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Study on Coal Flash Pyrolysis

Takafumi Kawamura*1 Hiroyuki Kozuru*1
Shigeru Hashimoto*1 Hiroshi Iida*1
Mitsuhiro Sakawa*1 Toshiaki Okuhara*2

Abstract:

The coal flash pyrolysis technology is expected to increase the yield of high-value-added gas and liquid components. The concept of utilization of coal pyrolysis products at steelworks is described as a comprehensive product utilization system. The features of conventional pyrolysis processes are outlined, and requirements for a next-generation pyrolysis process are presented. Also, the effects of pyrolysis reaction conditions (temperature, pressure, and atmosphere gas) on the yield of product gas, tar and char as well as the properties of such products are examined for several coal types, on the basis of basic experiments made by the grid heating method and entrained-bed flash pyrolysis method. The grid heating experiment indicates the temperature-dependence of primary pyrolysis products, with the yield of volatile matter standing about 30% higher than that determined by proximate analysis. In the entrained-bed experiment, the tar yield peaks at 700°C and drops in the high-temperature region owing to secondary pyrolysis. Increasing pressure decreases the tar yield and increases the gas yield. The effect of hydrogen concentration on the BTX yield is also discussed. An entrained-bed coal pyrolysis process is outlined.

1. Introduction

With its abundant reserves and stable supplies, coal will remain an important basic resource for Japan. Its efficient utilization will assume growing importance in the future when we consider the increase in energy consumption, supply limits of fossil resources including oil and natural gas, and the effects of energy use on the global environment. Noble use should be made of such easy-to-use fossil fuels as oil and natural gas as a precious asset for mankind, and earth-friendly technology must be developed in this country of vast energy consumption.

*1 Technical Development Bureau
*2 Technical Development Bureau (presently Nippon Steel Chemical Co., Ltd.)

Technology development has been carried out for the complete gasification, hydrogasification, and liquefaction of coal as fuel gas for electric power generation (IGCC), substitute natural gas (SNG), and liquid fuel. These coal conversion technologies were energetically researched into during the period from the 1970s to the 1980s, but not to the extent of commercial application because of great development difficulties, high investment costs, and low economics involved.

Coal can be used not only as a source of energy but also as a high-value-added raw material for chemicals and carbon-based materials. Effective utilization of coal best suited to its characteristics requires the development of a rational conversion technology for specific purposes. The pyrolysis of coal yields multiple products such as gas, liquid, and char by simply applying heat to coal. Since coal pyrolysis has lower development hurdles and incurs less equipment costs than coal gasification and liquefaction technologies, it has come to be highlighted as a mild gasification technology.

The gas, liquid, and char produced from coal can be used respectively as a fuel and chemical feedstock, as a chemical feedstock and fuel oil, and as a boiler fuel and ironmaking fuel (including reductant). The feasibility of converting these products into commercial products to meet market needs in both quantity and quality is a precondition for the commercialization of the coal pyrolysis process. A comprehensive system must be built whereby these products can be utilized in an effective and balanced way. Of particular importance is the application of coal flash pyrolysis technology from which an increase in the yield of high-value- added gas and liquid components can be expected. The steel industry is expected to provide the most advantageous field for developing a comprehensive utilization system for flash pyrolysis products of coal.

This paper outlines the coal flash pyrolysis process under research at Nippon Steel Corporation.

2. Comprehensive Coal Utilization System by Flash Pyrolysis

Conventional iron and steel-making processes utilized coal mostly in the form of coke charged into blast furnaces and by-products produced from coke manufacture. In recent years, coal utilization has diversified, as typically seen in the spread of pulverized coal injection (PCI) into blast furnaces, addition of coal into basic oxygen furnaces in the scrap steel melting process, and the development of the direct smelting reduction process as a new ironmaking process.

Technology of injecting large amounts of pulverized coal into blast furnaces (from the present rate of 100 kg/t-pig to the future rate of 200 kg/t-pig) and that of melting large amounts of scrap, both under development, will have the effect of lowering the coke rate in the blast furnace operation, reducing the supply of coke-oven gas (COG) to downstream processes, and tightening the supply of tar as a chemical feedstock. The direct smelting reduction process will eliminate the manufacture of coke-oven by-products.

Fig. 1 shows the coal flash pyrolysis process product utilization system as a complex centering on a steelworks and embracing peripheral industries. A COG-equivalent gas from the coal flash pyrolysis process (4,000 to 5,000 kcal/Nm^3) is supplied as a gaseous fuel for the hot and cold rolling processes and for the nearby gas energy-consuming industries. Benzene-toluene-xylene (BTX) and tar liquid components are utilized as chemical feedstocks at the chemical company. Char, a solid product, may be utilized as a substitute for PCI in blast furnaces, as a carbonaceous material in the direct smelting reduction process and scrap melting process, and as a fuel for private electric power generation boilers at the steelworks. It may also be used as a fuel for the thermal power plant operated by the local electric power company.

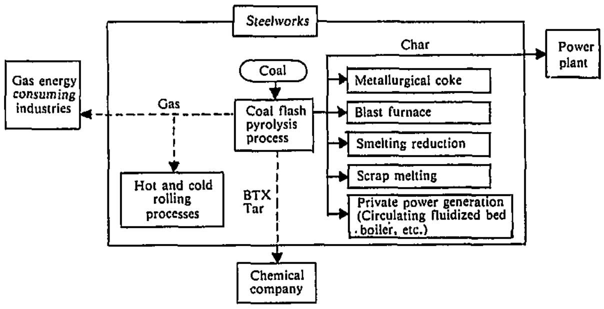

Fig 1 Coal flash pyrolysis process utilization system

3. Conventional Coal Pyrolysis Processes and Requirements of Next-Generation Coal Pyrolysis Process

Several technical points must be considered when commercializing a pyrolysis process for large-volume production of high-value-added gas and liquid from coal. They are how to avoid the agglomeration of coal of high caking property in the pyrolysis process and how to supply the heat required to accomplish the rapid heating of coal.

Representative coal pyrolysis processes developed to date are summarized in **Table 1**. They are the moving-bed (mixing-bed) Lurgi-Ruhrgas process[1], rotary-kiln Toscoal process[2], fluidized-bed COED process[3], fluidized-bed CSIRO process[4], and entrained-bed ORC process[5]. Heat is supplied by heated ceramic balls in the Toscoal process and by combustion heated char in

Table 1 Development of coal pyrolysis processes

Process (Developed by)	Toscoal (Tosco Corp.)	COED (FMC Corp.)	CSIRO (CSIRO, Australia)	ORC (Garrett/Occidental)	Lurgi-Ruhrgas (Lurgi-Ruhrgas)
Reactor type	Rotary kiln	Fluidized bed	Fluidized bed	Entrained bed	Moving bed (mixing bed)
Development period Development scale	1970s 25 t/d	1970s 36 t/d	1984-1985 0.5 t/d	1976-1978 4 t/d	1963 Commercialized
Description	Conversion of oil shale carbonization process; 500°C low-temperature carbonization by ceramic balls heated by combustion of product gas	Four fluidized beds at different temperature levels. Partial oxidation of char by oxygen; Movement and heat supply of hot char to upstream fluidized beds	Two fluidized beds; Generation of hot char by combustion of char in one fluidized bed; Circulation of hot char	Heating of char by combustion, separation of hot char in hot cyclone, and recycle of hot char to reactor. Ratio of recycled char to coal is about 10:1	Mixing and pyrolysis of char heated by combustion and coal in double shaft mixer; Another reaction in mixing bed
Feature Problem	Oil yield of 10% or less; Improvement of low-grade coal	Complex process with multiple fluidized beds; Low yield	Smooth hot charge movement between two fluidized beds	Uniform heating and dispersion of coal in recycle char are problems to be solved before scale-up	Lignite upgrading process; Low liquid yield

the Lurgi-Ruhrgas, COED, CSIRO and ORC processes. The combustion heated char used to supply heat and avoid agglomeration, and can be recycled to a great extent. None of these processes has been commercialized yet, except for the Lurgi-Ruhrgas process that has its aim in improving the lignite quality.

Some processes were developed with the aim of improving coals of low rank, but their development work was suspended for reasons of low gas and liquid yields, great scale-up difficulty, or low applicability (economy) of products obtained. In recent years, IGT, AMAX, and Carbon Fuels, all in the United States, have been developing coal pyrolysis processes in the process development unit (PDU) level. The details of their technologies are not yet known, however.

A next-generation pyrolysis process must:
- Produce high-value-added liquid as chemical feedstocks and gas products with high yields. (The yield of volatile matter can be increased by rapidly heating coal.)
- Produce gas with properties befitting the intended application.
- Be high in thermal efficiency.
- Be able to treat a large amount of coals (or easy to scale up).
- Be able to use many coal types.
- Be low in equipment cost.
- Be free from high development hurdles.
- Be flexible enough to meet the trend of product demand.
- Be environment-friendly (low in impact on environment).

4. Experimental Study of Coal Flash Pyrolysis Reactions

Flash pyrolysis is generally known to be an effective means of extracting large amounts of high-value-added gas and liquid products from coal, and the flash pyrolysis phenomena are aptly dealt with in literature[6-8]. Here are reported the coal flash pyrolysis phenomena by the grid heating method in which the secondary reaction of volatile matter is considered to be low, and the results of experimentation with entrained-bed coal pyrolysis.

4.1 Flash pyrolysis of coal by grid heating method[9]

Using the grid heating method adopted by Anthony et al.[10] and Solomon[11], a flash pyrolysis experiment was conducted in an inert atmosphere at a pyrolysis temperature of 500 to 1,000°C and heating rate of 30 to 300°C/s, and the char, gas and tar products were studied for temperature dependence. Since the volatile matter produced by the primary reaction of coal is liberated and rapidly cooled in the surrounding space, the secondary reaction of primary products of coal pyrolysis is extremely retarded. The grid heating method can thus determine the primary pyrolysis phenomena.

The experimental apparatus consists of a reactor made of glass, as shown in **Fig. 2**. The end of a copper support bar is covered

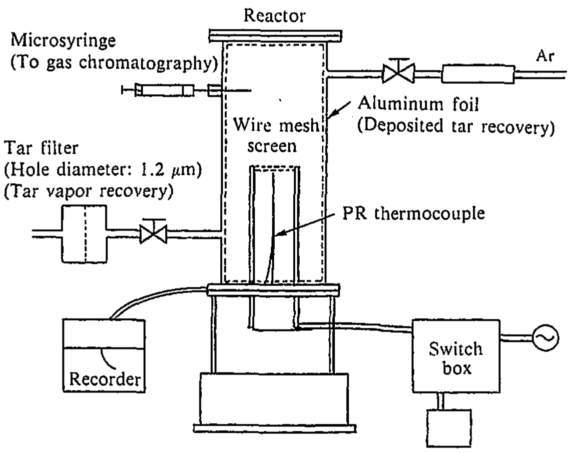

Fig 2 Experimental apparatus for grid heating method

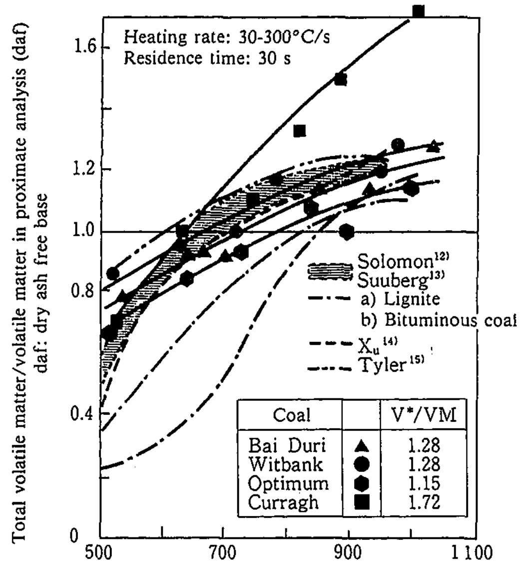

Fig 3 Effect of reaction temperature on total volatile matter yield (grid heating method)

with two stainless steel wire mesh screens, and a 20-mg coal sample is deposited on the stainless steel wire mesh screens and subjected to flash pyrolysis by electric heating. The pyrolysis is conducted in an argon atmosphere, and the temperature is measured with thermocouples across the coal layer. **Table 2** lists the analysis values of the coals used in the experiments.

Fig. 3 shows the effect of the peak pyrolysis temperature at a residence time of 30 s on the total weight loss (tar and gas),

Table 2 Analyses of coals (wt%)

Coal	Proximate analysis				Ultimate analysis				
	Volatile matter	Fixed carbon	Ash	Moisture	C	H	O	N	S
Taiheiyo	48.88	43.12	8.00	5.12	67.57	5.99	17.37	1.00	0.07
Wandoan	45.56	44.57	9.87	8.32	69.91	5.25	14.10	0.76	0.11
Bai Duri	45.35	50.42	4.23	8.41	68.31	4.91	20.39	1.41	0.75
Ikejima	38.19	53.58	8.23	1.42	74.93	4.50	10.11	1.40	0.83
Optimum	33.23	56.56	10.21	2.47	73.83	4.68	8.99	1.78	0.51
Witbank	32.14	59.58	7.88	2.01	76.65	4.96	8.02	1.90	0.59
Curragh	22.15	70.81	7.04	0.90	82.04	4.60	3.98	1.86	0.48

together with the experimental data of other researchers[12-15]. At the peak pyrolysis temperatures of 600 to 800°C, the total weight loss of each coal type exceeds the amount of volatile matter (VM) in the proximate analysis data. (The volatile matter (VM) equivalent liberation temperature is 725°C for Bai Duri, 775°C for Optimum, 650°C for Witbank, and 620°C for Curragh.) The ratio of the ultimate amount of pyrolysis (V*) to the volatile matter (VM) in the proximate analysis data at 1000°C for 30 s is 1.28 for Bai Duri and Witbank, 1.15 for Optimum, and 1.72 for Curragh. The increase of volatile matter yield (V*) from the proximate analysis data (VM)is about 30% or less, except for the low-volatile Curragh coal.

Anthony et al.[8] compiled the results of rapid heating experiments conducted by many researchers, and reported that the V*/VM ratio at a heating rate of 600 to 50,000°C/s and temperature of about 1,000°C falls within the range from 0.75 to 1.36 with most data exceeding 1.0. In the present experiment made at the heating rate of 300°C, the volatile matter yield differed little from that obtained at 300°C-plus heating rates. This means that beyond 300°C/s or thereabout the difference of heating rate has little effect on the volatile matter yield.

The effects of reaction temperature on the tar yield and gas yield are as shown in **Figs. 4** and **5**, respectively. The tar generation is almost constant at 500°C and over, except for Curragh. This indicates that tar forms mostly at low temperatures. The gas yield increases with increasing temperature, and the high-volatile Bai Duri coal produces the largest amount of gas. The coal samples are different in the forming of gas components but are very similar in the pattern in which gas components form at different temperatures. Saturated hydrocarbons CH_4 and C_2H_6 are generated in increasing amounts at 500 to 700°C, and unsaturated hydrocarbon C_2H_4 increases at 700°C and over. The H_2 and CO generation in increases at 700 to 900°C, while the CO_2 generation in increases at 600°C and lower. This is related to the fact that a particular functional group in each coal is decomposed and liberated at a certain temperature level.

4.2 Entrained-bed coal flash pyrolysis experiment[16]

The entrained-bed pyrolysis experimental apparatus (coal feed rates of 5 kg/h and 100 g/h) illustrated in **Fig. 6** was used to relate the entrained-bed pyrolysis reaction conditions to the product yields and to study the feasibility of the entrained-bed process.

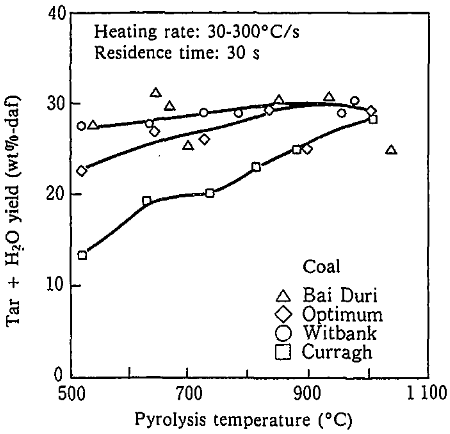

Fig 4 Effect of reaction temperature on tar yield (grid heating method)

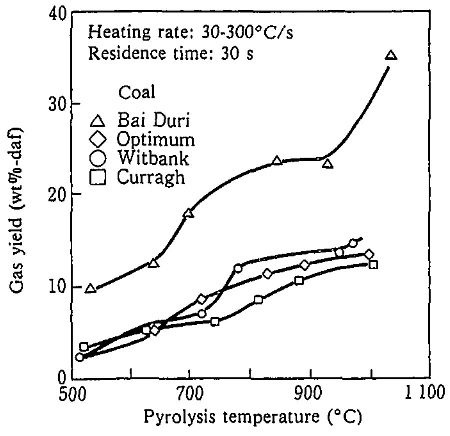

Fig 5 Effect of reaction temperature on gas yield (grid heating method)

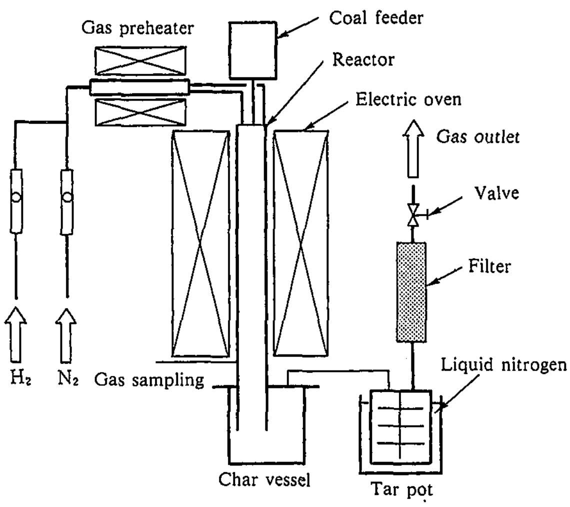

Fig 6 Experimental apparatus for entrained-bed flash pyrolysis of coal

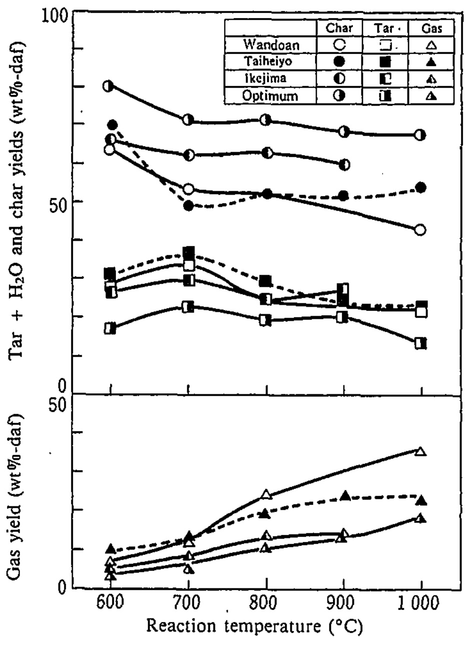

Fig 7 Effects of reaction temperature on char, tar, and gas yields (entrained-bed experiment)

The experimental conditions are a reaction temperature of 600 to 1,000°C, reaction pressure of 1 to 10 atm, and gas residence time of 2 s. The hydrogen concentration of the atmosphere, presumed to have the greatest effect on the properties of products, was changed from 0 to 75% and studied for changes in its effect. **Table 2** lists the analysis values of the coal samples used.

Fig. 7 shows the effects of reaction temperature on the char, tar, and gas yields in an nitrogen atmosphere at the atmospheric pressure. The char yield decreases with increasing temperature until reaches the vicinity of 50% at 700°C or over for Wandoan and Taiheiyo, both being subbituminous coals. Beyond the 700°C level, the reaction temperature-dependence of the char yield is not so large. The tar yield peaks at about 700°C and decreases with further increasing temperature for each type of coal. The tar yield increases with increasing volatile matter and exceeds 30% for subbituminous coals. The gas yield increases with increasing temperature. As is evident when compared with the results of the grid heating experiment without secondary pyrolysis reaction, gasification proceeds through the secondary pyrolysis reaction of tar in the high-temperature region. Also, increasing the gas residence time obviously decreases the tar yield and increases the gas yield.

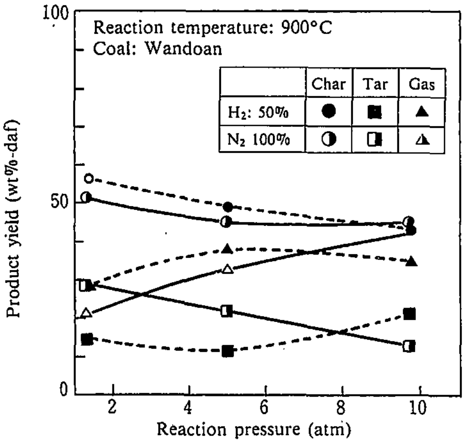

Fig 8 Effect of reaction pressure on product yield

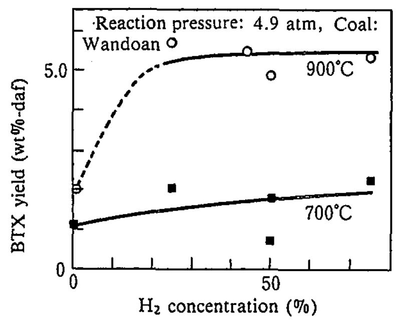

Fig 9 Effect of hydrogen concentration on BTX yield

The effect of the reaction pressure on the product yield at 900°C is shown in **Fig. 8**. As the reaction pressure increases, the tar yield decreases, and the gas yield increases. The effect of the reaction pressure appears to increase as the reaction temperature increases.

Fig. 9 shows the effect of hydrogen concentration on BTX generation. At the reaction temperature of 700°C, the BTX yield slightly increases with increasing hydrogen concentration. At 900°C, on the other hand, a BTX yield 2.5 times higher than obtainable in an nitrogen atmosphere is obtained when the hydrogen concentration is 25% or over. This suggests that, at high temperatures, partial hydrogenation proceeds where the hydrogen concentration is above a certain level. When the BTX composition is broken down by temperature, the benzene concentration is about 40% at 700°C and increases to nearly 80% at 900°C. These data clearly show that the methyl groups of toluene and xylene are liberated at high temperatures.

The gas composition is high in hydrocarbons at a low temperature of 600°C but in hydrogen and carbon monoxide at a high 1,000°C.

Mass spectra of tar produced from the flash pyrolysis of the

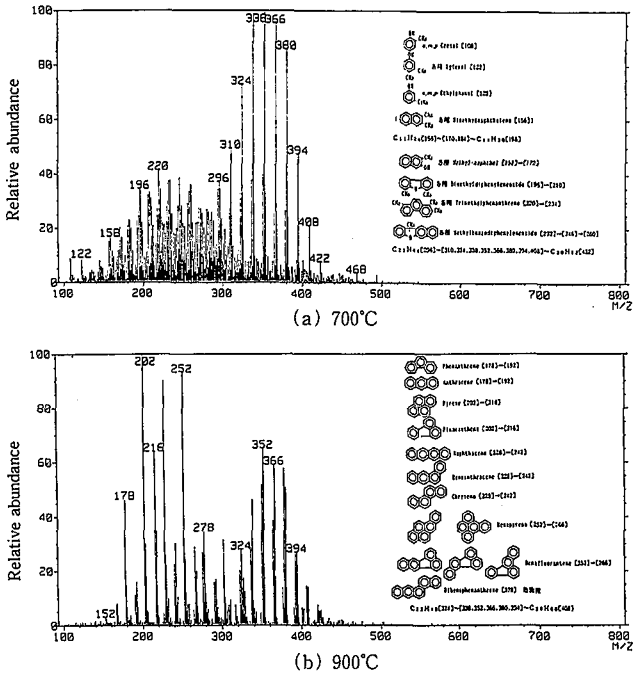

Fig 10 Mass spectra of tar produced from flash pyrolysis of Wandoan coal

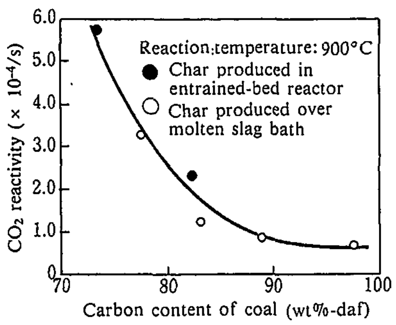

Fig 11 CO_2 reactivity of char

Wandoan coal are shown in **Fig. 10**. The low-temperature (700°C) tar contains extremely large amounts of side-chain compounds, indicating that secondary pyrolysis is yet to be advanced. The properties of the tar at the high temperature of 900°C are close to those of coke-oven tar with a small amount of alkyl side chains.

The CO_2 reactivity of char produced from the flash pyrolysis of coal was measured by thermorgravimetric analysis (TGA). **Fig. 11** shows the relationship between the carbon content of coal and the CO_2 reactivity of char under 900°C CO_2 reaction conditions. The CO_2 reactivity of char produced over a molten slag bath (char rapidly heated at 1,400°C)[17] is included. The CO_2 reactivity of char strongly depends on the carbon content of the parent coal, and is high when produced from a coal of low carbon content. The coals used for pyrolysis are generally high-volatile sub-bituminous and bituminous coals. The char produced from the flash pyrolysis of such coals is high in CO_2 reactivity.

5. Concept of Next-Generation Flash Pyrolysis Process

The entrained-bed coal flash pyrolysis technology has a high possibility of growing into a process that will offer a high yield of volatile matter, be easy to scale up, and be able to handle a wide variety of coals. To convert liquid products into high-value-added chemical feedstocks, the most desirable method is to transfer the hydrogen atoms of coal into liquid products in the reactor, instead of introducing hydrogen from outside the system.

An example of process flow is shown in **Fig. 12**.

Coal is injected into the high-temperature gas produced by the partial oxidation of char or gas produced and is put to the flash pyrolysis reaction. The formed char is separated in a hot cyclone, and its heat is recovered. Some of the char is partially oxidized by oxygen to supply heat for the reaction involved. The rest of the char is utilized as a fuel for electric power generation or iron production. Heat is recovered by oil flushing, for example, from the gas stream from the hot cyclone, containing gas and liquid products. Liquid products are recovered from the gas stream by water flushing, for instance. Heavy liquid products that condense in the heat recovery step can be recycled to the pyrolysis reactor and treated again there. The gas is removed of BTX, sulfur, ammonia, and other components in the gas treatment system before it is used as a fuel. To raise the hydrogen concentration in the pyrolysis reactor, the product gas is recycled to the partial oxidation furnace if required.

Among possible development themes are the gasification of char, injection of coal into the pyrolysis reactor, separation of hot char, and recovery of heat. Conventional technologies can be best utilized in these developments.

6. Conclusions

Coal flash pyrolysis will become the most economical coal conversion technology if a system is developed to utilize the flash pyrolysis products of coal. The authors intend to commercialize the process as early as possible through further basic research and process realization research.

References

1) Rammler, R.W. et al.: Energy Progress. 2, 121 (1982)
2) Carlson, F.B. et al.: Clean Fuels from Coal Symp., Chicago, 1975, IGT, p. 495
3) Jones, J.F. et al.: Clean Fuels from Coal Symp., Chicago, 1975, IGT, p. 323
4) Smith, I.W. et al.: Oil from Coal by Flash Pyrolysis End of Grand Report, 1985
5) Occidental Research Corp.: Final Report on DOE Contract No. EX-76-C-01-2244, 1979
6) Wen, C.Y. et al.: Coal Conversion Technology. Addison-Wesley, 1979, p. 57
7) Gavalas, G.R.: Coal Pyrolysis. Elsevier, 1982
8) Anthony, D.B. et al.: AIchE J. 22, 625 (1976)
9) Kawamura, T. et al.: CAMP-ISIJ. 2, 1049 (1989)
10) Anthony, D.B. et al.: 15th Symp. (Intern.) on Combustion, 1974, The Combustion Institute, p. 1303
11) Solomon, P.R.: 17th Symp. (Intern.) on Combustion, 1978, The Combustion Institute, p. 131
12) Solomon, P.R.: Rep. NSF/RA-770442, NTISPB278496/AS, 1977
13) Suuberg, E.M. et al.: 17th Symp. (Intern.) on Combustion, 1978, The Combustion Institute, p. 117
14) Xu, W.C. et al.: Fuel. 66, 632 (1987)
15) Tyler, R.J.: Fuel. 59, 219 (1980)
16) Kozuru, H. et al.: Intern. Conf. on Coal Science, Newcastle-upon-Tyne, September 1991, p. 624
17) Kawamura, T. et al.: Tetsu-to-Hagané. 78 (3), 360 (1992)

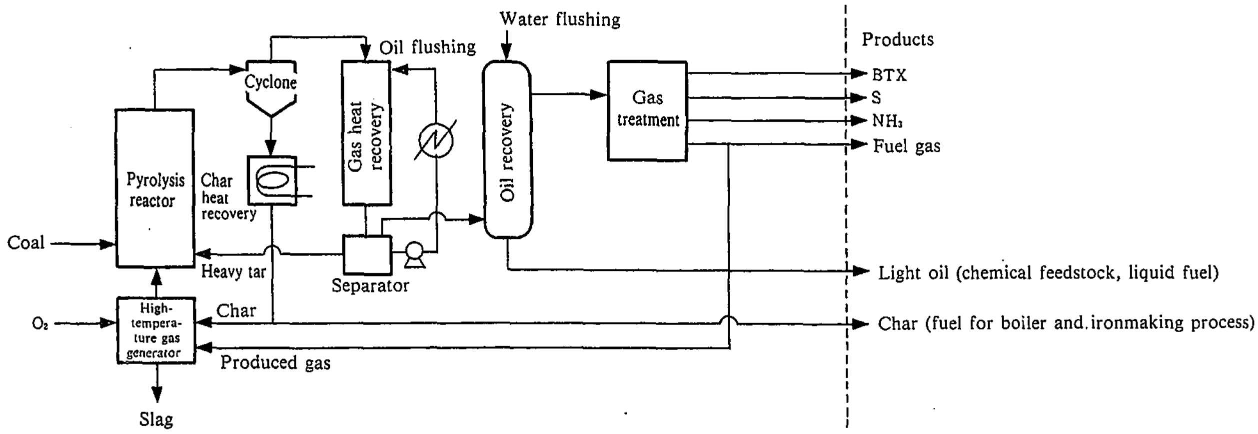

Fig 12 Coal flash pyrolysis process flow