

CHAPTER 1

GENERAL INTRODUCTION

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1.1 Significance of Coal in the Future Energy Supply

The growth of economy will depend largely on the development of its energy intensive industries. The energy consumption in the world is 7845 Mtoe (Million ton oil equivalent) in 1991 while it will be 11560 Mtoe in 2010¹⁾. It can be expected that a tremendous amount of energy is needed to support the growth of economy in the future²⁾. The problem what is our sufficient fuel for the future must be asked. The world energy composition in 1997 is listed in Table 1-1. It can be seen that oil, coal and natural gas are still main energy sources in the world.

Table 1-1 Energy composition in the world (1997)

Fuel resource	Oil	Coal	Natural gas	Nuclear energy	Hydropower
Composition %	39.5	27.0	23.5	7.4	2.6

World total resources of fossil fuels are shown in Table 1-2. Oil, the easy to be used fuel, has a consumption rate of 24.4 billion barrels/year while optimistic stock is only 997 billion barrels. That is to say, oil will be used up in just about 41 years. Recoverable reserve of natural gas is estimated to be 138 Gm³ and will be exhausted in 56 years³⁾. Some other fuels such as nuclear power, solar energy can not meet our increasing needs for the future energy supply because of some reasons of technologies, resource limitation and so on.

Coal is an abundant fuel resource worldwide, as shown in Table 1-2, with a historically stable price. The use of coal will increase, particularly in developing countries that have large coal reserves. A recent analysis from IEA1994¹⁾ has shown

Table 1-2 World total resources of fossil fuels

Energy	Quantity ($T \times 10^6$, except for natural gas)	Energy content	
		$J \times 10^8$	(%of world total)
Crude oil	257500	11134	2.8
Natural gas	$281743 \times 10^9 \text{ m}^3$	10509	2.6
Oil shale	2511600(as oil)	108502	26.9
Tar	364155(as bitumen)	15746	3.9
Peat	222378	1861	0.5
Coal	11769779	255246	63.3
Total		403098	100.0

that worldwide consumption of electricity from fossil fuels reached 63.0%. A net increase in the actual fossil energy component is predicted to reach 7500 TWh despite its drop to 58.3% of overall share of total electricity consumption by the year 2000. Among fossil fuels, the consumption of electricity from coal-based power plants is expected to increase from 39.5% of the total electricity consumption in 1987 to 5700 TWh, or 44.3% of electricity consumption by the year of 2000. These figures show that coal will remain as the largest single energy source for power generation, in spite of a projected increase in the nuclear based power generating capacity. Coal is the most abundant and widely dispersed fossil energy resource with an estimated worldwide production to reserve ratio of 238 years. Therefore it can be projected that coal will mainly fuel the world energy requirement in the middle of the coming century.

China is the largest coal producer and consumer in the world. Coal has played an important role in China's social and economic development. In 1994, China had 1947 state-owned coal mines and 67000 town/village-owned coal mines. The total

production in 1994 was 1240Mt accounting for 27.9% of world total⁴⁾. The Chinese estimated proven coal reserves at the end of 1993 were 1002Gt, in which bituminous coal accounted for 75%, anthracite 12% and lignite 13%. Steam coal accounted for 83% of the total reserves, coking and gas coals for 17%. Table 1-3 shows coal consumption during 1980-1994⁵⁾.

Table 1-3 Coal Consumption Mix (%) in China (1980-1994)

Consumer	1980	1985	1990	1992	1994
Power generation	20.37	20.15	25.78	29.33	31.17
Coking	10.95	8.95	10.14	9.89	10.85
Other Industries	41.11	43.38	41.34	42.05	42.23
Domestic & Commerce	19.72	20.05	16.83	13.80	10.95
Railway	3.16	2.83	2.05	1.65	1.45
Farming	2.54	2.71	1.99	1.55	1.35
Others	1.78	1.73	1.87	1.73	1.97
Total	100.00	100.00	100.00	100.00	100.00

The faster economic growth has brought along the development of the energy industry. China has become the second largest energy producer and consumer in the world after the USA. Coal is the most important energy resource in China and accounts for about three-quarters of China's primary energy consumption. The total primary energy production increased at an average annual rate of 3.6% from 1991 to 1995⁶⁾. The total primary energy consumption increased from 987 Mtce (million tonnes of coal equivalent) in 1990 to 1395 Mtce in 1996. The total consumption in 1994 was 1227 Mtce, in which coal shared 75%⁷⁾. At a GDP growth rate of 8-9%, the total primary energy consumption will increase to 1700-1900 Mtce by the year of 2000. Energy conservation and efficiency improvement has thus become important factors for China's sustainable development⁸⁾.

Japan has become a big economic country since 1980's and now has also become the 4th largest energy consuming country. In 1994, the General Energy Research Committee (GREC) reported that Japanese economic growth would increase at a rate of 3.5%/year from 1994 to 2000, followed by a rate 2.5%/year to 2010. Corresponding to future energy supply, the long-term outlook of the GREC projected an average annual increase in energy demand of over 0.9%/year from 1992 to 2010. Total primary energy requirements in 2010 will thus range from 735-800 Mtoe. Publicly supplied electricity generation is projected to rise from 788 TWh in 1992 to 946 TWh in 2000 and 1133 TWh in 2010. The targets for fuel share in 2010 are nuclear 42%, coal 15%, LNG 21%, hydro 11%, oil 10% and other fuel 1%. However, the Central Electricity Council projected that coal's share of the total generating mix would increase to over 20% in 2002, the coal import demand to more than double in 2002, and the coal consumption could rise to 72.5 Mt in 2002. Coal-fired generating capacity is expected to more than double over the next ten years. Overall thermal coal demand is likely to range 8 and 12 Mt/year, and the coal demand from the chemical, pulp, paper and other industries will range from 4 to 8 Mt over the period to 2010. Total coal demand is projected to range from 114 to 139 Mt in 2000 and 108 to 148 Mt in 2010.

Coal utilization for power generation usually brings on issues and problems which impact on environment since coal is a complex compound including pernicious elements and compounds. Accompanying with coal utilization, emissions such as SO_x , NO_x , CO_2 , fine particles and pernicious trace elements will let out. These emissions pollute the atmosphere, water and soil. Recently, acid rain has been found in many countries and it has become a global problem. The acid rain is threatening not only the economic development but also ecological balance of the world. Recently the global greenhouse effect due to excessive release of CO_2 is also an urgent problem. Therefore,

how to effectively and cleanly use coal at a competitive cost is today' task in many countries of the world. It seems that this task is particularly significant for those nations where coal is either abundant or deficient, for example, China and Japan. The development of advanced coal-based power generation systems as clean coal technologies for future energy supply is an urgent research topic in the world.

1.2 Advanced Coal-Based Power Generation Technologies and Environmental Aspects

Coal as an energy resource can be divided into two broad categories. One is direct burning in boiler to provide heat for direct heating, warm water and steam for power generation. The other is converting coal into gaseous fuel or liquid fuel to provide more efficient and clean use.

There have been some coal-fired power generation systems in recent years; the overall basis is a traditional power station in which a pulverized coal-fired boiler(PC) with flue gas treatment supplies steam to a dedicated turbo-generator set. The major developed and developing advanced coal power generation systems are described under main group headings as follows:

- (1) Fluidized bed combustion (FBC) featuring combustion of coal for steam turbine system for power generation, which includes bubbling fluidized bed (BFB) combustion, circulating fluidized bed (CFBC) combustion;
- (2) Pressurized Fluidized Bed Combustion (PFBC) combined cycle systems;
- (3) Integrated gasification combined cycle (IGCC) systems featuring conversion of coal to fuel gas followed by gas cleaning and combined cycle gas turbine/steam turbine system for power generation;

1.2.1 Fluidized Bed Combustion Technologies

Test on FBC of coal by bubbling bed was first started in England in 1960s and then in many countries. Crushed coal with under about 20mm size is fed together with crushed limestone or dolomite to a fluidized bed furnace, which has heat transfer tubes and a bed material – usually silica sand and limestone. The furnace temperature is controlled at 800-900°C.

The advantages of FBC are summarized as follows:

- (1) Limestone and dolomite are decomposed at an adequate temperature to form reactive CaO and MgO that absorbed SO₂ and SO₃;
- (2) The low combustion temperature prevents the damage of the furnace and the fusion of ash;
- (3) Coals with low melting point ashes can be used;
- (4) A low-grade coal can be burned because of the presence of the hot bed material.
- (5) A high heat efficiency can be expected because the hot bed material contacts with the tubes;

The major disadvantages summarized are as follows:

- (1) A large amount of limestone or dolomite, 3-4 times of the stoichiometry, is required to remove 80-90% of SO₂;
- (2) The combustion efficiency tends to be less than 95% because of the large coal size;
- (3) The boiler requires a large floor space, because the gas velocity is 1-3 m/s and much smaller than 10-15 m/s with a conventional boiler;
- (4) The gas pressure drop in the boiler is large because of the content of large amounts of bed material;
- (5) Erosion of the tubes contacting the bed material;

FBC has bubbling and circulating bed types. Both techniques have atmospheric and pressurized systems.

Bubbling FBC boilers are with a capacity of larger than 50ton/h. Most of these use 3-5 mol CaO to 1mol SO₂ to remove 50-80% of SO₂ and maintain NO_x below 200ppm. Coal combustion efficiency runs 85-90%. Some of them use carbon burn-up cell to increase the efficiency above 95%. Recently, a 350Mwe unit has been commercialized at Takehara of Japan¹²⁾.

A development in boiler practice, which has shown itself to be capable of meeting stringent standard for gaseous emissions¹³⁻¹⁴⁾ is the circulating fluidized bed system developed by Ahlstorm, Battelle, Deutsche Babcock, Foster-Wheeler, Lurgi and others. The maximum unit size of CFBC boiler has not yet reached 300MWe for hard coal. A unit rated at 125MWe, which has an unusually large furnace chamber, is in operation with peat firing in Finland¹⁵⁾. A 150Mwe hard coal unit is in operation at the Texas-New Mexico facility in the USA and a further hard coal unit rated at 165MWe is under construction at Point Aconi in Canada¹⁶⁾.

CFBC has advantages over conventional pulverized coal-fired boiler, such as the elimination of DeSOx plant by in-furnace DeSOx, smaller required equipment space, wide-ranging coal selection and upgraded economics. Operation efficiency is slight greater, by 0.3 to 0.5 percentage points than that obtained for the equivalent conventional pulverized coal-fired boiler system. However a higher calcium to sulfur ratio, 2:1 for CFBC systems as compared with 1:1 for FGD systems, is required to achieve 90% sulfur capture in this system. No saleable gypsum is produced and there is substantially greater production of residue. Disposal of residue from plants using a high sulfur fuel can also present problems.

1.2.2 PFBC combined cycles

Most advanced in this field is the bubbling bed version developed by ABB Carbon and others, with three commercial scale installations in operation. Although pressurized versions of circulating bed systems are under intensive development by Ahlstorm, Deutsche Babcock and Lurgi, none of these was considered to have a sufficiently mature stage.

Pressurized operation is arranged by enclosing the fluidized bed combustion and hot gas cleaning cyclones within a pressure vessel. Combustion air is supplied to the vessel from the compressor of suitable gas turbine and hot gases, after removal of particulates in a staged cyclone system, are returned to the engine to drive the turbine. This design is typical of gas turbine practice and eliminates any requirement for the use of refractory materials. In addition to the advantage of high cycle efficiency (about 45%) made it possible by its application in combined cycle operation, a PFBC boiler is substantially smaller than a conventional pulverized coal-fired boiler because of high-pressured operation resulting in increased combustion intensity. Heat release per unit of bed area is therefore much greater in pressurized system. With the high sulfur fuel, there is a significant increase in limestone consumption and residue production. Separately saleable sulfur or gypsum are not produced so that disposal of residues could be a problem.

1.2.2 IGCC systems

IGCC power generation uses coal gasification, followed by gas cleanup, to provide a fuel for a gas turbine. The hot exhaust gases from the gas turbine are used to generate steam, which is used, together with steam raised in gasification process, to generate additional electricity in a steam turbine.

IGCC results in the following advantages:

- (1) the potential for high cycle efficiencies;

- (2) low emissions of SO_x, NO_x, and particulates;
- (3) reduced water demand;
- (4) high cycle efficiency, which results in reduced CO₂ emissions per unit of power output relative to conventional coal fired plant.

Table 1-4 is a comparison of environmental aspects among IGCC, PFBC and pulverized coal-fired boiler. It is evident that IGCC has a greater superiority than pulverized coal-fired boiler and PFBC in the case of environmental technologies.

Table1-4 Comparison of environmental aspects among pulverized coal-fired boiler, PFBC and IGCC

	Efficiency [%]	SO _x [mg/MJ]	NO _x [mg/MJ]	Dust [mg/MJ]
PC	38-41	1634	516	43
PFBC	38-42	1505	172	34
IGCC	42-48	8	22	2

Different gasifiers produce slags and ashes with differing physical and chemical properties. The nature of the slag or ash depends both on process features and the type of coal used. The design of gasification reactors differs widely. Three main types are available:

- (1) moving bed systems: Lurgi (dry ash), British Gas/Lurgi (slagging);
- (2) fluidized bed systems: British Coal, HTW, KRW and U-gas;
- (3) entrained flow systems: Dow, GSP, NEDO, PRENFLO, Shell, Texaco, and VEW which are shown in Figure 1-1.

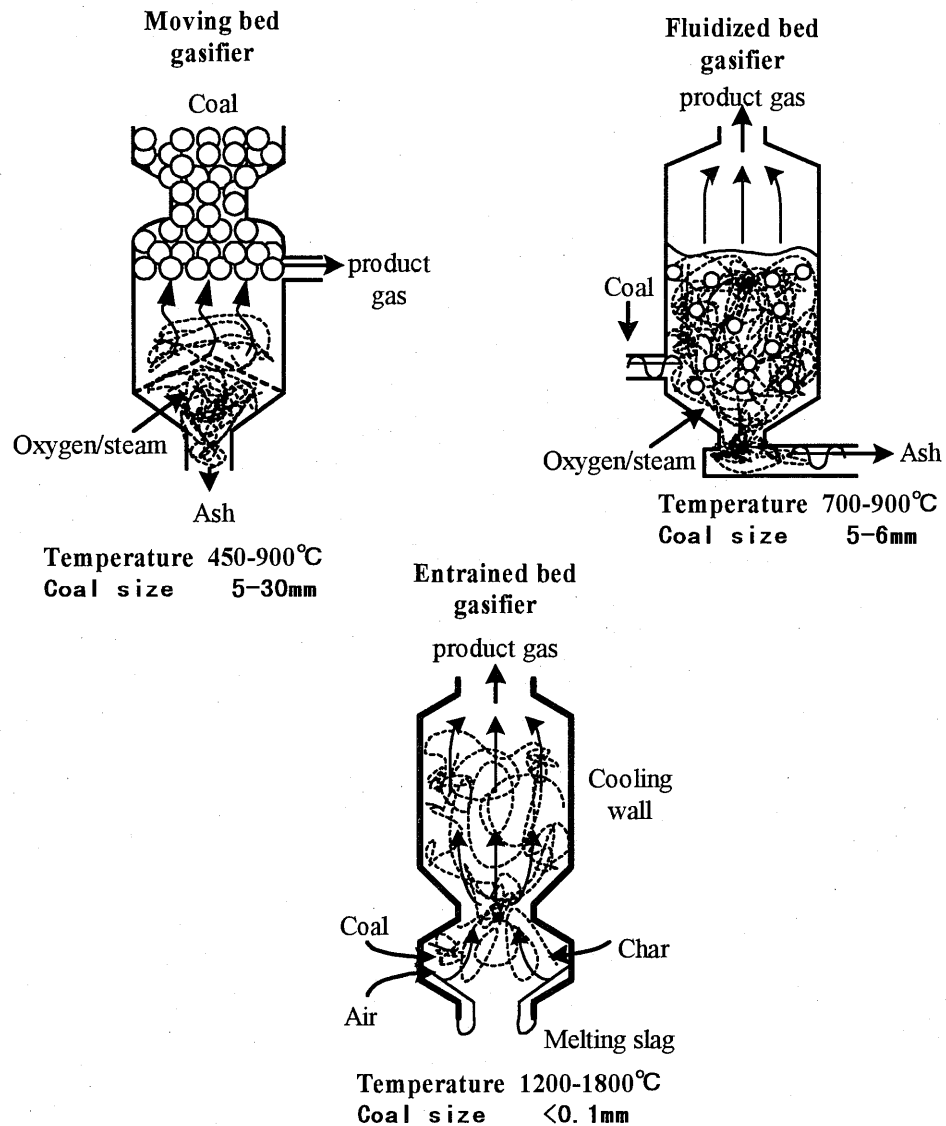


Fig.1-1 Main types of gasification process

Among these systems, a Lurgi fixed bed system and Texaco single stage wet feed entrained flow system had each been applied to commercial scale demonstration plants by utilities in Germany and the USA, respectively. The two stage wet feed entrained flow system developed by Dow was also used for internal power generation by the company on commercial scale at its large chemical plant complex in Louisiana. A further plant based on the single stage dry feed entrained flow system developed by

Shell had been designed by Demkolec in the Netherlands.

Fluidized bed gasifier must be operated at temperatures that do not cause ash fusion, and therefore it is operated at lower temperatures than slagging gasifiers. The gasifier residues from these lower temperature processes are either ash or partially agglomerated ash. Fluidized bed process which could scaled up to commercial IGCC operation includes the HTW, KRW and U-gas processes.

In slagging gasifiers the mineral matter in coal is melted and extracted as molten slag, usually at temperatures above 1350°C. The slag is then solidified and collected. Slagging gasifier systems which are at or near commercial-scale operation include the British Gas/Lurgi (BGL), Dow, Gaskombinat Schwarze Pumpe(GSP), Krupp Koppers Pressurized Entrained Flow(PRENFLO), Shell and Texaco processes.

In Japan, fluidized bed gasification was tested at the Yubari 40t/day-coal pilot plant from 1980 to 1987, and air blown entrained bed coal gasification tested at the Nakoso 200t/day-coal pilot plant in the 5 years from 1991 by the IGCC Research Association.

China has completed the pre-feasibility and engineering studies for a 200-400 MWe IGCC demonstration power plant. It has proposed to construct an IGCC demonstration power plant mainly by introducing foreign advanced technology to China. However, the ash agglomerating coal gasifier developed by Institute of Coal chemistry, Chinese Academy of Sciences (ICC,CAS) for IGCC system is near commercial-scale operation.

The temperatures in most fluidized bed gasification systems are not high enough to permit high carbon conversion, so that the residues from gasification process have a high carbon content char that should be withdrawn and burned in external boiler to raise steam to generate additional electricity. In addition, by products: ash and /or slag particles, sorbents and fluxes added to the coal and

desulfurization products also need to be treated before disposal. Therefore, it is reasonably proposed that the concept of the hybrid combined cycle systems as shown in Figure 1-2.

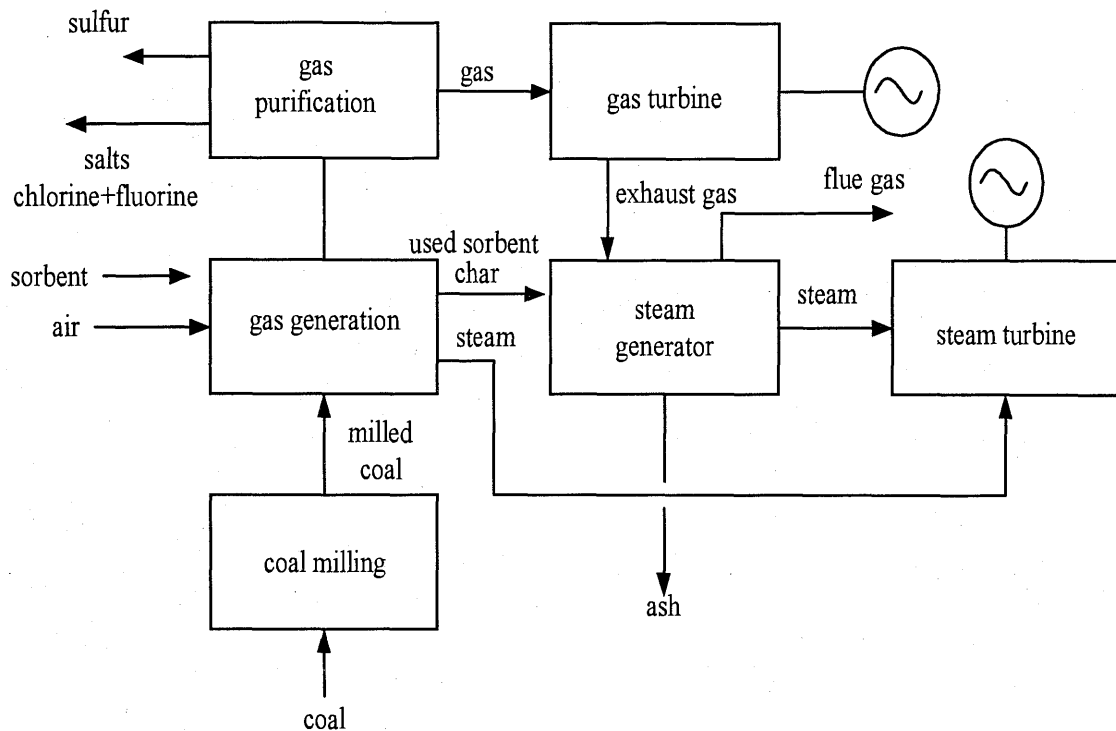


Fig.1-2 Hybrid combined cycle flow diagram

which incorporate partial coal gasification, fuel gas combustion in a gas turbine and combustion of residual char in a boiler for steam raising.

As shown in Figure 1-2, there involve some types of gasification stage, which is used to provide a cleaned fuel gas for the combustion turbine. Initial designs were based on relatively simple devolatilization of the coal for this purpose although more recent proposals involve some degree of gasification to increase carbon conversion and obtain enhanced performance. In all cases residual char from the gasification stage, possibly augmented by additional raw coal, is used as fuel for steam raising in a suitable char burn up stage. Therefore, besides carrying on the advantages of IGCC,

the hybrid combined cycle system has advantages of high carbon utility efficiency, excellent environmental performance, smaller quantity of solid residue, lower water consumption and capability of phased construction.

1.3 Development of Hybrid Combined Cycle

The concept of the hybrid combined cycle, or topping cycles, was first proposed as a means to overcome the limitations imposed on maximum cycle temperature that is found in basic PFBC combined cycles, mentioned above.

More recent design proposals have tended toward greater separation of the two-fuel streams¹⁷⁾. In this way, gas-cleaning requirements would be eased and clean fuel gas alone used to power the combustion turbine. Similarly the heat released from the solid residue that is recovered from the gasification stage is used exclusively for steam raising. Several designs propose the use of exhaust gas from the combustion turbine, which has a substantial oxygen content, as preheated forced draught combustion air for the char combustor. However, since this gas is slightly vitiated, supplementary air supplied by means of a forced draft fan may also be required in order to ensure high combustion efficiency. In some designs, heat exchangers alone are used to recover heat from the gas turbine exhaust and provision is made for a completely independent air supply for char combustion.

Continued development of the hybrid cycle approach has shown other potential advantages. For example, high carbon conversion in the primary gasifier may be less critical to overall system performance that is the case in IGCC systems. The use of steam in the gasification stage is also minimized and this brings additional advantages of reduced heat losses due to latent heat of water vapor in the product gas.

Provided only that enough fuel gas could be produced from the coal to ensure

correct operating conditions for the gas turbine, sole responsibility for efficient carbon conversion would not rest on the gasifier alone. The design and operating conditions of the gasification stage may therefore be less stringent than those required for IGCC systems. Against this, the combustion stage seems likely to produce a sulfated residue that could present disposal problems similar to those facing fluidized combustion systems. While the systems may not meet strict criteria for near term application, substantial development has taken place.

Recently A-PFBC technology has been developed to further improve PFBC plant efficiency in developed countries. Known as the PFBC topping cycle, this system features a high gas turbine inlet temperature. Advanced PFBC is currently being developed by a team of companies led by Foster Wheeler Development Corporation and funded by US DOE. British Coal Corporation in conjunction with GEC Alsthom and PowerGen, have worked on a Topping cycle linking a pressurized fluidized bed gasifier with a PFBC boiler. Early versions of the design used a PFBC unit for char combustion, although more recent designs have an atmospheric CFBC unit¹⁸⁻¹⁹).

In Japan, an original Japanese system had been selected based on the result of studies of various types by the A-PFBC R&D committee consisting of NEDO, the Center for Coal Utilization, Japan (CCUJ), academic circles and utilities as shown in Figure 1-3. This system, also known as a series type system, has several advantages such as system simplification by in-furnace DeSO_x and elimination of the complex topping combustor, higher plant efficiency (42-48%) through use of a gas turbine of a 1300°C class or more, USC steam condition and lower auxiliary power consumption. There also is the advantage of early commercialization due to the use of commercial or demonstration-stage technology.

Basic tests have been under way since 1995. Based on an evaluation of the

conceptual design and elemental test results, the Electric Power Development Co., Ltd. (EPDC) is in charge of R&D on the process development unit (PDU), which has a capacity of 15t/day-coal from 1996. The A-PFBC test operation by the PDU is planning during 2 years from 2001 to 2002.

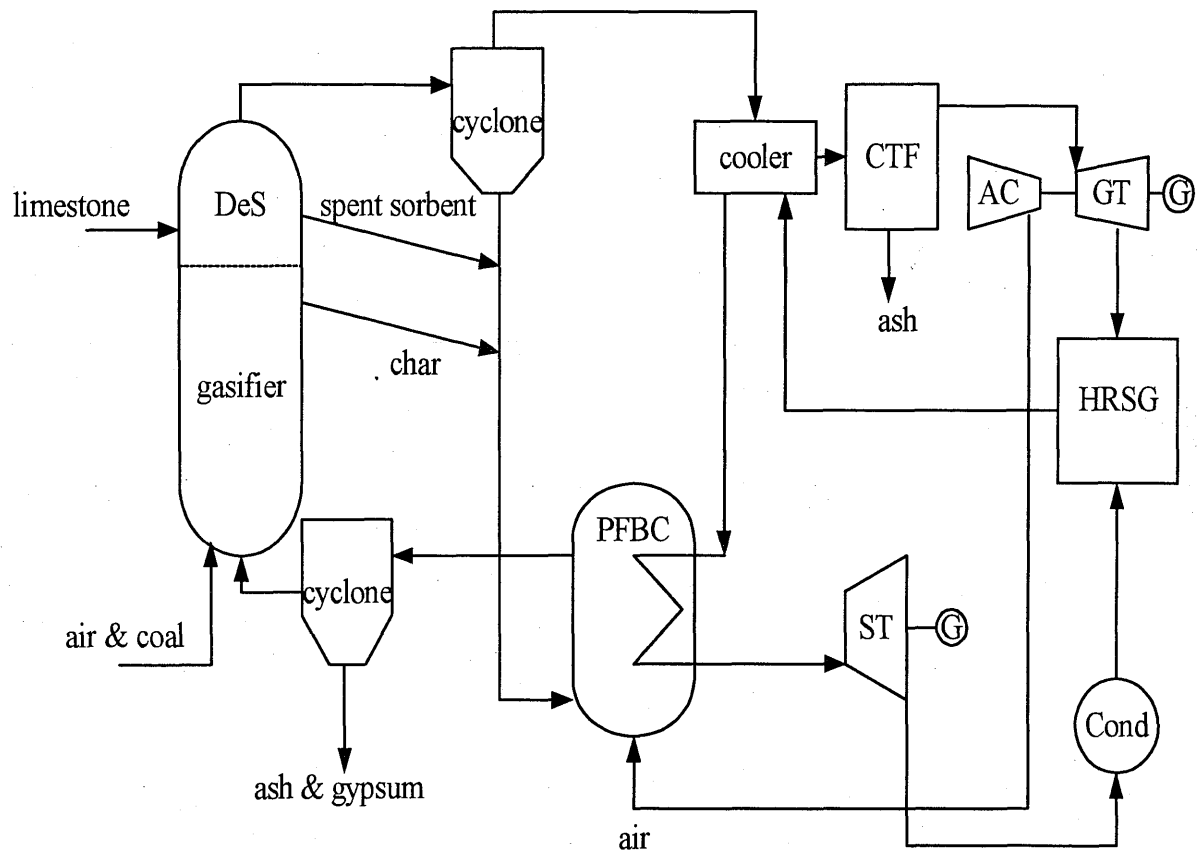


Fig.1-3 A-PFBC System

1.4 Formation and Reduction of Sulfur and Nitrogen Pollutants in A-PFBC

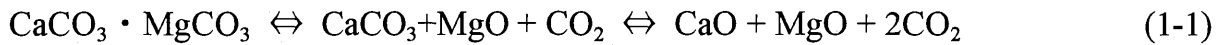
1.4.1 Sulfur pollutant

Sulfur in coal is found in both inorganic and organic forms. The inorganic sulfur is mostly pyrite (FeS_2). In addition to there may be marcasite (a different

morphological form of pyrite). The sulfate content is usually low except when the pyrite has been oxidized. The forms of organic sulfur are less well established. Since sulfur is either recovered in elemental form or fixed in one of several possible solid products, the quantities of solids produced depend upon both ash and sulfur content of the fuel. In many cases, reactions with low-cost limestone are used to retain the sulfur as calcium sulfate or calcium sulfide.

Under the reducing conditions found in the gasification system, the sulfur in coal is mostly converted to hydrogen sulfide (H₂S), with a small proportion of COS also formed. The sulfur clean-up system has been employed in coal gasification system with the use of calcium-based sorbents, such as limestone and dolomite as sulfur-capturing agents, operating at low temperature(<900°C). At low temperatures H₂S in the raw gas can be easily removed to very low levels,>99% sulfur recovery²⁰⁾.

Depending on the CO₂ partial pressure and the temperature in the gasifier, the sorbents may decompose to the respective oxides.



In fluidized bed gasifier, the conditions are such that MgCO₃ always calcines to MgO. However, the stability of CaCO₃ is dependent on the CO₂ partial pressure and the temperature²¹⁾. Depending on the conditions, sulfur absorbents are referred as follows: CaCO₃, uncalcined limestone; CaO, calcined limestone; CaCO₃ MgCO₃, uncalcined dolomite; CaCO₃+MgO, half-calcined dolomite; CaO+MgO, fully calcined dolomite. Thus, the two sulfidation reactions are:



If dolomite is used as a sorbent, the MgO will not react with sulfur compounds, because MgS is an unstable compound under gasification conditions. Reactions (1-2)

and (1-3) are both limited by thermodynamic equilibrium, not all H₂S can be captured with Ca-based sorbents²²⁻²⁶). Depending on the conditions, there still remains a H₂S equilibrium concentration of 100-500ppm.

Generally, the sulfidation of CaO under atmospheric pressure has been found to be relatively fast and conversions up to 100% have been achieved²⁷⁻²⁹). High conversions (80-90%) were also yielded for calcined limestones under pressurized conditions³⁰⁻³¹). There have been many reports³²⁻³⁴) where chemical reaction kinetics, reaction mechanism were studied. Effects of pressure, temperature, and sorbent type were also discussed³⁵⁻⁴⁰).

The use of in-bed desulfurization in gasification process results in the production of large quantities of residues, which include unburned char and used sorbent (calcium sulfide) and ash. Generally speaking, the residues can not be directly used for landfill or as materials for agriculture and industrial uses because that there is unsteady sulfur in the residue from gasification process.

Desulfurization in the hybrid power generation system is unlike that in unique coal combustion boiler. The reactants are the char by products: ash and /or slag particles, sorbents and fluxes added to the coal and desulfurization products, which need to be treated in combustor before disposal.

One of main problems in the treatment is oxidation reaction of calcium sulfide. It is desirable that the calcium sulfide after discharge from the gasifier is converted into the more stable calcium sulfate (CaSO₄) by oxidation in the combustor through



A critical objective will be to what extent the calcium sulfide (CaS) in the char stream introduced in the combustion unit will convert to calcium sulfate. This as well

as sulfation of calcium oxide is important if the solid waste produced is to be considered for landfill disposal⁴¹⁾.

Legislation in many countries now requires that utilization of residues should be considered before disposal is allowed. Therefore, the following criteria must be considered when deciding the suitability of the residues for disposal:

- (1) the health and safety of personnel working at a disposal site and local residents;
- (2) the long-term persistence of the residues and the implications for the future reuse of land;
- (3) the environmental aspects of disposal, particularly the potential pollution of water resources;

Of the various environmental criteria associated with the disposal of coal-use residues, the effect of air /water pollution has become an important concern. Problem arises because natural processes allow contaminants to leach slowly from residues, potentially allowing them to migrate through the soil to groundwater and surface waters. If there is calcium sulfide still remaining in the residues after oxidization, the calcium sulfide will slowly react with water to form H_2S , leading to the pollution of air and water resource. Therefore, calcium sulfide needs to be completely converted to stable calcium sulfate or calcium oxide during oxidization in the combustion process.

Diverse utilization options have been demonstrated for coal-use residues, which include agriculture uses, building and structural materials, industrial materials and specialist uses⁴²⁻⁴³⁾. For the all application, it is also needed that there is no calcium sulfide remaining in the residues after oxidization.

To sum up, complete conversion of calcium sulfide to calcium sulfate/calcium oxide in combustor is very important for power generation systems such as A-PFBC, a new clean coal technology. Due to the few research on oxidation reaction of calcium sulfide has been done, this study is imperative and significant for the development of

this new clean coal technology.

1.4.2 Nitrogen pollutant

An understanding of the physical and chemical mechanisms that influence the evolution and composition of nitrogenous species during early stages of coal combustion is essential to understanding and predicting the fate of coal nitrogen during combustion. The three crucial issues are:

- 1) partitioning among light gas products, tar, soot, and residual char during primary and secondary pyrolysis;
- 2) nitrogen evolution rates from the constituent phases;
- 3) initial nitrogen speciation of the solid and condensed phases;

A conceptual view of the key way fuel-nitrogen/nitrogen pollutant conversion pathways is shown in Figure 1-4.

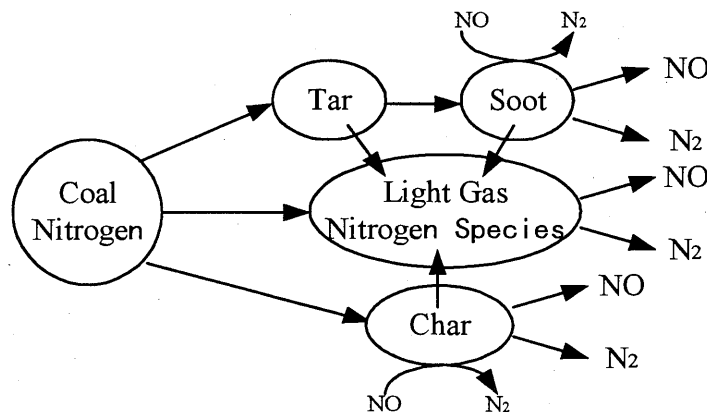


Fig. 1-4 Fuel nitrogen pathways leading to nitrogen pollutant formation during coal combustion

The non-homogeneous nature of coal, consisting of randomly fused aromatic clusters, heteroatom (O, N, and S) linkages and inorganic constituents, requires that a certain degree of empiricism be used when describing coal conversion processes.

Generalized coal devolatilization models, which predict char formation and gas evolution, are available; but at present, a coal-dependent method of accounting for

variation in nitrogen evolution pathways has not been demonstrated.

As stated in chapter 1.2.1, a common problem with FBC is N₂O formation with about 50ppm in the combustion gas, while conventional boiler flue gases contain less than 1ppm. The combustion temperature below 900°C favors the N₂O formation. Higher temperatures, however, give operation problems and also lower SO₂ and NO_x removal efficiencies. The mechanism of NO_x and N₂O formation during coal combustion is also an important topic nowadays.

1.5 Previous Works on Calcium Sulfide Oxidation and Mechanism of NO_x and N₂O Formation

1.5.1 Sorbent performance

Sulfur capture is achieved in the gasifier by addition of limestone or dolomite. This calcines to give calcium oxide (and magnesium oxide in the case of dolomite). The calcium oxide reacts with gaseous sulfur species released from coal to form solid calcium sulfide. The calcium sulfide (CaS), excess calcium oxide (CaO) and the char residue (which contains some unconverted sulfur) are passed to the combustor. During combustion the sulfur is released from char, and can be captured by the excess CaO to form stable calcium sulfate (CaSO₄). It is also desirable for the CaS to be fully oxidized to CaSO₄ during the combustion. This because the sulfided limestone or dolomite is not inert; its calcium sulfide component slowly liberates hydrogen sulfide gas if it is exposed to moist air. This creates an odour problem and makes disposal in landfill sites more difficult. In contrast, calcium sulfate is stable to the elements over geological time periods and can have uses as an aggregate or filter material.

In oxidizing environment of the combustor CaS is oxidized through:



Conversion of sulfide to sulfate via reaction (1-5) is favored at low temperatures and high partial pressures of oxygen. The onset of reaction has been detected at 400°C in air, and it was possible to form sulfate at temperatures up to 900°C if oxygen concentration was kept above 1%⁴⁴⁾. However, recent studies have shown that the oxidization of CaS to CaSO₄ is not so straightforward. A complete conversion of CaS to CaSO₄ can barely be reached because of the product layer diffusional resistance to the reactant gas. Ninomiya et al.⁴⁵⁾ studied the oxidization of sulfided lime, finding that the CaS oxidization began at 600°C, and below 1063°C, the outer shell of the sample was converted with a CaSO₄ product layer. The oxidization reaction eventually stopped due to the increase in the intraparticle diffusional resistance. As a result, 10-50% of the unreacted CaS remained in the inner shell. Abbasian et al.⁴⁶⁾ obtained different maximum conversions when partially sulfided lime particle (0.2mm diameter) with various sulfidation levels were oxidized at 815-900°C with 5.26% O₂. Davies et al.⁴⁷⁾ explored the oxidization of pure CaS of mean particle size of 45 μm with an atmospheric thermobalance. They reported that at 850°C the conversion of CaS to CaSO₄ was 10% in 30min. Above 850°C, the products were both CaSO₄ and CaO with the SO₂ evolution during the reaction. The conversion of CaS to CaSO₄ was 32% at 950°C after 30min. of oxidation with 4.2% O₂. Qiu et al.⁴⁸⁾ investigated the oxidization of CaS particles by the thermogravimetry and mass spectrometry coupled analysis and found that reaction (1-5) was controlled significantly by the product layer diffusion when a certain CaSO₄ product layer was formed. Several studies⁴⁹⁻⁵¹⁾ have shown that the conversion of sulfide to sulfate decreased with increasing temperature, and at temperatures above 900°C a weight loss was observed. This weight loss is due to the evolution of SO₂ by the reactions:



These reactions are undesirable in that they result in a net loss of sulfur and emission of SO₂ in the exit gas that may exceed environmental target. Reaction (1-6) proceeds rapidly at high temperatures(1300-1500°C) and low partial pressures of O₂. The apparent reaction(1-8) occurs above 900°C. Lynch et al⁵²⁾ studied CaS oxidation at a temperature range of 950-1580°C in 1-100% O₂. They observed that

- 1) weight loss with the formation of CaO and SO₂ through reaction(1-6) which occurred at high temperatures and low partial pressures of O₂
- 2) weight gain which occurred at low temperatures and high partial pressures of O₂ by the reaction



- 3) combination of 1) weight gain of overall formation of CaSO₄ and 2) weight loss with overall oxidation of CaS to CaO and decomposition of CaSO₄ leading to an oscillatory behavior which occurred at intermediate temperatures and intermediate to high partial pressure of O₂.

Rowena et al.⁵³⁾ reported their results on oxidation of 6.32 μm CaS in a laminar flow oxidation furnace at temperatures of 1123-1477°C in atmospheres containing 0-0.20% O₂ in He. They also found that the oxidation of CaS resulted in formation of CaO or both CaO and CaSO₄ as products.

1.5.2 Kinetics and modeling study

There have been some reports for kinetic studies of the above reactions. Davies et al.⁴⁷⁾ determined the kinetics of reaction (1-5) in the temperature range of 650-850°C. The order of the reaction with respect to O₂ was examined at 800°C and with O₂ concentrations of 4.2-80vol.%. Their results had shown that oxidation of CaS to CaSO₄ was first-order in O₂, with a rate constant of $(4.5 \pm 2.0) \times 10^{-4} \exp(-(5.7 \pm 1.5) \times 10^3/T)$ m/s. Torres-Ordonez et al.⁵⁴⁾ used the shrinking unreacted core model to

describe the oxidation behavior of CaS to CaO reaction in temperatures of 1123-1477°C, and concluded that the reaction (1-6) was first-order in the bulk O₂ partial pressure for $P_{O_2} \leq 0.2 \text{ atm}$ at 1123°C and for $P_{O_2} \leq 0.1 \text{ atm}$ at 1227-1477°C. They found that at temperature >1227°C reaction (1-6) was largely under kinetic control and considered that the CaO product layer formed may be sufficiently porous so that the reaction is not hindered by any product layer diffusion resistance. The rate constant $8.2276 \times 10^6 \exp(-20411/T) \text{ cm}$ was yielded at 0.1 atm of O₂ and 1277-1477°C.

The kinetics for apparent solid-solid reaction (1-8) had been characterized by Qin et al.⁵⁵⁾, the activation energy of this reaction was estimated as 301 kJ/mol. Chen and Yong⁵⁶⁾, Kikuchi et al.⁵⁷⁾ and Kamphuis et al.⁵⁸⁾ also gave the activation energy 343, 242 and 358 kJ/mol, respectively.

Hasatani et al.⁵⁹⁾ studied the reaction of CaO and SO₂ by means of a thermal gravimetric analyzer with various kinds of limestone particles (5-294 μm) in the temperature range of 600-1200°C, yielding the activation energy of this reaction 27.0 kJ/mol. A mathematical model including intraparticle transport and chemical reaction within the particles (grain model) had been developed to simulate this sulfur oxide sorption reaction. Several works.⁶⁰⁻⁶³⁾ also had developed a modified grain model including grain and micrograin to simulate the reaction (1-7), the satisfactory agreement between the experimental and theoretical results was achieved.

1.5.3 Mechanism of NO_x and N₂O formation

There is considerable recent interest in the reaction pathways whereby fuel-nitrogen evolves as NO_x and N₂O in combustion of heavy fuels such as coal and biomass. These fuels contain nitrogen in heterocyclic structures comprising pyridine and pyrrole ring systems⁶⁴⁾. During devolatilization, fuel nitrogen is divided between char-nitrogen and volatile nitrogen compounds, mainly in the tar and as NH₃ and HC

$\equiv\text{N}$. The char-nitrogen is thought to be primarily in the form of the same aromatic heterocyclic structures as that found in the original materials. The tar nitrogen was bound in the same ring structures as the nitrogen in the parent coal. Solomon and Colket⁶⁵), performing rapid pyrolysis experiments on coal with a heated-grid reactor, found that at low temperatures ($<700^{\circ}\text{C}$) no substantial amounts of $\text{HC}\equiv\text{N}$ or NH_3 were formed and the tar nitrogen was the main nitrogenous volatile product. The major nitrogen-containing components of the tars were pyridine, methylpyridines, pyrrole, quinoline, methylquinolines, indole, methylindoles, benzonitrile, and cyanonaphthalens^{66, 67}). Most of the nitrogen species in the gas phase resulted from secondary reaction of the tar. High-temperature secondary pyrolysis reactions of tars yielded $\text{HC}\equiv\text{N}$ as a primary product. During combustion, $\text{HC}\equiv\text{N}$ and NH_3 may be converted to NO , N_2O or N_2 or may play a part in the reduction of NO and N_2O together with CO and H_2 either in homogeneous or heterogeneous conditions.

Most of the nitrogen oxides emitted to the atmosphere by combustion systems is in the form of nitric oxide (NO), with only a small fraction appearing as nitrogen dioxide (NO_2). Other nitrogenous compounds, such as ammonia, hydrogen cyanide, amine compounds, and nitrous oxide (N_2O) are air pollutants whose anthropogenic origin includes combustion systems.

Nitric oxide is formed in flames predominantly by three mechanism; thermal NO (the fixation of molecular nitrogen by oxygen atoms produced at high temperatures), fuel NO (the oxidation of nitrogen contained in the fuel during the combustion process) and prompt NO (the attack of a hydrocarbon free radical on molecular nitrogen producing NO precursors).

N_2O can be formed by a number of paths in gaseous and coal-laden reactors; however, it rapidly reacts with radicals to form N_2 . The N_2O levels in coal combustors are generally less than 5 ppm and are not related to the nitrogen oxide levels in the

flue gas^{68,69}). NO_2 is only significant in combustion sources such as gas turbine⁷⁰). In most combustors, NO_2 concentrations are highest near the flame zone where NO reacts with HO_2 but are then quickly converted back to NO in the presence of high radical concentrations⁷¹). Thus, NO_2 only exists as a transient species, which is quickly destroyed in the post-flame region.

Neither N_2O nor NO_2 reach high concentration in coal flames. Hence, NO is normally the only significant nitrogen oxide species emitted from practical combustors.

Fuel NO is by far the most significant source of nitric oxide formed during the combustion of nitrogen-containing fossil fuels. Fuel NO accounts for 75-95% of the total NO_x accumulation in coal flames. Fuel NO is formed more readily than thermal NO because the N-H and N-C bonds common in fuel-bound nitrogen are weaker than the triple bond in molecular nitrogen, which must be dissociated to produce thermal NO. Nitrogen is primarily evolved from tars as HCN and from amines as NH_3 ^{72, 73}). At typical combustion temperatures, heterocyclic compounds of pyridine, quinoline, pyrrole, and benzonitrile are mostly pyrolyzed to HCN. Once the fuel nitrogen has been converted to HCN, it rapidly decays to NH_i ($i=0,1,2,3$), which reacts to form NO and N_2 .

Much research has focused on the elementary steps leading from HCN to NO and N_2 . Although concepts for the dominant network steps have been explored by a number of investigators, an exact determination of the complete mechanism is presently not available for generalized types. Many of the reactions involve immeasurable intermediate and radical species.

1.6 Scope and Constitution of this Study

As discussed above, there are a few important problems for calcium sulfide oxidation and the mechanism of NO_x and N₂O formation during coal uses, such as reaction mechanism analysis, conditions for complete conversion of CaS to CaSO₄/CaO, model simulation on reactions of CaS to CaSO₄ and CaS to CaO/CaSO₄, and the change of nitrogenous compounds in coal during coal combustion. The optimal reaction conditions such as particle size, reaction temperature, O₂ concentration, feeding position and the method of NO_x reduction must be made clear for effective process development and the establishment of rational design methodology. It is the objective of the present study to provide scientific information concerning the factors list above.

This study consists of six chapters summarized in the following:

Chapter 1 General introduction

In this chapter the general introduction has been devoted for stressing on the significance and necessity of power generation systems, deriving the subjects of research based on the review of previous works and evaluation of the calcium sulfide oxidation, and the mechanism of NO_x and N₂O formations.

Chapter 2 Calcium sulfide oxidation under constant heating rate conditions

In this chapter was analyzed the reaction process of calcium sulfide oxidation by a Thermogravimetric Analyzer (TGA) with 5, 10 and 15 °C/min constant heating rates. The oxidation process was classified into three different regions according reaction temperature: (1) weight gain (< 900°C); (2) weight loss and SO₂ release (900-1150°C); (3) oscillation (1150-1200°C). In addition, effects of type of limestone, oxygen concentration particle size and heating rate had also been discussed. The reaction mechanism of oscillation process was reasonably deduced. The detailed discusses of oxidation in the reaction region (1) and (2) are presented in chapter 3 and 4, respectively.

Chapter 3 Oxidation mechanism of calcium sulfide between 600 and 900°C

In this chapter, the oxidation reaction has been found that at temperatures of 600 to 900°C calcium sulfide was only converted to sulfate. The sulfation reaction of calcium sulfide was discussed being focused on effects of limestone type, particle size, and O₂ concentration. The reaction rate constant and reaction order with respect to oxygen was also studied. A grain model has been applied to simulate this reaction process and the predictions are given that the reaction conditions (initial calcium sulfide content, particle size) for complete conversion of calcium sulfide to sulfate.

Chapter 4 Oxidation mechanism of calcium sulfide between 900 and 980°C

In this chapter the oxidation process was discussed by means of a quartz tube reactor at temperature of 900 to 980°C, within which the calcium sulfide was converted to calcium oxide and sulfate. The effects of calcium sulfide content, particle size, temperature has been analyzed. The modified grain model used in chapter 3 has been also used to simulate the two reactions, and the model predictions of optimal reaction conditions for complete conversion of calcium sulfide were given.

Chapter 5 Theoretical study on the thermal decomposition of pyridine

For better understanding of mechanism of fuel NO formation, in this chapter semi-empirical PM3 molecular orbital calculations have been used to investigate the reaction pathways of pyrolysis of pyridine. All the transition states and intermediates of the reaction path were optimized. The probable pathways are estimated from the activation energies calculated and compared with known experimental results. The heats of formation of pyridine radicals are calculated to be 76.1, 80.6, and 79.5 kcal/mol for 2- (2A), 3- (3A) and 4-pyridyl radicals (4A), respectively. The weakest bonds on the radicals were assumed to be broken and gave the decomposition fragments successively.

Chapter 6 General conclusions

The main results in this thesis are summarized.

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