to test possibilities for gradually introducing hydrogen into large-scale industrial use outside the chemical and petrochemical industries - in other words, as an energy source. The problem is being examined worldwide; the present survey is based on two sources:

In 1986 an expert committee established by DECHEMA (German Society for Chemical Technology and Biotechnology) drew up a comprehensive study on the subject "Hydrogen Technology - Perspectives in Research and Development", which was published by DECHEMA.

In 1986/1987, too, on behalf of the Commission of the European Community, a DECHEMA project group carried out a "Technological and Economic Study of the Production, Intercontinental Transport and Use of Solar Hydrogen", which has been published by the EEC.

The paper will report about results as well as open technical problems and research needs.

Dimerization and Oligomerization of Olefins

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The metal catalyzed oligomerization of olefins is of considerable academic and industrial interest for the synthesis of linear and branched higher monoolefins. The linear olefins are key intermediates for detergents, plasticizers, and a variety of fine chemicals. The branched ones represent potential candidates for improving octane numbers.

Since many years, we are working on the linear oligomerization of olefins. For our catalyst selection square planar nickel complexes containing chelate ligands were chosen [1]. A chelate was selected for the following reasons: exploitation of the chelate effect; selection of distinct structures; impact on redox properties; ease of reductive elimination. This concept has proven quite successful having led to the linear oligomerization of ethene to α-olefins (SHOP-Process) which will be practized in 1990 in 1 mio.t per year by Shell.

In close cooperation, funded by VW foundation (Stiftung Volkswagenwerk), the Dalian and Aachen group extented the chelate concept to $\overset{\frown}{O\ O}$ chelates, such as acetylacetone. Catalysts could be developped which for the first time dimerized olefins such as propene, 1-butene and higher α-olefins to predominantly linear products [2].

Also other metals could be applied. Good results for linear oligomerization of ethene could be obtained with zirconium by Ren He. His results are summarized in the following: The results of ethylene oligomerization under the catalysis of zirconium complexes needs improvements. Though the zirconium Ziegler-Natta system can be used to catalyse the oligomerization of ethylene, the oligomer thus obtained has a wide distribution of products [3].

In He's work lower linear α-olefins (i.e. linear C_4 to C_{10} α-olefins) were prepared by homogeneous oligomerization of ethylene under low pressure using zirconium compounds as catalyst. A binary catalyst composed of $ZrCl_4$ and an organoaluminium compound is one of the simplest system. It was found that organoaluminium compounds of different kinds effect both the activity and selectivity. $ZrCl_4/Et_3Al$ catalyst gives high activity but the oligomers formed are in a wide molecular distribution. $EtAlCl_2$ or $Et_3Al_2Cl_3$ is even a poorer activator than Et_2AlCl. Generally the selectivity for lower linear α-olefins is not satisfactory when a binary catalyst system is employed. It is important to select some suitable reaction conditions such as aging and reaction temperature to obtain lower α-olefins.

A ternary catalyst system consisting of the binary catalyst with the addition of small amounts of third component RONa behaves in a better catalytic manner both in activity (1300 g oligomer/Zr(g)h), and in selectivity ($C_{10}^{=}$ > 85 %, linear α-olefins > 85 %) [4].

The IR spectrum of $ZrCl_4$ and RONa in cyclohexane indicates the existence of a Zr-O bound. Therefore, one can can infer that $ZrCl_{4-n}(RO)_n$ is formed in situ.