

Development of Coal Partial Hydrolysis Process

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Abstract

Coal partial hydrolysis process aims at co-production of high yield of light oil and synthesis gas from a low rank coal under a mild hydrolysis condition. The characteristic of this process is in the hydrolysis reactor composed of the reformer and gasifier. So far, in order to evaluate the process concept a small-scale basic experiment and a 1t/d process development unit study were carried out. The experimental results showed that coal volatiles were partially hydrogenated to increase the light oil and hydrocarbon gases at the condition of partial hydrolysis. This process has a possibility of producing efficiently and economically liquid and gas products as chemicals and fuel for power generation. As a further development, a 20t/d pilot plant study called ECOPRO has been started to establish the process technologies for commercialization.

1. Introduction

Coal is the most abundant energy source on the Earth, and because of its economical advantages, it is presently used worldwide as one of the important primary energy sources. Its consumption is expected to continue to grow with the increase in the world's population and the improvement of the quality of life mainly in developing countries. Coal still accounts for about 20% of the primary energy sources for Japan, and its importance will not decrease in the near future.

On the other hand, problems relating to the global environment, such as global warming caused by CO₂ emissions, constitute a serious concern to the whole of mankind. In this sense, because coal undoubtedly places enormous loads on our environment with its emissions of greenhouse gases, there is a serious attempt to establish and develop technologies that enable its clean and efficient use. These technologies are often referred to as clean coal technologies. It should be noted that various coal conversion technologies have been devel-

oped in Japan and other countries. Such technologies include integrated coal gasification combined cycle (IGCC) power generation aiming at enhancing power generation efficiency and environmental friendliness of coal, direct coal liquefaction aiming at producing transportation fuels, and coal hydrogasification aiming at producing substitute natural gas (SNG).

Coal Flash Partial Hydrolysis Technology, proposed by the authors as one of such technologies, is a new coal conversion technology that subjects pulverized coal to instantaneous pyrolysis reactions in a hydrogen atmosphere under a prescribed pressure of 2 to 3 MPa. This process, which utilize only one reaction furnace, co-produces synthetic gas, which is usable as a power generation fuel, and a chemical material, and light oil, which are also usable as fuels, and a chemical material, with high efficiency. Unlike the coal hydrogasification technology^{1,2)}, which is a conventional method, the proposed technology does not require very severe processing conditions, such as high pressures, high temperatures and high hydrogen concentrations as required for the conversion of coal mainly

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into methane. For this reason, the technology allows for simpler equipment configurations, reduced operating costs by reducing hydrogen consumption and improved processing efficiency.

The authors have already established a coal flash pyrolysis process. That is a multi-purpose coal conversion process named CPX^{3,4}. CPX is a low-pressure process mainly intended for use in steel works to produce COG-substitution gas, tar and char. On the other hand, the newly proposed process uses a high pressures, and therefore, the product gas is expected to have wider applicability while the product liquid is expected to have higher added value because of the lighter oil components.

Table 1 shows the development schedule of the proposed process. Preliminary studies began in 1996, basic tests on a small-scale test facility in 1997, and thereafter, verification tests were applied to the reactions on a process development unit (PDU) in 1999. Based on the test results, studies on a pilot plant for the purpose of technical evaluation with a view to commercial application began in December, 2003.

The object of this paper is to explain the basic concept of the Coal Flash Partial Hydrolysis Technology, the results of the research and development of the technology done so far and the future plans for its commercial application.

Table 1 Development schedule

	1995	2000	2005
1) Preliminary study	↔ (1996-1998)		
2) Small-scale basic experiment	↔ (1997-1999)		
3) PDU study (1t/d)		↔ (1999-2002)	
4) Pilot plant study (20/d)			↔ (2003-2008)

2. Process Outline

Fig. 1 shows the overall flow of the process of the subject technology. In a partial oxidizer, which forms the lower part of a partial hydrolysis reactor, pulverized coal and recycled char are gasified by oxygen and steam under a pressure of 2 to 3 MPa and a temperature of 1,500 to 1,600°C into high-temperature gases composed mainly of CO and H₂. Pulverized coal is injected also at a reformer, which connects to the partial oxidizer through a throat, together with recycled H₂ into the high-temperature gases from the partial oxidizer. Instantaneously, and reforming reactions (partial hydrolysis reactions) are completed under a pressure of 2 to 3 MPa, at a temperature of 700 to 900°C. Hydrogen concentration was 30 to 50% (the sum of the H₂ in the high-temperature gas and the recycled H₂). Here, the high-temperature gases from the partial oxidizer serve also as the source of the heat required for the reactions that take place in the reformer. The hydrolysis reactions to transfer H into the primary pyrolysis products such as tar that are devolatilized from the pulverized coal proceed in situ at the reformer. The heavy tar is then converted into light oils.

The mixture of the gases, light oils and char having formed in the partial hydrolysis reactor pass through a cyclone separator to separate char, then heat exchangers to recover sensible heat and gas treatment facilities to separate the oils and remove sulfur. Thus, syngas is finally obtained. A part of the syngas is converted into hydrogen-rich gas through shift conversion reactions and CO₂ removal, and after preheating through heat exchange with the syngas from the reformer, the hydrogen-rich gas is recycled to the reformer of the partial hydrolysis reactor. The final product syngas is a hydrogen-rich gas composed mainly of H₂, CO and CH₄ and having a H₂/CO ratio approximately of 1, and is usable as a fuel or raw material for IGCC, gas-to-liquid (GTL) conversion and chemical processes. The light oils consist mainly of mono- or bicyclic aromatic compounds such as benzene and naphthalene, and are usable as a chemical raw material or a power plant fuel.

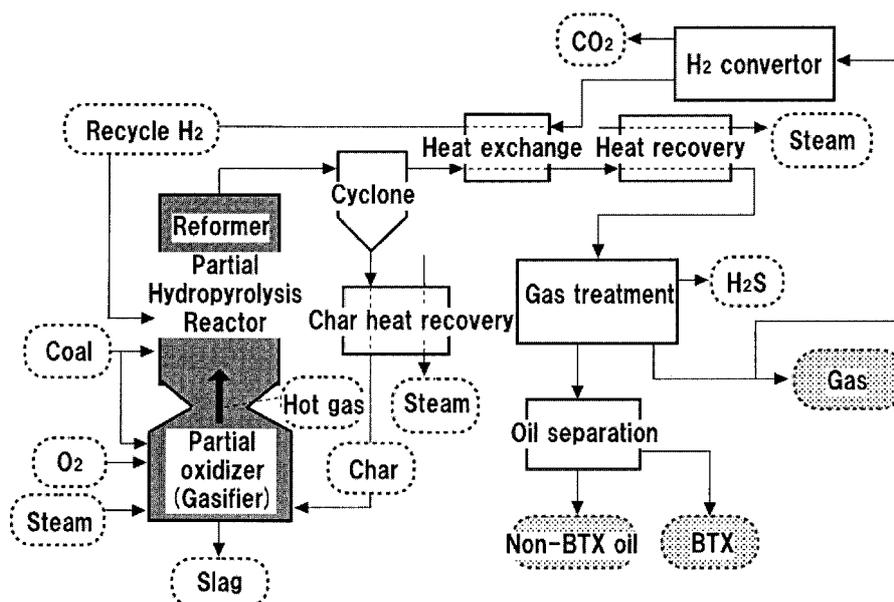


Fig. 1 Process flow diagram of coal partial hydrolysis

3. Fundamental Tests on Small-scale Test Equipment^{5,6)}

3.1 Object

For clarifying the yields and properties of the pyrolysis products obtained under the comparatively mild reaction conditions of the hydrolysis atmosphere envisaged in the subject technology, fundamental tests were carried out using an up-flow, continuous-coal-feeding type test pyrolysis reactor.

3.2 Test method

Fig. 2 shows the outline of the test equipment. The reactor is an up-flow type tubular gas reactor having a heating zone 60 cm in length. Pulverized coal is fed into it continuously through a feeder at a rate of 0.5 g/min together with reaction gas that contains 0 to 100% hydrogen and is preheated to approximately 500°C, and the coal is cracked under prescribed processing conditions at a pressure of between 0.3 to 3.0 MPa, a temperature from 700 to 870°C, and a gas residence time of 1 s. From the pyrolysis product, which is a mixture of char, oil and gas, char is separated and recovered by a char collector, oil by a liquid collector (cold trap), and a part of the gas by a gas bag. Removed properties were analyzed. Tanito Harum coal sample (Indonesian subbituminous coal), known as a low-grade coal, was used in this experiment. Table 2 shows the analysis results of the coal.

3.3 Results and discussion

As examples of the test results, Fig. 3 shows the effects of the hydrogen concentration (0 to 100%) of the pyrolysis atmosphere on the yields (carbon conversion rates) of the pyrolysis products. The temperature was 870°C, and the pressure was 3.0 MPa.

The total yield of gases composed of CO, CO₂, CH₄, C₂H₆ and C₂H₄ increased with increasing hydrogen concentration, but whereas the yields of CH₄ and C₂H₆ tended to increase, those of CO, CO₂ and C₂H₄ showed a tendency to decrease. Besides the above components, C₃H₆ formed by a small amount (less than 1%) when the hydrogen concentration was 0 and 20% (not shown in the graph). The total yield of liquid, which consisted of benzene, toluene, xylene (BTX) and non-BTX oils, decreased with increasing hydrogen concentration, but whereas the yield of BTX increased, that of non-BTX

oils decreased. The yield of char decreased markedly from the level with 0% hydrogen as the hydrogen amount increased. This seems to indicate that the re-polymerization of unstable radicals having formed through the pyrolysis into char was suppressed even under the conditions of the mildly hydrogenating atmosphere.

Among the pyrolysis product components (BTX, CH₄ and C₂H₆) the yields of which increased with increasing hydrogen concentration, CH₄ showed an especially large yield increase. However, their yield increase in the hydrogen concentration range from 50 to 100% was smaller than that in the range from 0 to 50%. This seems to

Table 2 Analyses of coal (Tanito Harum)

Proximate analysis [wt%]				
Moisture	Volatile matter	Fixed carbon	Ash	
3.8	45.4	48.2	2.7	
Ultimate analysis [wt%-daf]				
C	H	N	S	O
76.4	5.6	1.8	0.1	16.2

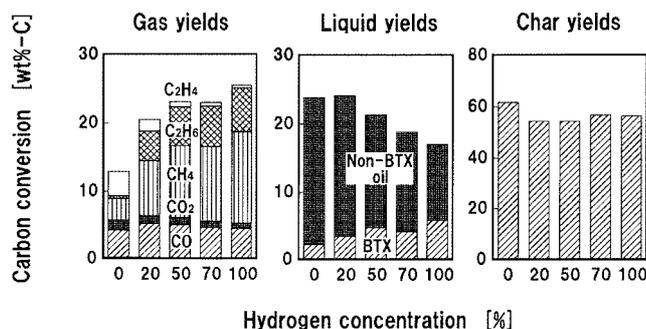


Fig. 3 Effect of hydrogen concentration on product yields

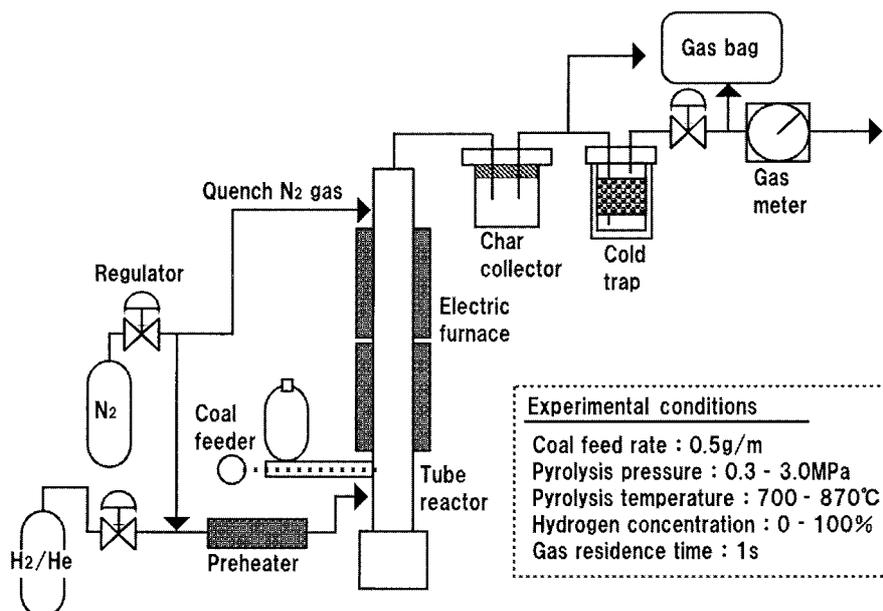


Fig. 2 Laboratory-scale experimental apparatus

indicate that the influence of hydrogen concentration on the yield increase is not significant when the hydrogen concentration is at a certain level or more. It should be noted that mass spectrometry of non-BTX oil components revealed that the molecular weight distribution of the oils decreased as the hydrogen concentration increased. This indicates that the product oils tended to become lighter.

These test results made it clear that the hydrolysis reactions of coal proceeded sufficiently well even under the comparatively mild reaction conditions envisaged in the subject technology, contributing to the production of light liquid oils and the increase in the yields of saturated hydrocarbon gasses (CH_4 and C_2H_6). It can be presumed from the above that a high hydrogen concentration (meaning a high hydrogen consumption), which leads to a cost increase in commercial operation, is not necessarily required for increasing the yields especially of light oils such as BTX.

4. Tests on Process Development Unit⁷⁾

4.1 Object

For clarifying the reaction characteristics of the core equipment of the subject technology, namely the partial hydrolysis reactor composed of a reformer and a partial oxidizer, process verification tests were carried out using a 1-t/d process development unit (PDU).

4.2 Test method

Fig. 4 shows the process flow diagram of the PDU, and Photo 1 is an overall view thereof. Pulverized coal injected through burners together with oxygen into the partial oxidizer, which constitutes the lower part of the partial hydrolysis reactor, gasifies (partially oxidizes or partially burns) at high temperatures of 1,550 to 1,650°C and converts that into gasified gas composed of H_2 , CO , CO_2 and H_2O . Ash in the coal melts at the gasification to form molten slag, and is discharged through a slag tap at the reactor bottom. For preventing the tap from clogging with slag, it is heated with a slag tap burner.

The high-temperature gasified gas having formed in the partial oxidizer goes immediately through the throat to the reformer, where

pulverized coal is injected through coal nozzles into the gas. Thus, the coal and gas undergo hydrolysis and reform using the sensible heat of the gasified gas. In hydrogen addition tests, hydrogen is injected into the reformer through the coal nozzles together with the pulverized coal. The product discharged from the reformer, which is a mixture of the gasified gas from the partial oxidizer and gas, oils and char forming in the reformer, is cooled through a double-tube, water-jacket type gas cooler, rid of char through cyclone separators, and cooled and dedusted through a venturi scrubber. The gas finally obtained is burned through a flare stack. A part of the gas is extracted after the second-stage cyclone separator and cooled through cold traps, which are indirectly cooled with liquid nitrogen, to condense the oils contained therein. The oils are recovered as samples for analysis.

The cycle time of the PDU test operation was approximately 10 hours at the longest including approximately 2 hours each for raising



Photo 1 Experimental apparatus (1t/d PDU)

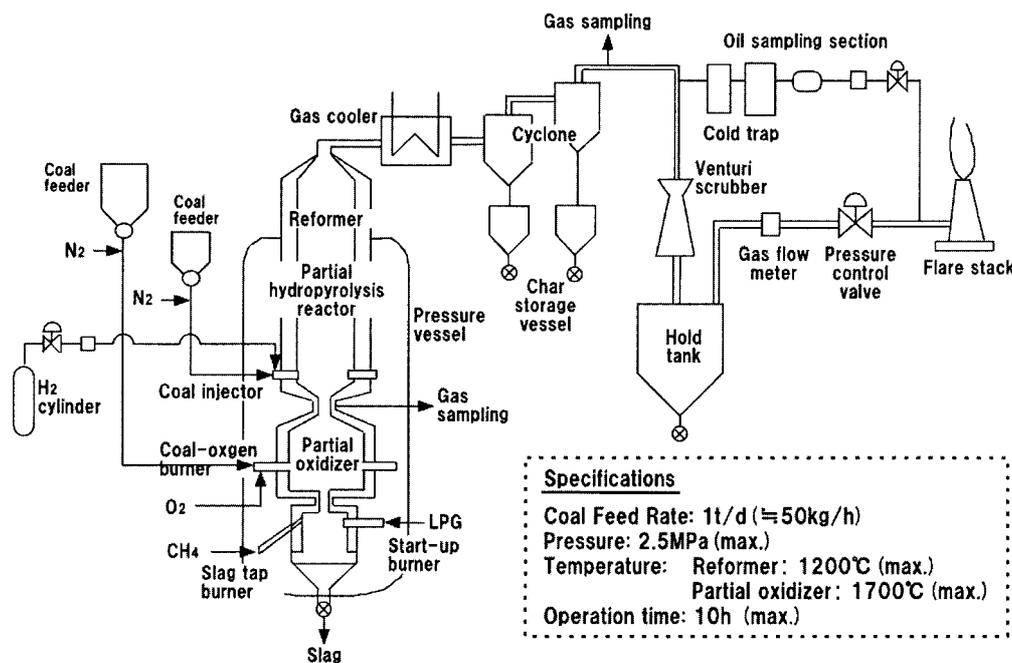


Fig. 4 Experimental apparatus (1t/d PDU)

Table 3 Experimental conditions (1t/d PDU)

CASE	1	2
Reformer		
Coal	Tanito Harum	Tanito Harum
Pressure [MPa]	2.0	2.0
Temperature [°C]	700-800	900-950
Hydrogen concentration [%]	31	33
Gas residence time [s]	2	2
Gasifier		
Coal	Tanito Harum	Tanito Harum
Pressure [MPa]	2.0	2.0
Temperature [°C]	1,550-1,650	1,550-1,650
Gas residence time [s]	2	2

and lowering of the pressure. Gases were sampled from the throat between the partial oxidizer and reformer, the middle of the reformer and after the second-stage cyclone separator for composition analysis by gas chromatography. The char and oils separated at the cyclone separators and the cold traps, respectively, were discharged after the end of each test operation cycle for analyses (proximate analysis and ultimate analysis for the char, and element analysis, composition analysis, distillation analysis by gas chromatography, etc. for the oils).

Table 3 shows the test conditions. The change of the yields of the products of the coal pyrolysis reaction in the reformer was studied by changing the reformer temperature in cases 1 and 2. The Tanito Harum coal was used as the feed stock also for the tests at this stage.

4.3 Results and discussion

Fig. 5 shows the yields of the products of the pyrolysis reactions in the reformer in terms of the carbon conversion rates on the amount of coal injected into the reformer. The yield of CO and CH₄ increased with the higher temperatures; the increase in the yield of CO was especially conspicuous. Whereas hydrocarbon gases other than CH₄, namely C₂H₆ and C₂H₄, formed in case 1, they did not form in case 2 where the reformer temperature was higher. As for the yields of liquid oils, while that of BTX increased with higher temperature, that of non-BTX oils decreased instead, which seems to indicate that they converted into lighter oils. Incidentally, it was confirmed by the authors that the non-BTX oils cease to form at yet higher reformer temperatures (approximately 1,050°C), almost all of them converting into gases.

Most of the BTX obtained was benzene, and the amounts of tolu-

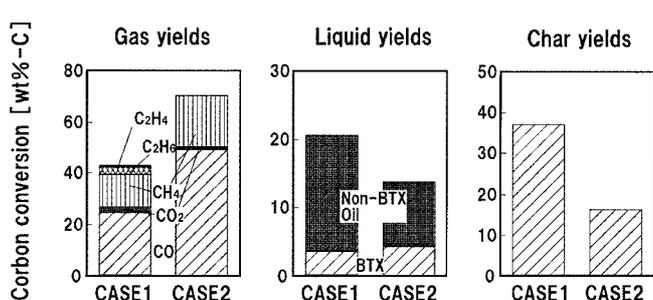


Fig. 5 Product yields at the reformer

ene and xylene were insignificant. The yield of char decreased with higher reformer temperature, and the decrease in the char yield nearly corresponded to the increase in the CO yield explained earlier. This seems to indicate that the gasification reactions of char to form CO ($C + H_2O \rightarrow CO + H_2$ and $C + CO_2 \rightarrow 2CO$) take place also in the reformer, pronouncedly especially in case 2 where the temperature is higher.

Fig. 6 shows the distillation curve of the non-BTX oils recovered in case 1 by distillation analysis. Compared with common tar from coke ovens, the oils obtained through the test generally had lower boiling temperatures: distillates at 360°C or lower accounting for 90% or higher. This indicates that the oils consisted mainly of light components. The flat portion of the curve a little above 200°C corresponds to the distillation of naphthalene, providing evidence that the oils of the subject technology contain a high concentration of naphthalene, which has an especially high added value among various components of tar. The composition analysis of the oils showed that the content of an isomer, methyl naphthalene, which coexists with naphthalene in a high percentage in common coke oven tar, was very low. One can presume from this that the side chains (methyl radicals) of naphthalene were cut off during the hydrolysis process. Judging from the fact that the amounts of coexisting isomers are small, the subject technology is expected to have an advantage of low processing loads in the processes of naphthalene separation and refining when the technology is commercially applied.

Fig. 7 shows the coal gasification (partial oxidation) performance of the partial oxidizer. While the results differ slightly depending on the operating conditions, such as the temperature and coal feeding rate, it was possible to stably produce gas containing H₂ and CO by approximately 70% in total on a N₂-free basis, virtually at a carbon

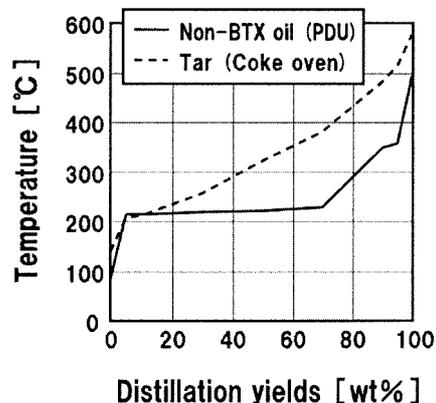


Fig. 6 Distillation curve of non-BTX oil

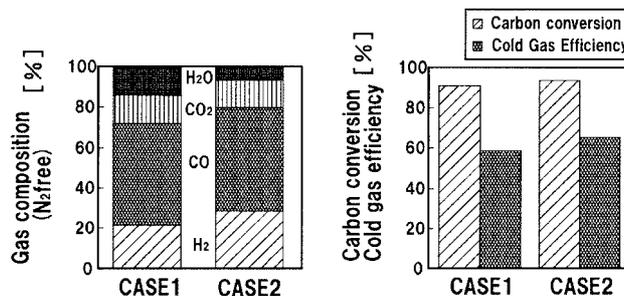


Fig. 7 Performance of the partial oxidizer

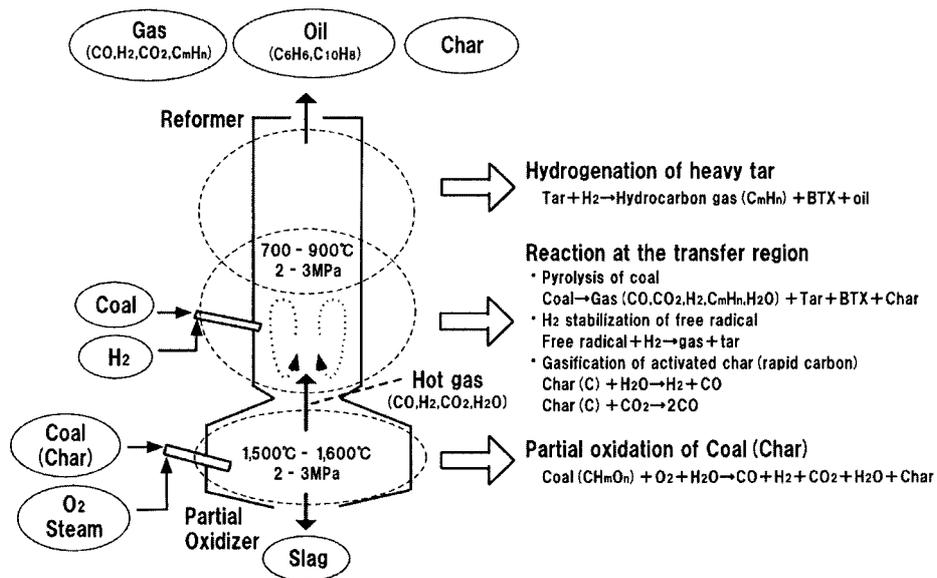


Fig. 8 Reaction mechanism in the partial hydrolysis reactor

conversion rate of 90% or higher and a cold gas efficiency of approximately 60%. Although the average temperature of the partial oxidizer, which functions also to supply heat to the reformer, was set as high as 1,600°C in the PDU tests to maximize the coal feeding rate into the reformer, a lower gasification temperature would not pose any practical problem in relation to ash melting temperature. A lower gasification temperature will make it possible to further increase cold gas efficiency.

Fig. 8 schematically shows the reaction mechanism in the partial hydrolysis reactor estimated based on the results of the PDU tests. The high-temperature gasified gas, which forms in the partial oxidizer through the gasification of coal by oxygen, goes immediately to the reformer, in which coal is injected together with hydrogen into the high-temperature gasified gas, and the injected coal undergoes hydrolysis, namely the flash pyrolysis of coal and the stabilization of unstable radicals by hydrogen. In the reactor zone, called a transfer region, where the high-temperature gasified gas and the injected coal first react with each other, extremely active char, or rapid carbon, will form⁸⁻¹⁰⁾ and stay there. As a consequence, char gasification reactions, or the reactions of char with steam or CO₂ contained in the gasified gas, are presumed to proceed in spite of the comparatively low temperature.

Heavy tar (or volatile matter) discharged from the transfer region converts at the upper part of the reactor into lighter oils and partially gases through further hydrolysis. For maintaining the above functions of the partial hydrolysis reactor at a high level, it is essential to adequately control the conditions of the transfer region, as is true with CPX.

5. Prospect of Commercial Application

Fig. 9 shows the process balance of a commercial plant of the subject technology having a coal processing capacity of 1000 t/d, estimated based on the results of the tests described above. In the case where the char is recovered and all the recovered char is recycled to the partial oxidizer, it is possible to produce 61,000 Nm³/h of gas and 3 t/h of light oils as final products. The product gas is a

medium-calorie gas composed mainly of H₂ and CO, containing a small amount of CH₄. The energy conversion efficiency, corresponding to the cold gas efficiency, defined by equation 1 is estimated to be as high as 88%, by far surpassing the same of conventionally proposed coal conversion technologies.

Energy conversion efficiency (defined on a low heating value basis) = Calorific value of products (gas and light oils) / Calorific value of coal × 100 ... (1)

Fig. 10 shows examples of the applications of the pyrolysis products of the subject process. Different from conventional coal gasification processes, the process is capable of co-producing gas and light oils using one plant, and its products have wide applications. For instance, the product gas is a high-pressure gas, and as such, is usable as a fuel for high-efficiency, combined-cycle power generation (IGCC) or a raw material for synthesizing methanol, dimethyl ether (DME), etc. The light oils can be used as a high-value-added chemical material for producing a variety of aromatic chemicals. When combined with gas power generation, for example, the process allows reduction of power generation costs with the profit from the sale of the light oils.

The subject process is promising also in the application to a power plant that has to cope with the fluctuation of power demands. That is to say, using of the product gas for the base-load power generation and the easily stocked light oils for coping with peak power demands will make it possible to follow the daily fluctuation of power demands without having to turn down the operation of the coal conversion plant, which leads to a significant decrease in the efficiency⁵⁾.

6. Test on Pilot Plant (ECOPRO)

For solving various problems related to the commercial application of the subject technology, a 6-year research study began in fiscal year (April to March) 2003 using a pilot plant having a coal processing capacity of 20 t/d. This stage of study, nicknamed ECOPRO after Efficient Co-production with Coal Flash Partial Hydrolysis Technology, is being carried out jointly by the Japan Coal Energy Center (JCOAL), the National Institute of Advanced Industrial Sci-

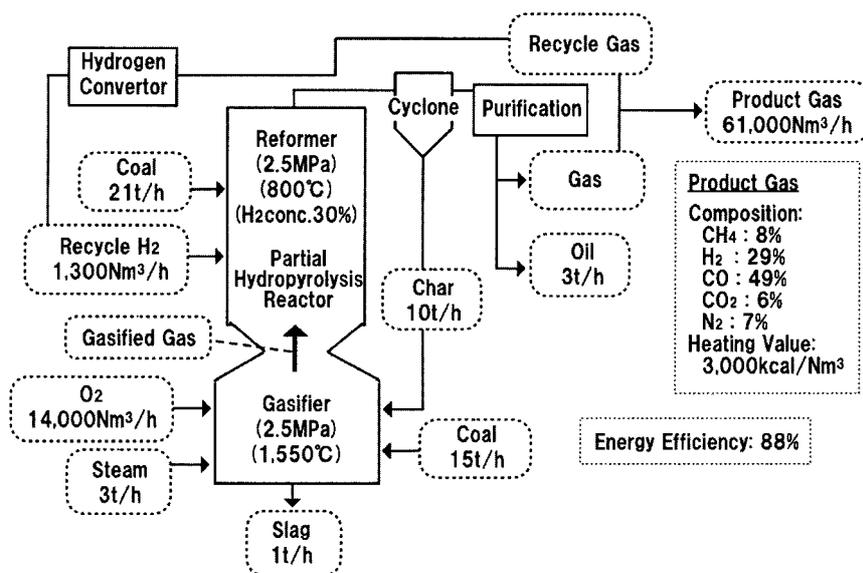


Fig. 9 Estimated yields in commercial full scale plant

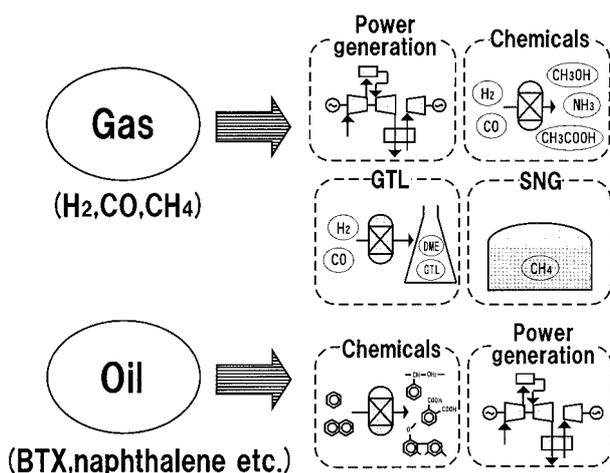


Fig. 10 Product utilization

Table 4 Technical issues

Technical issues	Contents
Verification of the reaction in the partial hydrolysis reactor	-Quantification of reaction in the reactor such as hydrolysis and gasification -Establishment of reactor conditions for optimum transfer region
Evaluation of the additional key process technologies	-Establishment of technologies for char recycle and heat recovery
Evaluation of total system and estimation of a full-scale commercial plant	-Establishment of long stable operation technology -Confirmation of scale-up factor for demonstration unit design

ence and Technology (AIST), Babcock-Hitachi K.K., Mitsubishi Chemical Corp. and Nippon Steel, under the auspices of the Agency for Natural Resources and Energy, and the Ministry of Economy, Trade and Industry. The design and construction of the pilot plant, which will be built in the premises of Nippon Steel's Yawata Works, will be completed by the end of March, 2006. Its operation technologies will be developed in fiscal years 2006 to 2007, and researches of peripheral technologies will be carried out in parallel using the 1t/day PDU and simulations. The subjects of the studies at this stage are listed in Table 4.

The target operation parameters of a commercial plant having a coal processing capacity of 2000 t/d, estimated based on the results of the pilot plant tests and aimed at in the pilot plant tests, are as follows.

- Energy efficiency defined by equation 1: 85% or more in terms of low heating value
Target for the pilot plant: 78% or higher
- Liquid product ratio to feed stock coal (dry and ash-free): 8 wt%

Target for the pilot plant: 5 wt%

- Liquid product properties: the light and medium oil distillates having a boiling temperature of 360°C or lower accounting for 80% or higher
- Economical efficiency: the product syngas being price-competitive at present and in the near future against similar gasses for the same applications

7. Closing

The coal flash partial hydrolysis technology is capable of co-producing high-value-added gas and liquid products efficiently and economically making the most of the reaction characteristics of coal. The technology is expected to dramatically improve the total efficiency of energy utilization by materializing coal-based interdisciplinary business encompassing the electric power generation, chemical and steel industries.

The authors intend to actively contribute to the smooth progress of the pilot plant test (ECOPRO) to solve the technical problems and accelerate the commercialization of this technology.

Acknowledgement

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