

กระบวนการร่วมของลีกไนต์และยางธรรมชาติโดยใช้ตัวเร่งปฏิกิริยาซัลเฟตเซอร์โคเนีย
ในบรรยากาศไฮโดรเจน



นาย ชัยพงษ์ เยาวภักดิ์

สถาบันวิทยบริการ

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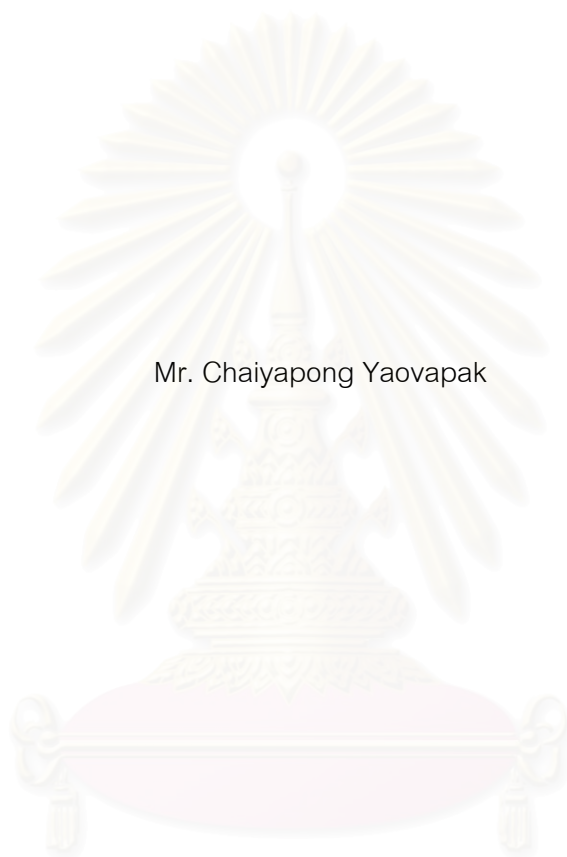
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

COPROCESSING OF LIGNITE AND NATURAL RUBBER USING SULFATED ZIRCONIA
CATALYSTS IN HYDROGEN ATMOSPHERE



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ชัยพงษ์ เยวรักษ์ดี: กระบวนการร่วมของลิกไนต์และยางธรรมชาติโดยใช้ตัวเร่งปฏิกิริยาซัลเฟตเซอร์โคเนียในบรรยากาศไฮโดรเจน. (COPROCESSING OF LIGNITE AND NATURAL RUBBER USING SULFATED ZIRCONIA CATALYSTS IN HYDROGEN ATMOSPHERE) อาจารย์ที่ปรึกษา: รศ. ดร. ธราพงษ์ วิทิตสานต์: 85 หน้า.

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กระบวนการร่วมระหว่างลิกไนต์และยางธรรมชาติด้วยไฮโดรเจนบนตัวเร่งปฏิกิริยาซัลเฟตเซอร์โคเนีย ทำในเครื่องปฏิกรณ์ขนาดเล็ก เส้นผ่านศูนย์กลางภายใน 30 มิลลิเมตร ความจุ 75 มิลลิลิตร โดยทำการศึกษาการเปลี่ยนแปลงค่าตัวแปรต่อไปนี้คือ อัตราส่วนระหว่างสารตั้งต้นลิกไนต์ต่อยางธรรมชาติจาก 100 ต่อ 0 ถึง 30 ต่อ 70 ความดันแก๊สไฮโดรเจน 20 ถึง 50 บาร์ อุณหภูมิในการทำปฏิกิริยา 325 ถึง 400 องศาเซลเซียส เวลาในการทำปฏิกิริยา 30, 60 และ 90 นาที ปริมาณของตัวเร่งปฏิกิริยา 0, 1, 3 และ 5% โดยน้ำหนักของสารตั้งต้น จากผลการทดลองพบว่าภาวะที่เหมาะสมต่อกระบวนการผลิตเชื้อเพลิงเหลวของกระบวนการร่วมระหว่างลิกไนต์และยางธรรมชาติคือที่ อัตราส่วนสารตั้งต้นเป็น 30 ต่อ 70 ความดันแก๊สไฮโดรเจน 40 บาร์ อุณหภูมิของปฏิกิริยา 375 องศาเซลเซียส เวลาของการทำปฏิกิริยา 60 นาที และปริมาณของตัวเร่งปฏิกิริยา 3% ได้ปริมาณของเชื้อเพลิงเหลวสูงสุดที่ 72.12% โดยน้ำหนักและยังพบอีกว่าความดันของก๊าซไฮโดรเจนมีผลต่อกระบวนการร่วมน้อยมาก

การวิเคราะห์ผลิตภัณฑ์เหลวที่ได้จากการทดลองด้วยเครื่องแก๊สโครมาโทกราฟี (Simulated distillation gas chromatography) พบว่าภาวะที่เลือก ให้ผลิตภัณฑ์เหลวที่มีองค์ประกอบของแก๊สโซลีน 20.19% เครโซลีน 12.26% แก๊สฮอยล์ 22.36% และโมเลกุลสายโซ่ยาว 17.31% จากการเปรียบเทียบกระบวนการร่วมระหว่างลิกไนต์และยางธรรมชาติ แบบใช้ตัวเร่งปฏิกิริยากับแบบเติมตัวทำละลายที่ให้ไฮโดรเจนอะตอม พบว่ากระบวนการร่วมแบบใช้ตัวเร่งปฏิกิริยา ให้ปริมาณเชื้อเพลิงเหลวและการกระจายตัวขององค์ประกอบในเชื้อเพลิงเหลวดีกว่าแบบกระบวนการที่เติมเตทราลินเป็นตัวทำละลาย

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CHAIYAPONG YAOVAPAK: COPROCESSING OF LIGNITE AND NATURAL RUBBER USING SULFATED ZIRCONIA CATALYSTS IN HYDROGEN ATMOSPHERE. THESIS

ADVISOR: Assoc. Prof. Dr. THARAPONG VITIDSANT, 85 pp. ISBN 974-03-0829-5

The conversion of coprocessing of lignite and natural rubber with hydrogen gas on sulfated zirconia catalyst in a microreactor with 30 mm. inside diameter and 75 ml was investigated. The experiment has been set up at conditions by the following variables: ratio of lignite: natural rubber from 100:0 to 30:70, pressure of hydrogen gas range of 20-50 bar, reaction temperature ranging from 325 to 400 °C, reaction time 30, 60 and 90 min. and amount of catalyst 0%, 1%, 3% and 5% starting materials. The results have shown the appropriate conditions of coprocessing of lignite and natural rubber at the ratio of lignite: natural rubber were 30:70, hydrogen pressure was 40 bar, reaction temperature was 375 °C, reaction time was 60 min and amount of catalyst was 3%. The highest yield of oil was 72.12% by weight; however the results show that hydrogen pressure was insignificant in coprocessing.

The analyzed liquid products from Gas Chromatography (G.C. Simulated Distillation) was found that the liquid products of proper condition consists of 20.19% gasoline, 12.26% kerosene, 22.36% gas oil and 17.31% long residue. Coliquefaction was compared by using catalyst reaction and hydrogen donor solvent (tetralin). The yield of oil and product distribution obtained from ZrO_2/SO_4^{2-} solid super acid catalyst in coliquefaction obtaining higher than coliquefaction using tetralin solvent.

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Academic year.....2001..... Co-advisor's signature.....

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จุฬาลงกรณ์มหาวิทยาลัย

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ABBREVIATIONS

°C	:	Degree Celsius
C/R	:	Weight ratio of coal and natural rubber
FT-IR	:	Fourier Transform Infrared Spectrophotometer
FBP	:	Final boiling point
IBP	:	Initial boiling point
NR	:	Natural rubber
min.	:	Minute
ml.	:	Milliliter
mm.	:	Millimeter
%wt	:	Percent by weight
SD-GC	:	Simulated distillation gas chromatography
ZrO ₂ /SO ₄ ⁻²	:	Sulfated zirconia

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CHAPTER I

INTRODUCTION

Coal has been believed to be the major energy source among fossil resources in the coming century because there is a large reserved quantity of coal which located all over the world, resulting in a relatively low price in market place. On the other hand, a petroleum shortage is inevitable in a near future. The liquefaction of coal is a promising technology for producing alternate fuels that may eventually replace petroleum-based fuels.

Presently, the economic of coal liquefaction is not favorable because of intense processing conditions, used of a costly catalyst, low quality product^[1]. Many efforts have spent to increase the efficiency and reduce the cost of coal liquefaction process. Catalyst and reduction of hydrogen consumption are two ways to reduce cost of process.

The present work concerns coliquefaction of lignite with natural rubber (NR) using a sulfated zirconia catalyst ($\text{ZrO}_2/\text{SO}_4^{2-}$). NR can also be well used as coliquefaction agents for conversion of coal to liquid fuels. The NR was expecting to improve the quality and yield of the liquid products from coal under moderate conditions. Sulfated zirconia catalyst was expecting to improve the efficiency and selectivity in coal conversion. Gasoline, kerosene and diesel of transportation fuels were major targets.

1.1 Objectives of this study

The objectives of this study are:

1. To investigate the coliquefaction process of lignite and NR to liquid fuel by $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst under the pressure of hydrogen gas.
2. To study the suitable conditions of coliquefaction of lignite with NR into liquid fuel that generates maximum liquid product and high quality of oil.
3. To compare a consequence of the processes with and without catalyst.

1.2 The scopes of this study

1. Experimental study in laboratory scale.
2. Selecting a suitable conditions of coliquefaction process by varying these following parameters :
 - Lignite and NR feed ratio
 - Reaction temperature
 - Residence time
 - Hydrogen pressure
 - Amount of sulfated zirconia catalyst (0%, 1%, 3% and 5%)
3. Liquid products from coliquefaction were determined by SD-GC.
4. Comparing the results from different kind of process of liquefaction to those reported for the best coliquefaction process conditions.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Coal conversion

In the past, most of coals were burned directly, but in the present an increasing amount is converted to gas and liquid fuels and to petrochemicals. The current conversion technology is the basic process of many industries.

The term “conversion” implies a change in physical state and/or extensive alternation of composition and chemical reaction to cause conversion. The technology of coal conversion is divided into 3 methods pyrolysis, gasification and liquefaction.

1. *Pyrolysis* is a decomposition of organic matter by heat in the absence of air.
2. *Gasification* is a process that transforms solid or liquid substance into useful gases.
3. *Liquefaction* is a process that converts solid or heavy hydrocarbon into lighter “synthetic oil” by controlled molecular degradation.

2.1.1 Coal Liquefaction

Liquefaction has advantages in both thermal efficiency and economics. Both advantages convert solid coal into liquids products more than gaseous fuels. Liquid fuels have higher energy and therefore they are cheaper to store and transport. There are two methods for converting liquid products form coal, direct liquefaction aims to produce liquid products from coal directly, but indirect liquefaction produces gas products which is processed into liquid fuels.

The experiment was designed for converting lignite and NR to liquid fuels under direct-liquefaction process, using $\text{ZrO}_2/\text{SO}_4^{-2}$ catalysis in hydrogen pressure. The main difference between naturally occurring petroleum flues and coal was deficiency of hydrogen. Therefore, conversion of coal into liquid fuels involved the addition of hydrogen. The mass ratio of hydrogen to carbon for variety of fuels is showed in Table 2.1.

Table 2.1 Compositions of coal and various fuels ^[2].

Fuel	H/C atom ratio
Anthracite	0.31
Bituminous	0.67
Lignite	0.69
Benzene	1
Gasoline	2

Research and development on conversion of coal to petroleum-like hydrocarbon liquids and chemical feed stocks are important for secure supply of liquid transportation, residential, commercial, and industrial fuel requirements ^[31]. Coal liquefaction contains less sulfur, nitrogen and ash; this is easier to transport. These liquids are suitable refinery feedstock for manufacture of gasoline, heating oil, diesel fuel, jet fuel, turbine fuel, fuel oil and petrochemicals.

2.1.2 Parameters in characterizing process performance

1. Coal rank and type: Coal liquefaction behavior depended on the rank of coal. Anthracites produce low liquid yields; lignite liquefies were most readily but gave lower liquid yields than bituminous ^[4].

2. Reaction temperature: Reaction temperature range between of 325-400 °C and rate of heating must high.
3. Catalyst: Catalyst in reaction must operate in reaction condition.
4. Pressure: Initial hydrogen pressures in this experiment range between of 20 - 50 bar.
5. Residence time: Long residue time reduce oil product because of thermal decomposition.

2.1.3 Reaction in coal direct liquefaction

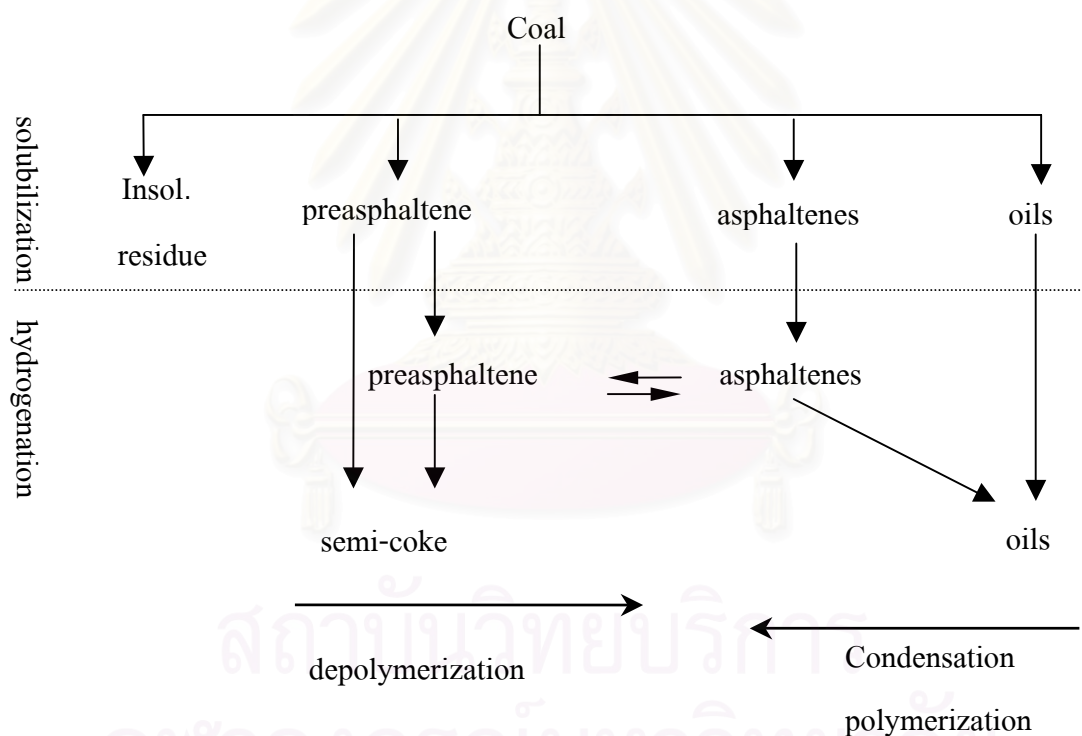


Figure 2.1 Conceptual reaction sequences in coal liquefaction ^[3].

Figure 2.1 showed the general reaction model for coal liquefaction. This reflects potential reversibility at different stages of liquefaction due to concurrent thermal and hydrocracking reactions ^[3].

Direct liquefaction process may be distinguished by whether the products were produced in one or two stages. In two-stage process, dissolution or primary liquefaction in the first stage and upgrading of primary products in the second stage to produce liquids that like synthetic crude oils. Primary liquefaction involves thermal cracking of coal macromolecular structure to produce free radicals followed by hydrogenation by hydro aromatic or other hydrogen-donation species in coal itself, in solvent and in gas-phase H_2 lead to products consists of preasphaltene, asphaltene and oil along with C_1 - C_4 hydrocarbon gas and inorganic gases.

2.1.4 Mechanism of cracking processes

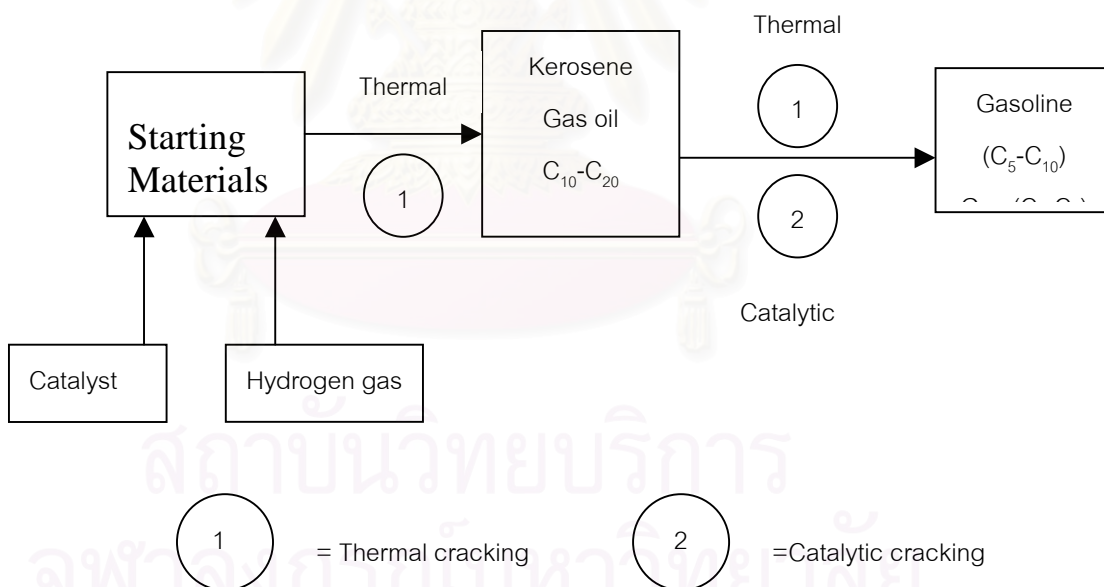


Figure 2.2 Thermal cracking and catalytic reaction ^[8].

Cracking process was assigned to two fundamental classes of thermal cracking and catalytic cracking, as showed in Figure 2.2.

1. Thermal cracking

This is process used to reduce the molecular weight of hydrocarbons by breaking molecular bonds. Thermal cracking depended on a free-radical mechanism to cause scission of hydrocarbon carbon-carbon bonds and reduction in molecular size. Hydrogen atoms from hydrogen gas and hydrogen donor were contacting to the hydrogenation, with the formation of kerosene and gas oil^[31]. Gas oil and kerosene from reaction have a molecular size just enough to transfer in the pores of the supported catalyst.

2. Catalytic reaction

Primary objective of catalytic cracking was production of maximum yields of gasoline. But, normally gas was produced at the same time. Hydrocracking converted intermediate and high molecular weight molecules such as kerosene and gas oil to gasoline^[8]. Two methods of hydrogenation additions are distinguished as following:

1. Hydro liquefaction or catalytic liquefaction
2. Solvent extraction (hydrogen donor solvent)

The general directions of approaches for converting heavy materials with lower hydrocarbon contents increased the hydrogen-to-carbon ratio by either hydrogen addition or carbon rejection. Direct liquefaction of coal by hydrogenation is also called hydroliquefaction. In hydroliquefaction, the hydrogen was added directly from gas phase in the presence of catalyst. In solvent extraction process, a coal-derived liquid, which may or may not be separately hydrogenated, transfers the hydrogen to the coal without external catalyst addition.

The present work concerns catalytic liquefaction using $\text{ZrO}_2/\text{SO}_4^{-2}$ catalysts in catalytic hydrogenation, NR were added as another source of hydrogen in order to reduce hydrogen consumption. The conditions of coliquefaction by $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst by studying its influences to conversion percentage of the products and yielded oil composition have the following variables: percentage of $\text{ZrO}_2/\text{SO}_4^{-2}$, temperature, a ratio of lignite/NR, initial pressure of hydrogen gas and reaction time. The processing conditions of the experiments are showed in Table 2.2.

Table 2.2 Processing conditions.

Coal rank	Lignite (250 mesh)
Hydrogen donor	Hydrogen gas and NR
Heating rate	0.9 °C/second
Rate of shaking	60 time/min.
Catalyst	$\text{ZrO}_2/\text{SO}_4^{-2}$
Temperature range	325-400 °C
Hydrogen pressure range	20 – 50 bar
Reaction time	30 – 90 min

2.2 Raw material for coliquefaction process

2.2.1 Coal

2.2.1.1 The origin of coal.

Coal is a heterogeneous material found in sedimentary rock. Coal is burned to produce energy. It used to for an important source of chemicals and make pharmaceuticals, fertilizers and other products. Coal is a complex

mixture of organic chemical substances containing carbon, hydrogen and oxygen in chemical combination, together with smaller amounts of nitrogen and sulfur. The organic part of coal has associated with it various amounts of moisture and minerals^[39].

Coals are from by plant substance preserved from complete decaying in environment and later chemically and physically by environmental effect. There are two stages in the process of coal formation: (1) the biochemical and peat stage, and (2) the dynamo chemical or metamorphic.

The accumulation of plant remains as peat deposits is considered as biological process. Plants are heterogeneous in composition and contain cellulose, hemicelluloses, lignin, resins, waxes, and fats. Cellulose is easily oxidized into carbon dioxide and water through simple sugars by aerobic organism. In anaerobic fermentation, cellulose is a source of oxygen for the organisms and the products are on longer simply CO_2 and H_2O . Lignin is more resistant to bacteria action and it slowly oxidized by aerobic organism to complex humic acids that are a large part of peat. Decomposition of lignin can produce in swam which is unsuitable for growth of bacteria.

The metamorphic stages of coals differ considerably in composition and other properties. As burial depth increased, overburden pressure causes an increasing in compaction (reduction in porosity and expulsion of moisture), and temperature increases promoting chemicals changes of organic components of coal. Peat is transformed into coal through the process of coalification. Their "type" and "rank" classify coals. Coal type is determined by the nature of plant material of which it is composed.

2.2.1.2 Classification of coals by rank

Coalification is the name given to the development of the series of substances known as peat, lignite or brown coal, sub-bituminous coal, bituminous coal, and anthracite. The degree of coalification, also called the rank of the coal, increases progressively from lignite to low rank coal, to high rank coal, to anthracite. The carbon content increases, while the oxygen and hydrogen contents decrease throughout the series. The hardness increases, while the reactivity decreases. Different amounts of heat and pressure during the geochemical stage of coal development cause these differences in rank. It is not due to the kind of plants the coal is formed from.

The properties of coal of particular importance are its *heating value*, the amount of *fixed carbon* and *volatile material*, and the amount of *moisture*, *sulfur*, and *ash*. The definition described these properties^[39]:

1. *Heating value* of coal is amount of heat liberated by complete combustion at constant volume under specified conditions. Heating values are determined by bomb calorimeter. The heat property is important in coal conversion.
2. *Fixed carbons* refer to the weight loss on combustion of a devolatilized coal.
3. *Volatile material*, when coal heated above 400 °C, some of the coal material decomposes and is given off gas. This is referring to as the volatile material in coal.

4. *Moisture*, the state of water content in coal and its quantitative determinations have been the subject of investigation. The moisture content is an important factor in the storage and utilization of coals. The moisture contents of coal increase with decrease in rank.
5. *Sulfur* in coal may occur as pyritic (FeS_2), organic, or sulfate. In low sulfur coal, the sulfur is mainly organic. In high-sulfur coal, the added sulfur is mainly mineral (pyritic). The sulfur can be determined without a full ultimate analysis. The percentage of sulfur in coal ranges from a trace to 12%. Most commercial coals have between 0.3 and 5.5%.
6. *Ash* is non-combustion residue after burning the coal and coke. Ash obtained differs in composition from mineral and organic matter.

The ASTM (American Society for Testing and Materials) standard specifications for classifications of coal by rank have 4 main groups: anthracite, bituminous, sub-bituminous and lignite. The characteristics of coal in differing ranks have widely different chemical property^[27]. Coal was classified into ranks as showed in Table 2.3.

In Table 2.4 these properties are showed for coals of different rank. It can be seen that the lower the coal rank, lower its fixed carbon content and the higher its oxygen and hydrogen contents, although the hydrogen content may drop somewhat from bituminous to lignite coals. Generally, the lower coal rank, the lower also is the calorific value and the higher the fraction of moisture and volatile matter^[2].

Table 2.3 Classification of coals by rank

		Fixed carbon limits,%		Volatile matter limit,%		Calorific value limit, % Btu/lb	
Class	Group	Equal or grater than	less than	Equal or grater than	less than	Equal or grater than	less than
I. Anthracite	1.Meta-antracite	98	2
	2.Anthracite	92	98	2	8
	3.Semianthracite	86	92	8	14
II. Bituminous	1.Low volatile	78	86	14	22
	2.Medium volatile	69	78	22	31
	3.High volatile A	...	69	31	...	14,000	...
	4.High volatile B	13,000	14,000
	5. High volatile C	11,500	1,3000
III.Subbituminous	1.Subbituminous A	10,500	11,500
	2.Subbituminous B	9,500	10,500
	3.Subbituminous C	8,300	9,500
IV. Lignite	1.Lignite A	6,300	8,300
	2.Lignite B	6,300

Source. ASTM Standard D –388 (ASTM D-388)

Table 2.4 Chemical change with coal rank ^[2].

<i>Material</i>	Mass Percent		
	Carbon	Hydrogen	Oxygen
Wood (cellulose)	44	6	50
Peat*	59	6	35
Lignite	71	5	24
Bituminous coal	84	5	11
Anthracite	94	3	3
Graphite*	100	—	—

*Not a coal,

2.2.1.3 Structure of coal

Many researchers have investigated the structure of coal and it is generally agreed to consider coal as highly cross linked polymer, which consist of a large number of stable aggregates connected by relatively weak hydrogen bond crosslink.

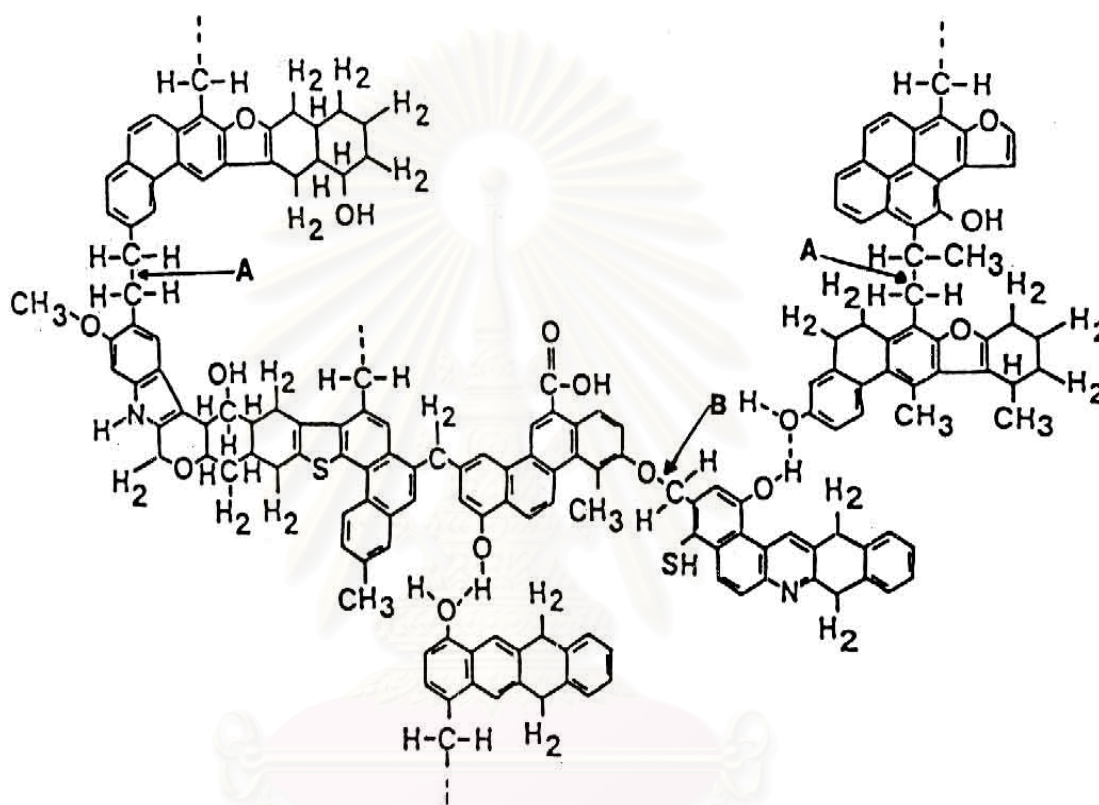


Figure 2.3 Possible chemical structure of coal^[4].

The decomposition products in Figure 2.3 are obtained after the weak link in the structure is ruptured. For example, the bond between aliphatic carbons (A) or between the oxygen and an aliphatic carbon (B) are most likely to break. The breaking of these bonds releases the ring clusters with their attached functional groups. These large molecules comprise the coal tar.

2.2.1.4 Coal in Thailand

Most of coals in Thailand are lignite type, with a total volume 2,128 million tons. The main resource is Mae Moh basin in Lampang province in the north of Thailand, with reserve of 1,240 million tons. In 1999, total coal consumption in Thailand was about 22.8 million tons. Coal used in electricity generation accounted for almost 70% of the total domestic coal consumption. The rest was used fuel in industrial sector, paper mill, fiber factory, etc^[29]. The sources of Thailand energy consumed over the last 3 years as showed in Table 2.5.

Table 2.5 Thailand sources of energy consumed (%)^[30].

	Primary energy demand		
	1992	1996	2001
Lignite (Coal)	13.9	11.6	19.0
Hydraulic Power	2.8	1.8	1.9
Natural Gas	20.8	15.2	14.5
Petroleum	62.5	71.4	64.6

Thailand consumption of lignite seems to be growing steadily each year. The trend of lignite demanded for energy sources and others as showed Figure 2.6.

Due to the comparatively low cost of supplies and low political risk of supply disruptions compared with other major energy source, it is foreseeable that coal will remain a major fuel, next to oil and natural gas.

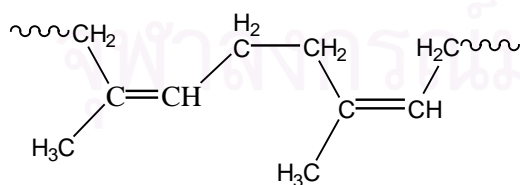
Table 2.6 Demand of lignite and trend in the future ^[30]. Unit: 1,000 tons

		1992	1996	2001	2006
Electric Power	Domestic Coal	12,554	15,305	18,388	31,932
	Imported Coal	0	0	9,770	19,250
<i>Cement</i>	Domestic Coal	1,893	4,500	4,930	5,520
	Imported Coal	370	1,480	1,480	1,480
Others	Domestic Coal	1,290 (7.9)	1,310 (5.8)	1,440 (4.0)	1,500 (2.5)
Total	Domestic Coal	15,737	21,115	24,758	38,952
	Imported Coal	370	1,480	11,250	20,730

2.2.2 Natural Rubber

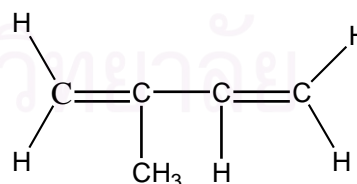
Natural rubber (NR) is a bio-polymer consisting of *cis*-1,4-polyisoprene at 99% produced from Para rubber, although NR may be obtained from hundreds of different plant species, the most important source is the rubber tree (*Hevea brasiliensis*).

When the bark of the *Hevea* tree is partially cut trough (tapped), a milky liquid extrudes from the wound and dries to yield a rubber film. The biological function of this latex is still obscure: it may help wound healing by protecting the inner bark. The latex consist of an aqueous suspension of small particle, about 0.1~0.5 micrometer in diameter, of *cis*-1,4-polyisoprene (Figure 2.4), containing approximately 5000 isoprene units (Figure 2.5) in the average polymer chain ^[27].



(I)

Figure 2.4 *Cis*-1,4-polyisoprene



(II)

Figure 2.5 Isoprene units

A wide variety of products have a rubber, or elastomer, as an essential component. The most important forms in which NR is processed and marketed are the following:

- Sheets
- Crepes
- Block rubber
- Preserved latex concentrates

NR in sheet forms is the oldest and the most popular type. Being the simplest and easiest to produce on small scale, small holder's rubber in the most of countries are processed and marketed as sheet rubber.

NR is one of the most important produce of Thailand. Thailand is currently the leader in the production and export of NR in the world with exporting volume of approximately 2.031 million tons in the years 1999 as showed in Table 2.7. While the capacity for the NR production is estimated to be 2.150 million tons currently. Trends of NR production is reported that there are 22 countries in this world that do process altogether about 24,403,760 acres of rubber land, Thailand has about 4,960,000 acres^[26].

Table 2.7 Thailand NR production export and capacity^[26].

Year	Production (tons)	Export (tons)	Local Usage (tons)	Stock (tons)
1995	1,804,788	1,635,533	153,159	113,030
1996	1,970,265	1,762,989	173,159	147,669
1997	2,025,000	1,837,150	185,000	59,374
1998	2,065,002	1,839,396	185,700	200,000

World consumption of NR seems to be growing steadily each year; however, there still exists the oversupply trend throughout the years. Thus, rubber price will continue to suffer in the immediate foreseeing future.

2.3 Catalyst and catalysis

2.3.1 Definition of catalyst

The word catalysis comes from two Greek words, the prefix *cata-*, meaning down, and the verb *lysein*, meaning to split or break. The Chinese words *tsoo mei* which are used for a catalyst, and which also mean ‘marriage broker’ Berzelius introduced the term “catalysis” as early 1836 in order to explain various decomposition and transformation reactions.

A definition that is still valid today is due to Ostwald (1895): “a catalyst accelerates a chemical reaction without affecting the position of equilibrium”. While it was formerly assumed that the catalyst remained unchanged in the course of reaction, it is now known that catalyst is involved in chemical bonding with the reactants during the catalytic process^[10].

In theory, an ideal catalyst would not be consumed, but the case is not practical. Owing to competing reactions, the catalyst undergoes chemical changes, and its activity becomes lower (catalyst deactivation). Thus catalyst must be regenerated or eventually replaced. Catalytic cycle was showed in Figure 2.6.

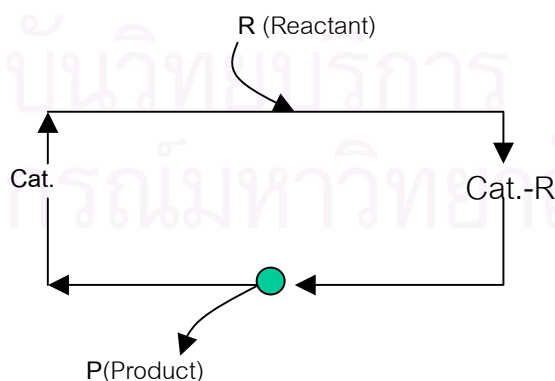


Figure. 2.6 Catalytic cycle.

2.3.2 Classification of catalysts

Most of the catalytic reactions can be classified as homogeneous and heterogeneous reactions. Both of these classes have different conditions and end effects. Catalytic reactions involve catalyst and reactants to produce products and unchanged catalyst in the ideal sense. The two systems, homogeneous, and heterogeneous, are differentiated as follows in Table 2.8.

Table 2.8 Comparison of homogeneous and heterogeneous catalysis^[11].

Homogeneous catalysis	Heterogeneous catalysis
<ol style="list-style-type: none"> 1. Catalysis and components of reactants and products are in the same physical state and remain only in one phase. 2. Catalyst is uniformly distributed throughout the system and the mobility of catalyst is same as that of the other component. 3. Catalyst acts by its mass and the velocity coefficient is proportional to the concentration of the catalyst in the system. 	<ol style="list-style-type: none"> 1. Catalysts and components of reactants and products are in different physical states or, if in the same physical states, they have different phase separated by a phase boundary. 2. Catalyst is not uniformly distributed throughout the system and mobility of catalyst is different from that of the other component. 3. Catalyst acts by its surface and the velocity coefficient is proportional to the catalyst area exposed for the reaction.

The differences of two types of catalysts, as heterogeneous catalysts are most important in petroleum process, such as hydrocracking, hydrotreating, reforming, polymerization and hydrogenation. In the hydrogenation of oil, a heterogeneous catalyst was selected in experiment.

2.3.3 Heterogeneous catalysis

Heterogeneous catalyst is in different phases from reactant, generally the catalyst is a solid, and the reactants are gases or liquids. The major advantages of heterogeneous catalysts are they can separate from product automatically, or they can separate by simple process for example, filtration and centrifugation^[10]. The following reaction steps are showed in Figure 2.7

The heterogeneous catalytic reaction can be divided into 7 steps:

- 1) Mass transfer of the starting material from bulk fluid to the catalyst surface.
- 2) Mass transfer of the reactants in to the pores of the catalyst.
- 3) Adsorption of the reactants on the inner surface of the pores.
- 4) Chemical reaction on the catalyst surface.
- 5) Desorption of the products from the catalyst surface.
- 6) Mass transfer of the products out of the pores.
- 7) Mass transfer of the products to bulk fluid.

The reaction of heterogeneous consists of chemical and physical reaction steps. For the starting reaction, the reactant must transfer from liquid phase (or gas phase) to the catalyst surface. That is the ends of catalytic reaction. The products diffuse from catalyst surface to liquid phase.

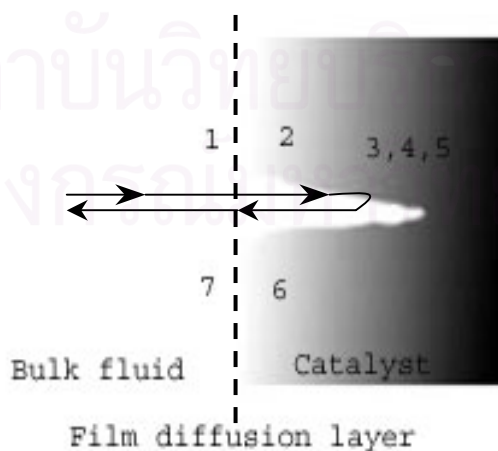


Figure 2.7 Catalytic reactions^[10].

2.3.4 Adsorption in heterogeneous catalysis

The term “adsorption” was defined by the accumulation of atom (molecules) on the surface of solid without percolation into bulk of solid. The particle (atom or molecule) is adsorbate and solid is adsorbent.

Generally process of adsorption must distinguish between physical and chemical adsorption (physisorption and chemisorptions)

1. Physical adsorption is the adsorption by physical forces only; major force is resulted by Van Der Waals forces.
2. Chemical adsorption, particle are formed the chemical bond between the surface of solid and starting material.

Both types of adsorption are exothermic, such as raising the temperature of reaction decreases the quantity of adsorbate. Physisorption is faster than chemisorptions and equilibrium is rapid at low temperature. Chemisorptions requires high activity energy. The rate of adsorption is proportion to temperature, then the rate of adsorption is low at low temperature, but rapid at high temperatures. Chemical adsorption can form monolayer on the solid surfaces, whereas physisorption can form multilayer on surface, whereas the physisorption is a first step to chemisorptions. The two types of adsorption are differentiated as follows (Table 2.9):

Table 2.9 Comparison of physisorption and chemisorptions ^[10].

	Physisorption	Chemisorption
Temperature required	low temperature	high temperature
Rate	very fast	depends on temperature
Activation energy	low	high
Number of layers	multilayer	monolayer

2.3.5 Production of heterogeneous catalyst^[5]

The production of heterogeneous catalysts consists of numerous physical and chemical steps. The conditions in each step have a decisive influence on the catalyst properties. Catalysts must therefore be manufactured under precisely defined and carefully controlled conditions. General methods of catalyst preparation most often used impregnation and precipitation.

- Impregnation

One of the best known methods for producing catalysts is the impregnation of porous support materials with solutions of active components. After impregnation the catalyst particles are dried, and the metal salts are decomposed to the corresponding oxides by heating. The process is showed schematically in Figure 2.8.

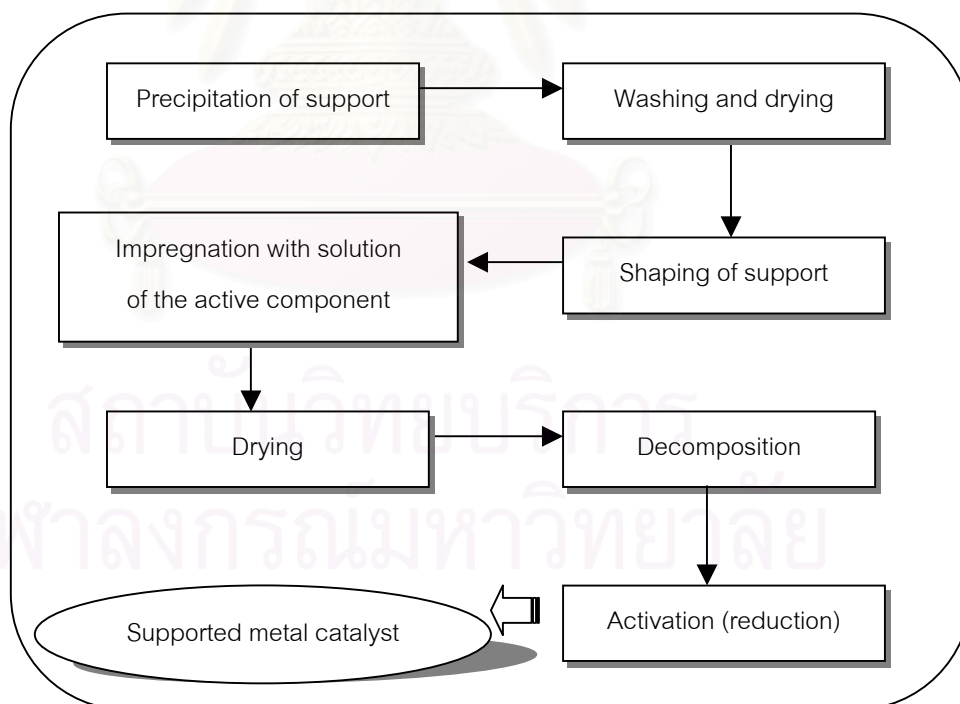


Figure 2.8 Production of supported metal catalysts by impregnation^[5].

- Precipitation

Bulk catalysts are mainly produced when the active components are cheap. Since the preferred method of production is precipitation, they are also known as precipitated catalysts. Precipitation is mainly used for pure support materials. One or more components in the form of aqueous solutions are mixed and then co-precipitated as hydroxides or carbonates. An amorphous or crystalline precipitate or a gel is obtained, which is washed thoroughly until salt free. Further steps then follow this: drying, shaping, calcination, and activation (Figure 2.9).

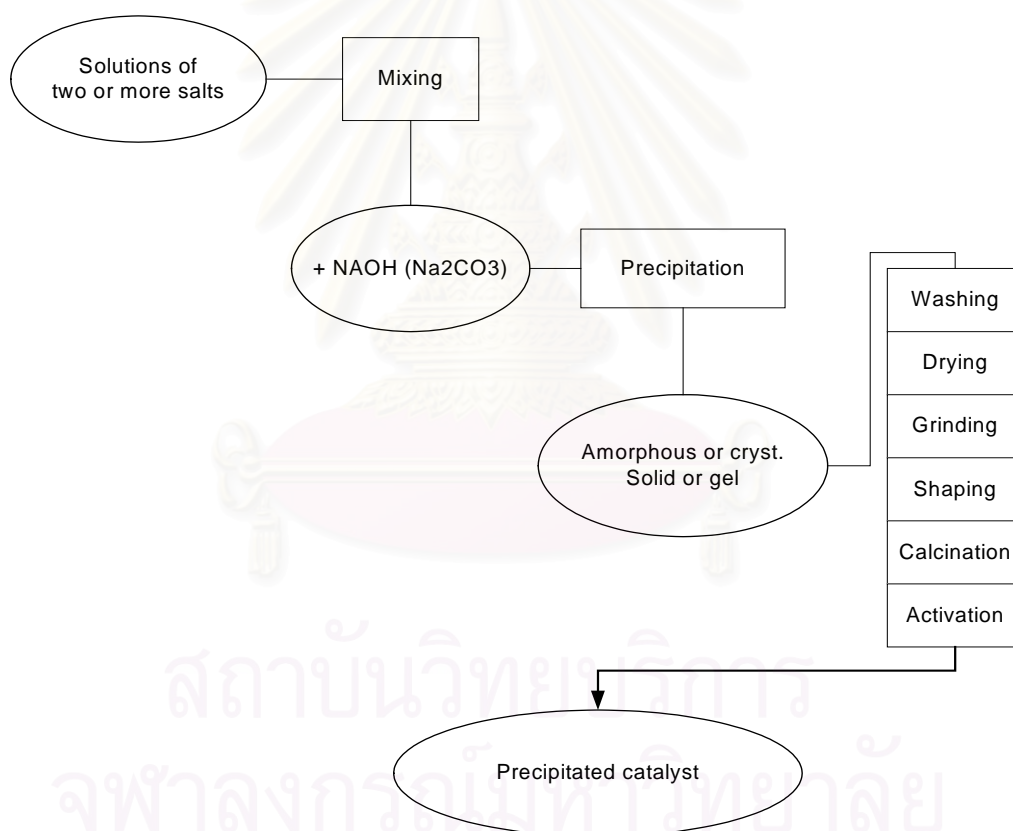


Figure 2.9 Production of a precipitated catalyst ^[5].

The production conditions can influence catalyst properties such as crystallinity, particle size, porosity, and composition.

2.4 Catalysts in direct coal liquefaction by sulfated zirconia

Catalysts for the coal liquefaction have been extensively needed for many years. They classified into several types: metal oxide, metal sulfides, metal halides and others. Metal halides, highly active, but the disadvantage is corroding reactor materials and difficulties in catalyst recovery. Research of metal oxides and sulfides has increased ^[33]. In the field of catalysis, solid super acids, acids stronger than 100% H₂SO₄, have been prepared by the addition of sulfate ion to oxides of Fe, Ti, Zr, Hf, Sn, Si and Al. The strong hydrogenation and hydrocracking ability for C—C and Ar—O bond are required for liquefaction of coal.

2.4.1 Zirconium catalysts and catalysts ^[33].

2.4.1.1 Occurrence and distribution of zirconium

Zirconium (Zr) is transition metal group 4 and average atomic mass is 91.224. Zirconium is one of more abundant elements, and is widely distributed in the earth's crust and has been present in the earth's crust (about 0.02%) in the forms of zircon (ZrSiO₄), baddelyite (ZrO₂) and complex oxides and silicates.

Atomic structure

- Atomic Radius : 2.16 Å^o
- Covalent Radius : 1.45 Å^o
- Crystal Structure : Hexagonal
- Electron Configuration: 1s² 2s²p⁶ 3s²p⁶d¹⁰ 4s²p⁶d² 5s²

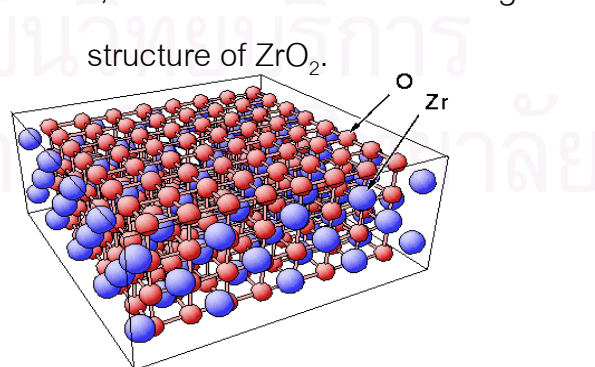
2.4.1.2 Physical and chemical properties

At room temperature zirconium is unreactive to a wide range of chemicals and it is very corrosion resistant. The good mechanical properties combined with resistance to corrosion and low neutron absorption have given zirconium an important place in nuclear reactor technology. Zirconium seems to be non-toxic and compatible with tissue, and it is a competitor with tantalum as component of artificial joint and limbs. Some of physical properties of zirconiums are showed in Table 2.10.

Table 2.10 Physical properties of zirconium ^[33].

Physical properties	Value
Melting point (°C)	2,128 ± 15
Boiling point (°C)	3,578
Density	≈6.46
Specific heat (cal /g)	0.066

The main oxide formed by zirconium is dioxide; the dioxide is naturally occurring as the mineral baddelyite and is usually contaminated with zircon, silica and oxide of iron, aluminum and titanium. Figure 2.10 showed



ZrO_2 lattice

Figure 2.10; Structure of ZrO_2

2.4.2 Sulfated zirconia catalysts

In the study of Zmierczak et. al. [35], they study activity of superacids catalysts, i.e., $\text{Fe}_2\text{O}_3/\text{SO}_4^{-2}$ and $\text{ZrO}_2/\text{SO}_4^{-2}$, for hydrogenolysis of coal compounds at temperature range of 350-400 °C. The solid super acids found are high activity and effective hydrogenolysis catalysts in the low-temperature depolymerization-liquefaction of coal.

In the study of addition metal cation to $\text{ZrO}_2/\text{SO}_4^{-2}$ in n-butane isomerization [36] and study effects of sulfur content for ZrO_2 catalyst on the Fischer-Tropsch synthesis [37]. The results showed $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst leading to an increase in isomerization rate and also gave high selectivity when the catalyst was used.

Zirconium oxide, or zirconia, when modified with anions such as sulfates ions for a highly acidic or super acids catalyst depend the treatment conditions. This catalyst is found to be well suited for catalyzing reactions, e.g. hydrocarbon isomerization, methanol conversion to hydrocarbons, condensation, cyclization, oligomerization, Fischer-Tropsch reaction, cracking and hydrocracking reaction [38].

Two main objects for selected $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst in this research can be expected:

- Improvement of coliquefaction process: increasing the yield, selectivity and energy saving in the production process.
- Development of new processes: use of lignite in Thailand and NR.

2.5 Literature reviews

Several studies of liquefaction include both developing new type of catalyst and seeking a more suitable condition. The studies include a coprocessing between coal and other substances which contain carbon and hydrogen as its major components such as plastic and tires, etc.

Emir, H., Karaduman, A. and Olcay, A.^[1], studied liquefaction of Turkish coals in tetralin with microwaves for 10 min. The yield of oil obtained from the 10 min microwave heating is higher than those obtained from liquefaction experiments carried out at 375 °C in tetralin under H₂ atmosphere for 30 min. Those results support earlier starting that the coal liquefaction goes through the formation of free radicals.

Karaca, F., and Bolat, E.^[7], studied coprocessing of Turkish lignite with a waste materials. Waste material may improve the overall economics of coal liquefaction by fulfilling one or more of the roles of an expensive solvent. The results have showed that the coprocessing of coal with sawdust increases liquefaction yields.

Vatcharahirun, T.^[8], studied the coliquefaction of lignite and used tires with hydrogen by used iron/active carbon, nickel/molybdenum on alumina and cobalt/molybdenum on alumina as catalyst at 350 - 400 °C, residence time of 30 - 60 min and H₂ pressure range of 30 to 60 bar. It was found that appropriate conditions at 80% tire 20% coal mixture feed, 400 °C, 60 min and 60 bar of hydrogen pressure, obtaining liquid oil yield of 52.54% by using Ni/Mo catalyst. The components in the product were composing of 39% gasoline, 16% kerosene, 30% gas oil and 15% residue.

Kittiroungtong, T. ^[9], investigated the direct liquefaction of lignite and polypropylene using iron on active carbon from palm-oil shell. Coal can be converted into distillable liquid fuels with addition of polymer. Polypropylene contains hydrogen approximately fourteen percents, in principle; provide the hydrogen to aid in the liquefaction of coal. The lignite and polypropylene were reacted at 420 °C, hydrogen gas pressure of 62 bar and reaction time at 30 min. Under this condition lignite and polypropylene gave maximum naphtha in liquid product. The product consists of 35.6% naphtha, 7.41% kerosene, 5.45% gas oil and 0.99% long residues.

Charusiri, W. ^[12], studied coprocessing of polypropylene and anthracite using iron on active carbon in micro reactor by varied operating condition as ratio of polypropylene with anthracite rang of 1:0 to 0:1, reaction temperature range of 380 – 430 °C, pressure of hydrogen gas range of 30 -60 bar, reaction time 30 – 75 min. The results established that the ratio of polypropylene with anthracite 0.8:0.2, temperature 400 °C pressure of hydrogen gas 50 bar, reaction time 60 min was the best condition that giving oil yields of 59.40%. The components in the product were composing of 32.07% gasoline, 7.84% kerosene, 8.82% gas oil and 5.08% long residue.

Kano, T. and others ^[21], studied coprocessing between coal and polyethylene (PE) using Fe (CO)₅-S as catalyst at 400 - 425 °C with tetralin mixed as solution. The situation without catalyst provides a higher liquid product than a situation with 11-12% of catalyst because Fe (CO)₅-S interrupted H₂ transport from polyethylene to coal.

Artanoto, Y. and others ^[22], studied properties of various types of catalyst in different circumstance which reacts to the coal located in different parts of Indonesia. It was found that in the case that the catalyst is Mo in the presence of S for solvent-free hydrogenation, yielded a maximum value at 79-88% of coal starting weight with the same capacity as Ni/Mo catalyst.

Ikenaga, N., and others ^[23], studied coliquefaction of micro algae with Australian Yallourn brown coal under pressurized H₂ in 1-methylnaphalene at 350-400 °C for 60 min with various catalysts. Coliquefaction of Chlorella with Yallourn coal was successfully achieved with Fe (CO)₅-S catalyst. In the reaction with a one to one mixture of Chlorella and Yallourn coal giving conversion at 99.8% and 65.5% of oil yields were obtained at 400 °C.



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CHAPTER III

EXPERIMENTAL

The experimental was in laboratory scale which studied condition of coliquefaction of lignite with NR. The products were analyzed by SD-GC. The result brought to information for production and suitable advantages.

3.1 Apparatus

Reactor was a micro-reactor that showed in Figure 3.2. The micro reactor is a stainless steel tube SS 316 with an inner volume of 75 ml, 30-mm inside diameter. Figure 3.3 showed the reactor with heating coil 450 watt, and the temperature was measured by thermocouple. The temperature was controlled to accuracy of +/- 5 °c by digital temperature controller. Rota-meter is used to control shaking of micro-reactor (Figure 3.4). The oil product was separated form solid by using vacuum filter. Filter paper was fiberglass that reduces time and efficiency showed in Figure 3.5.

3.2 Raw materials and chemicals

3.2.1 Lignite from Mae Moh Mine

3.2.2 Natural rubber (dry rubber sheet)

3.2.3 Hydrogen gas 99.5% / Praxair (Thailand) co., ltd.

3.2.4 Sulfated zirconia (ZrO_2/SO_4^{2-})/ Wako pure chemical Industries.

3.2.5 Toluene / Analytical grade / Lab scan

3.2.6 1,2,3,4 –Tetrahydronaphthalene (tetralin)/Analytical grade; Merck

3.3 Procedure

3.3.1 Lignite analysis

- The proximate analysis was used to determine the percentages of volatile matter (VM), fixed carbon, ash and moisture content.

3.3.2 Study reaction conditions of coliquefaction on ZrO_2/SO_4^{-2} catalyst, the parameters were;

- Lignite and rubber feed ratio (C/R ratio); 70:30, 60:40, 50:50
- Reaction temperature; 325, 350, 375, 400 °C
- Reaction time; 30, 60, 90 min
- Hydrogen pressure; 20, 40, 50 bar
- Amount of catalyst; 0%, 1%, 3%, 5%

3.3.4 Study reaction conditions of coliquefaction between lignite and NR by using solvent extraction method (H-donor solvent).

3.4 Experimental

Dried samples of natural rubber were used as hydrogen donor and lignite were employed. All coal samples were dried, ground to pass 250 mesh sieves, and stored in dry place. The proximate analyses of feed stocks are shown in Table 4.1. Sulfated zirconia (ZrO_2/SO_4^{-2}) was employed as catalyst.

Lignite, NR and catalyst were placed into a 75 ml micro-reactor. Hydrogen was charged in micro-reactor at room temperature and reactor was heated to required temperature (325-400 °C) within 60 min. The reaction time was counted from the time when temperature of mixture had reached the

required temperature. After the reaction the reactor was rapidly cooled to room temperature with an electric fan, the gaseous products were released and the weight of gas was measured.

The products were separated by filter glass. Conversion was calculated by the difference between the charge feed and the amount of residue. The oil fraction, including water, was calculated from the difference between the coal conversion and the gas fraction.

- The components of oil fractions were analyzed by simulated distillation by gas chromatography at PTT Research and Technology Institute.

- Fourier transform infrared (FT-IR) spectra were analyzed functional group obtained by transmission mode using Perkin Elmer; FTIR 1760x.

Experimental Method

1. Clean and dry the micro-reactor, weigh lignite, NR and catalyst in into the reactor.
2. Close the reactor and inject initial pressure of hydrogen gas, after that weight the reactor.
3. Install a micro-reactor with the reaction unit and settle the desired condition. The micro-reactor was wrapped by insulator.
4. After reaction was over, cool down the reactor to room temperature by an electric fan and then weighed the reactor.
5. Liquid production was strained by vacuum filter. Solid part was dried and the liquid product was collected in a bottle. Then the solid and liquid products were weighted. Finally the micro-reactor was washed with toluene.
6. Oil product was analyzed to find the composition by SD-GC.

3.5 Coliquefaction condition.

This study addressed the reaction conditions necessary for coliquefaction of lignite with NR and determined the conditions under which the synergistic conversions and oil yields. Coliquefaction was carried out under the following conditions.

1. Coal and NR feed ratio (C/R ratio)
2. Reaction temperature
3. Residence time
4. Hydrogen pressure
5. Amount of $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst
6. Effect of hydrogen donor solvent (tetralin)

The experimental results showed the amount of oil production in the different factors and composition analysis of liquid product by SD-GC. The product expressed in form of total conversion, oil yield and gas yield that the component of product was divide into 3 types:

1. Oil products (gasoline, kerosene, residues and gas oil).
2. Gas products.
3. Solid.

The conversion was calculated by difference between the charged feed and the amount of residue.

The second part, an evaluation method of oil fractions is proposed based on the boiling point distribution obtained from the SD-GC. Knowledge of boiling point distribution data for crude oil and refined petroleum products is essential for process control and quality assurance. A simulated distillation by

gas chromatography (SD-GC), standardized by the American Society for Testing and Materials (ASTM D2887) [19], has been well accepted as rapid way of determining a boiling range distribution. However, SD-GC method is only applicable to petroleum fractions boiling between 373 K and 811 K.

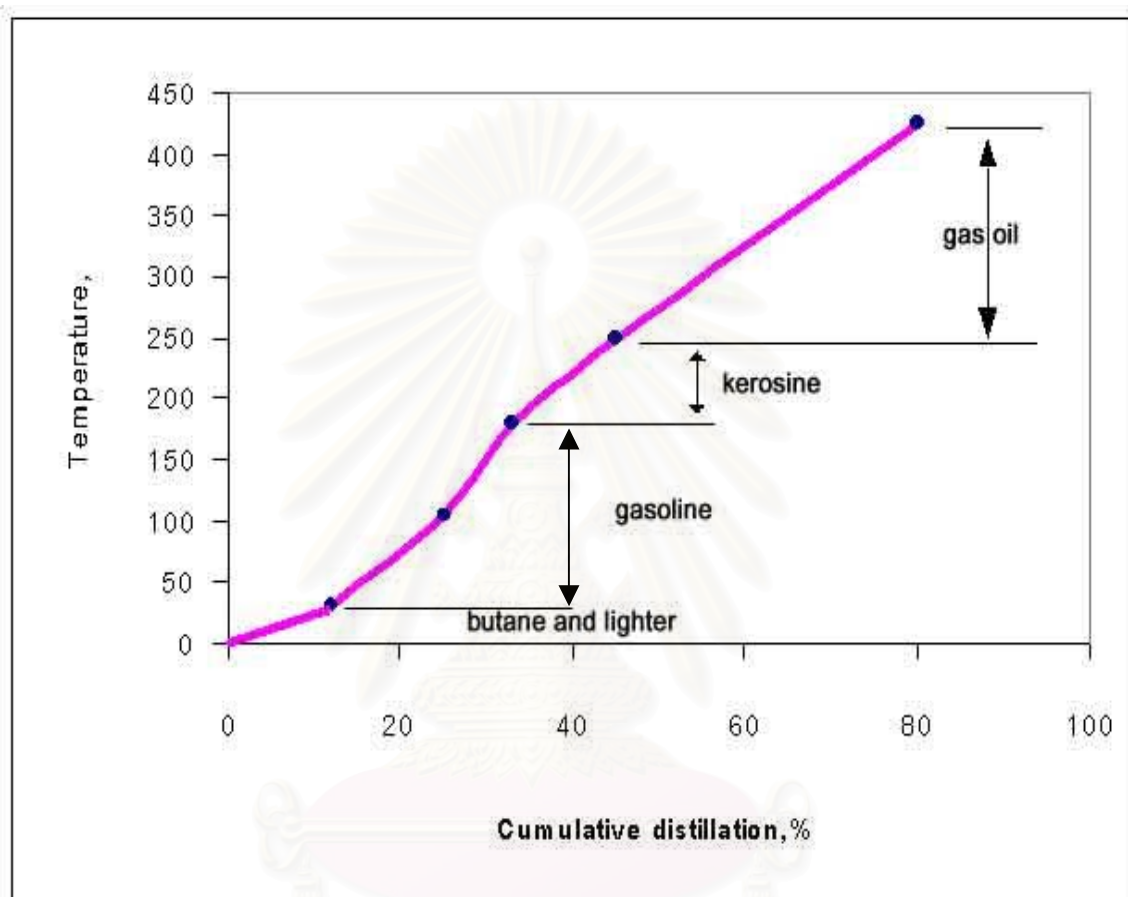


Figure 3.1 Simulated distillation curves obtained according to SD-GC and boiling point calculation for coal derived oil ^[3].

The SD-GC was also prepared by the boiling point prediction of components identified in oils. The distillation curve was obtained by accumulating the contents of all identified components in order of their boiling points (Figure 3.1).

Table 3.1 Boiling ranges and disposition of oil fractions ^[3].

	Carbon number	Boiling range	Uses
Gas	C ₁ -C ₄	<32 °C	Fuel
Gasoline	C ₅ -C ₁₂	32-180 °C	Gasoline
Kerosene	C ₉ -C ₁₅	180-250 °C	Jet fuel
Gas oil	C ₁₁ -C ₂₁	250-370 °C	Diesel fuel
Residues	>C ₂₂	>370 °C	Heavy fuel, asphalt

Since boiling points increase with molecular weights, specific oil cuts produced by fraction of a crude oil showed pronounced composition shift. The fundamentals of modern fraction practices and the major product streams generated by them are showed in Table 3.1.

The fractions of oils in this experiment were separated into 4 types:

1. Gasoline : boiling range from IBP to 180 °C
2. Kerosene : boiling range from 180 °C to 250 °C
3. Gas oil : boiling range from 250 °C to 370 °C
4. Residue : boiling ranges over 370 °C – FBP

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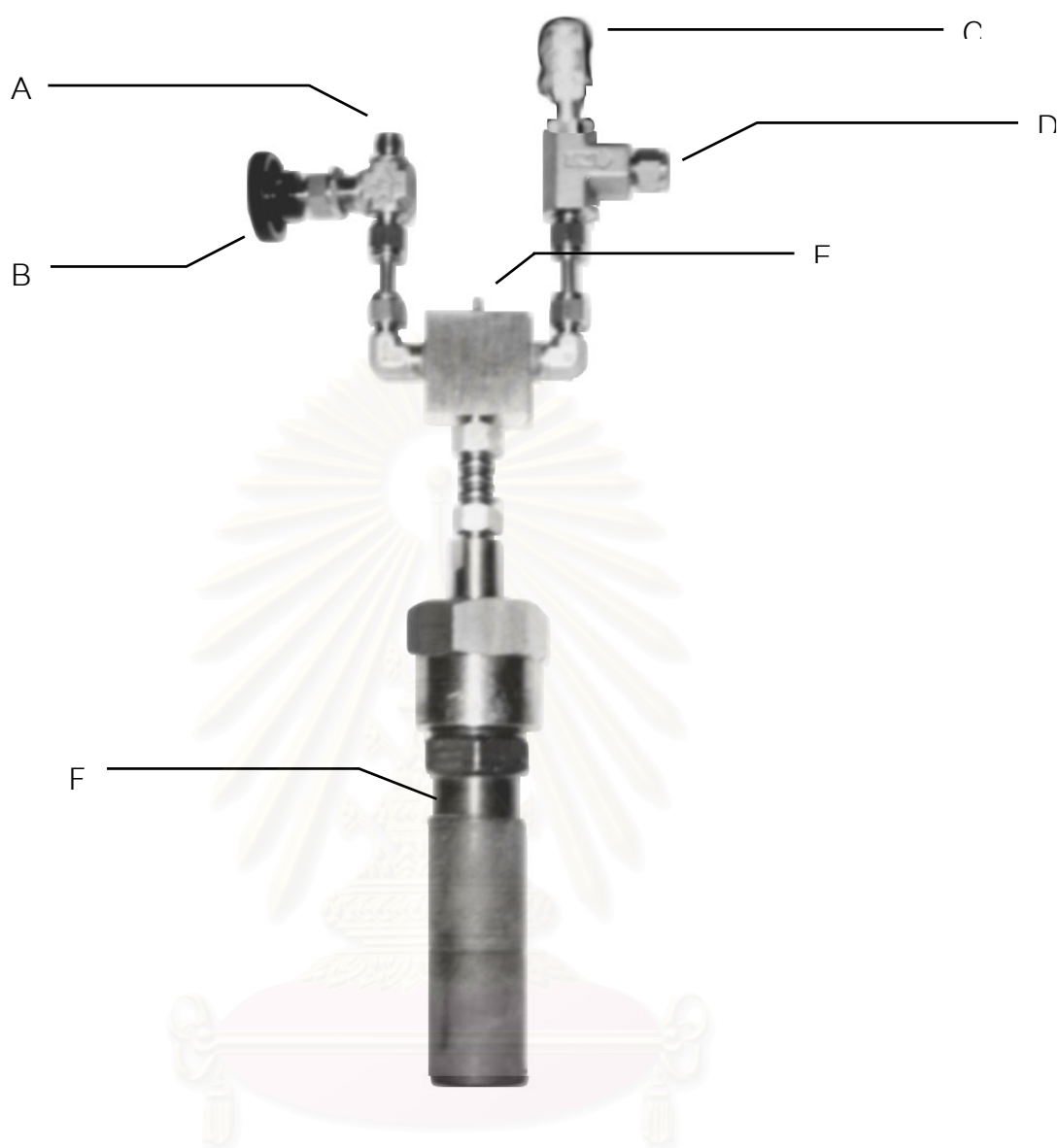


Figure 3.2 Reactor and fittings

The parts of micro-reactor are indicated with the following letters.

- A. A gas injection and release tube
- B. A gas gate valve
- C. A safety valve
- D. A gas release safety valve
- E. A thermocouple
- F. A heating column



Figure 3.3 Shaker

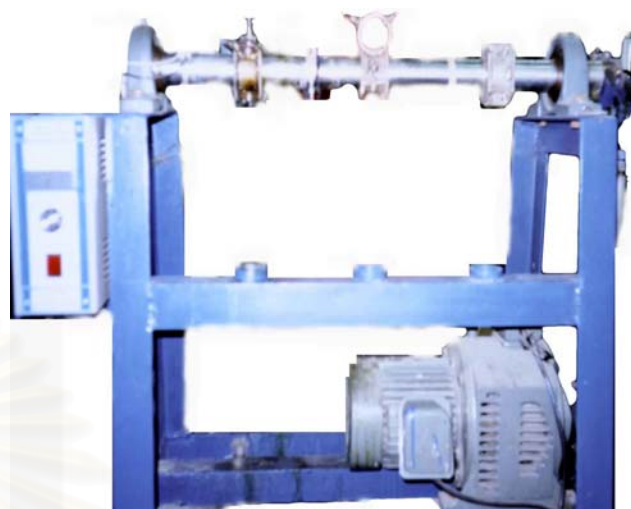


Figure 3.4 Reactor shaker



Figure 3.5 Filtration set

CHAPTER IV

RESULTS AND DISCUSSION

The experiment studied the effect of parameters that influence to oil product conversion of coliquefaction lignite and rubber on ZrO_2/SO_4^{-2} catalyst. The main objective of this research was aimed to study the suitable condition of coliquefaction of lignite with natural rubber.

4.1 Properties of starting materials

4.1.1 Properties of lignite

The coal used in this study was lignite from Mae Moh Mine. The coal particle size was ≤ 60 mesh (sieve opening: $\leq 250 \mu\text{m}$) and stored in a sealed, dry container.

Table 4.1 Proximate analysis for lignite^a: ASTM 3172-3175 (see Appendix A)

	Lignite (1*)	Lignite (2*)	Lignite (3*)
Volatile matter (V), %	42.31	37.10	42.10
Fixed carbon (FC), %	23.83	21.89	47.44
Ash (A), %	33.86	40.40	10.46

a = dry basis

(1*) Lignite in experimental

(2*) Data of coal from Kittiroungtong, T., Master's thesis ^[9]

(3*) Data of coal from Karaca, F.; Bolat, E., ^[7]

The properties of lignite (Table 4.1) compared with different sources. Research from Kittiroungtong showed the same low quality of lignite because it has low percent of fixed carbon (23.83%) and high amount of ash (33.86%).

4.1.2 Composition of dry rubber

Raw natural rubber is a major amount of rubber hydrocarbon (94%), while protein and neutral lipid are the same at about 2%. The remainder is not significant showed in Table 4.2.

Table 4.2 Composition of dry rubber

<i>Composition</i>	Dry rubber (%)
Rubber hydrocarbon	93.7
Protein	2.20
Carbohydrates	0.40
Neutral lipid	2.40
Glycolipids & phospholipids	1.00
Inorganic constituents	0.20
Other	0.10
Water	—

By heating, the NR is decomposed and resulted in the cracking of long chains in the core structure of rubber. Through the coal transformation process, NR can be added in the order to lower required hydrogen gas needed in processing. In consequence, it is to cheapen the cost of fuel production.

4.2 Coliquefaction condition

4.2.1 Effect of lignite and natural rubber feed ratio on the coliquefaction.

The liquefaction of lignite alone was studied at temperature range of 325 °C to 450 °C, 0-60 bar, 30-120 min. The results indicated that the oil product was not produced in the liquefaction of lignite alone.

The variation of lignite natural rubber feed ratio from 50:50, 40:60, 30:70 was investigated by fixing the condition at reaction temperature of 375 °C, H₂ pressure of 40 bar, reaction time 60 min and 3 %wt catalyst. It was found that a decrease feed ratio of lignite/NR induced an increase of the percentage of oil from 52.09% to 72.12%. The percentage of conversion was also increased, because the liquid from lignite could do more coprocessing with NR. While the solid content decreased, produced gases rested stable about 10%. Figure 4.1 illustrates the effect of the feed ratios of lignite/NR on the oil yield in the coliquefaction.

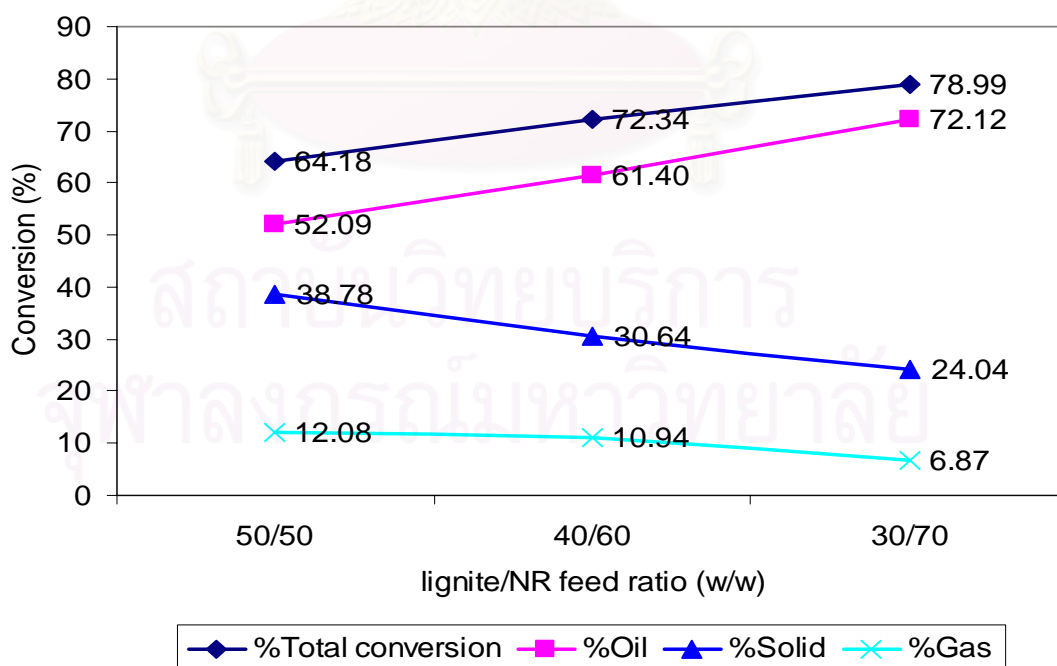


Figure 4.1 Effect of lignite and NR feed ratio on the coliquefaction. Reaction using $\text{ZrO}_2/\text{SO}_4^{-2} = 3\% \text{wt}$, 375 °C, 60 min, P (H₂) 40 bar.

For lignite and NR feed ratio of 30:70, the conversion and oil yield in coliquefaction were highest. The product distribution of oil component showed in Figure 4.2 which supports the assumption that NR was hydrogen donor for coal liquefaction to increase the amount and quality of liquid product, as measured by an increasing in the amount of gasoline in liquid product.

The ratio of 30:70 gave the maximum amount of gasoline because the composition of NR was cis-1,4-polyisoprene, and methyl free radicals generated by thermal cracking. The free radical initiators of chain reaction cause medium size molecules to low molecular weight products such as gasoline and kerosene were highly produced. These results strongly supported the above assumption that NR fragment radicals behaved as an initiator of coal cracking.

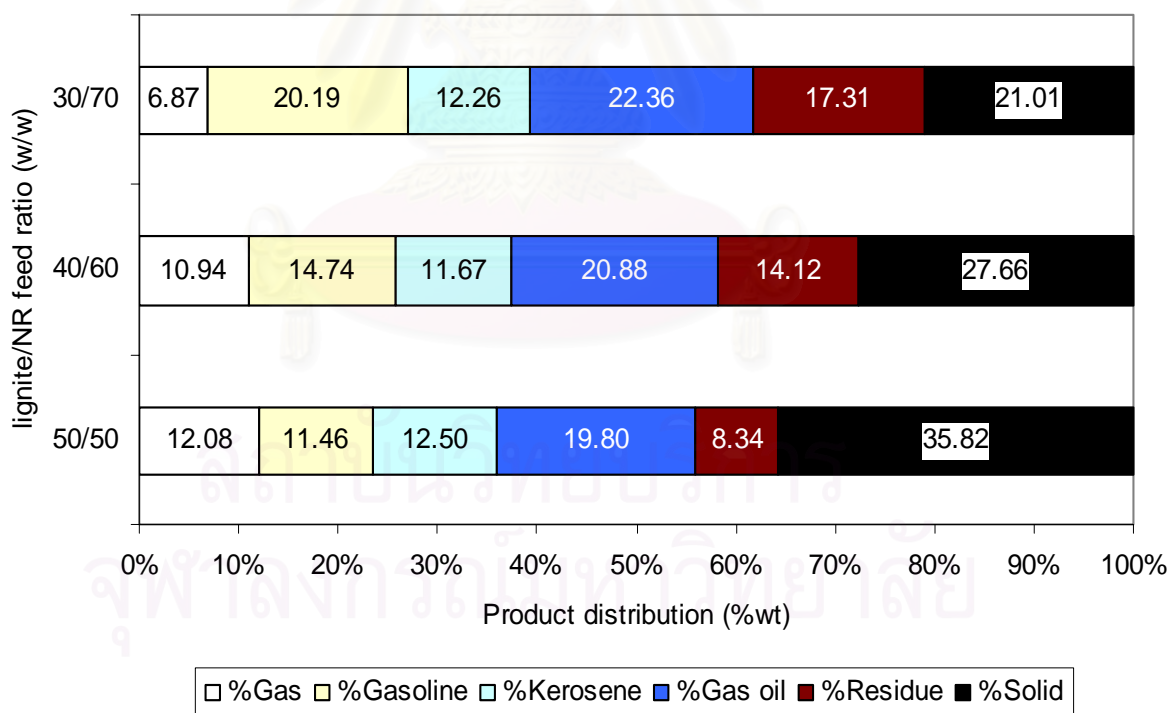


Figure 4.2 Effect of lignite and NR feed ratio on the product distribution in coliquefaction. $\text{ZrO}_2/\text{SO}_4^{-2} = 3 \text{ \%wt}$, $375 \text{ }^\circ\text{C}$, 60 min, $P(\text{H}_2) 40 \text{ bar}$.

In all cases of experimental conditions, the total conversion, oil yield and gasoline fraction at high amount of NR were greater than at low amount of NR. The highest lignite/NR feed ratio effect was observed when lignite/NR ratio of 30/70 was coliquefied. The conversion of 78.99% and the oil yield of 72.12% obtained were higher than those of other ratios.

4.2.2 Effect of reaction temperature on the coliquefaction.

The reaction temperature was investigated from 325 to 400 °C being fixed the condition at H₂ pressure 40 bar, reaction time of 60 min and 3 %wt catalyst. When the temperature was increased from 325 °C to 400 °C, the increase of the total conversion from 75.82 % to 78.99 % and oil yield from 70.45% to 72.12% were observed in Figure 4.3.

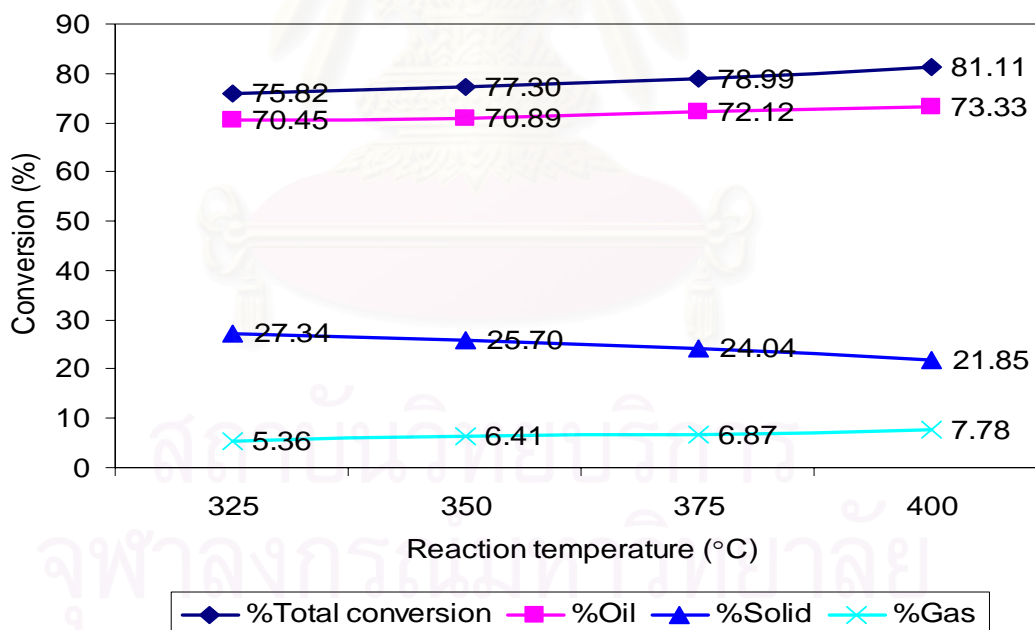


Figure 4.3 Effect of reaction temperature on the coliquefaction. Reaction using lignite/NR = 30/70, ZrO₂/SO₄⁻² = 3 %wt, 60 min, P (H₂) 40 bar.

It was found that the coliquefaction of lignite with NR slightly increased the conversions and oil yields at these temperature ranges. When reaction temperature increased over 375 °C, it was found a lot of hydrocarbon gas coming from depolymerization and cracking of NR. It could be explained that the temperature over 375 °C was higher ceiling temperature of NR, therefore temperature reaction for coliquefaction of lignite with NR was range of 300 - 400 °C. In the liquefaction of lignite with NR, a high conversion (78.99 %) and oil yield (72.12 %) were obtained even at reaction temperature of 375 °C in reaction with catalyst.

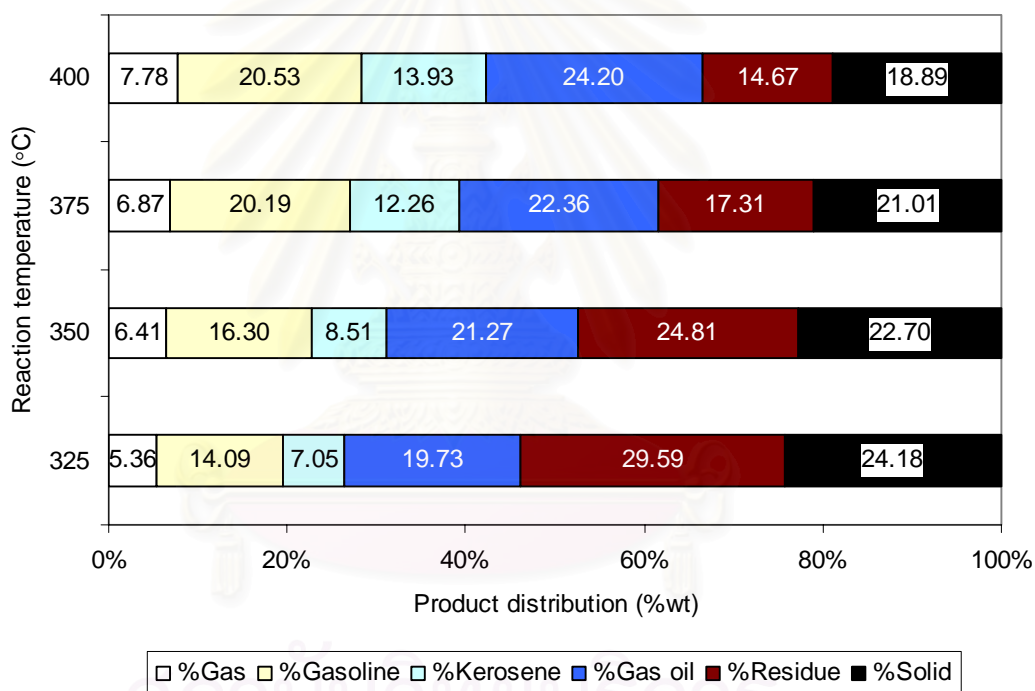


Figure 4.4 Effect of reaction temperature on the product distribution in coliquefaction. Lignite/NR =30/70, ZrO_2/SO_4^{2-} = 3 %wt, 60 min, $P(H_2)$ 40 bar.

The component distribution of oil product was showed in Figure 4.4. When the temperature increased from 325 °C to 375 °C it caused a larger amount of thermal cracking of NR and lignite, as a result, the compositions of

gasoline, kerosene and gas oil have a trend to be increased from 14 to 20 %, 7 to 12 % and 19 to 22 %, respectively.

The results from Figures 4.3 and 4.4 showed that temperature is important factor of coal conversion. Because of their higher contents of heterocyclic and polynuclear aromatics, coal liquids are, as rule, more difficult to hydrocrack than petroleum feedstock ^[3]. Typical condition for reaction is over 300 °C.

In conclusion, the suitable temperature is 375 °C because of high oil yield and low solid. The composition of product is gasoline, kerosene, gas oil, residue and solid at 20.19 %, 12.26 %, 22.36%, 17.31% and 21.01%, respectively with 72.12% of oil yield.

4.2.3 Effect of reaction time on coliquefaction.

Figures 4.5 and 4.6 showed the influence of variation of reaction time range from 30 to 90 minutes on percentage of product yield and composition by fixing the condition at C/R ratio = 30:70, H₂ pressure 40 bar, reaction time of 60 min and 3 %wt catalyst.

The experimental results indicated that the increasing of reaction time from 30 to 90 min increased the total conversion from 77.68% to 79.70%, whereas oil yield was decreased from 72.73% to 71.73%. The increasing of reaction time caused much increase in thermal cracking rate. Therefore, it was observed that the amount of oil was slightly decreased while the reaction time was increased. However, if the longer reaction time was set up (especially at 60 min), the required product would occur in high quality, while gas yield was also increased, as illustrated in Figure 4.5.

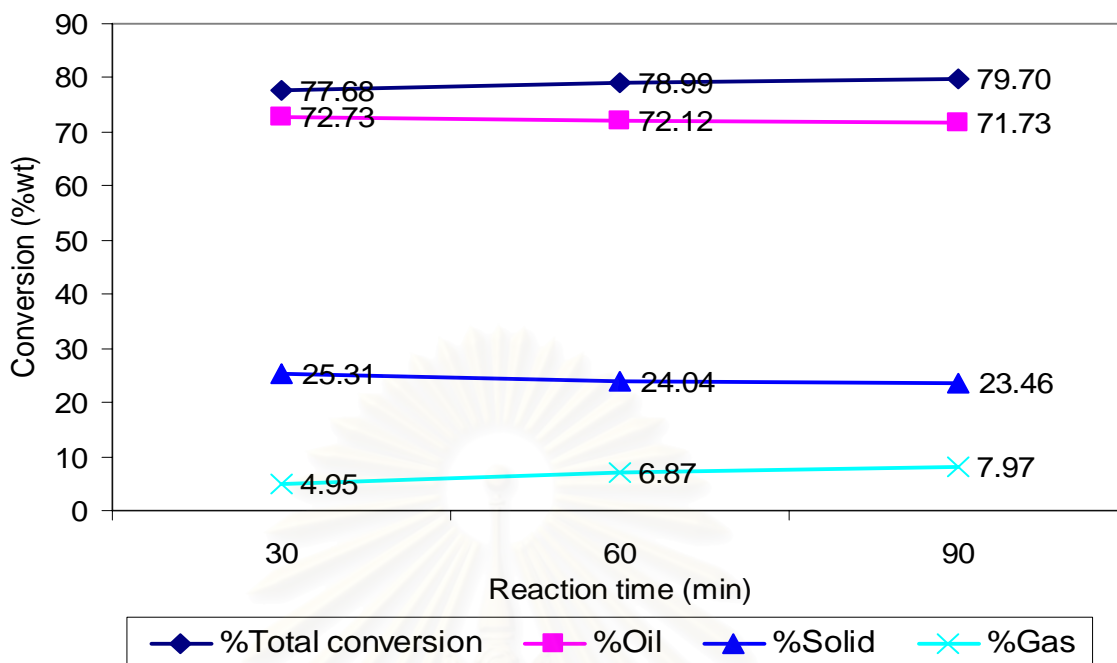


Figure 4.5 Effect of reaction time on the coliquefaction. Reaction using lignite/NR = 30/70, $\text{ZrO}_2/\text{SO}_4^{-2}$ = 3 %wt, 375 °C, P (H_2) 40 bar.

In term of product distribution, gasoline and kerosene increased from 17.45 wt% and 9.45 wt% to 20.19 wt% and 12.26 wt% when increasing of reaction time form 30 min to 60 min. This resulted in increasing of low molecular weight oil components. However, when reaction time increased from 60 min to 90 min gasoline yield decreased from 20.19 wt% to 15.78 wt% and kerosene decreased from 12.26 wt% to 11.48 wt%. It is because oil component shift to low molecular weight during longer thermal and catalytic cracking. It can be conclude that the optimum reaction time for coliquefaction of lignite with NR should be 60 min because it gave the highest amount of gasoline and kerosene.

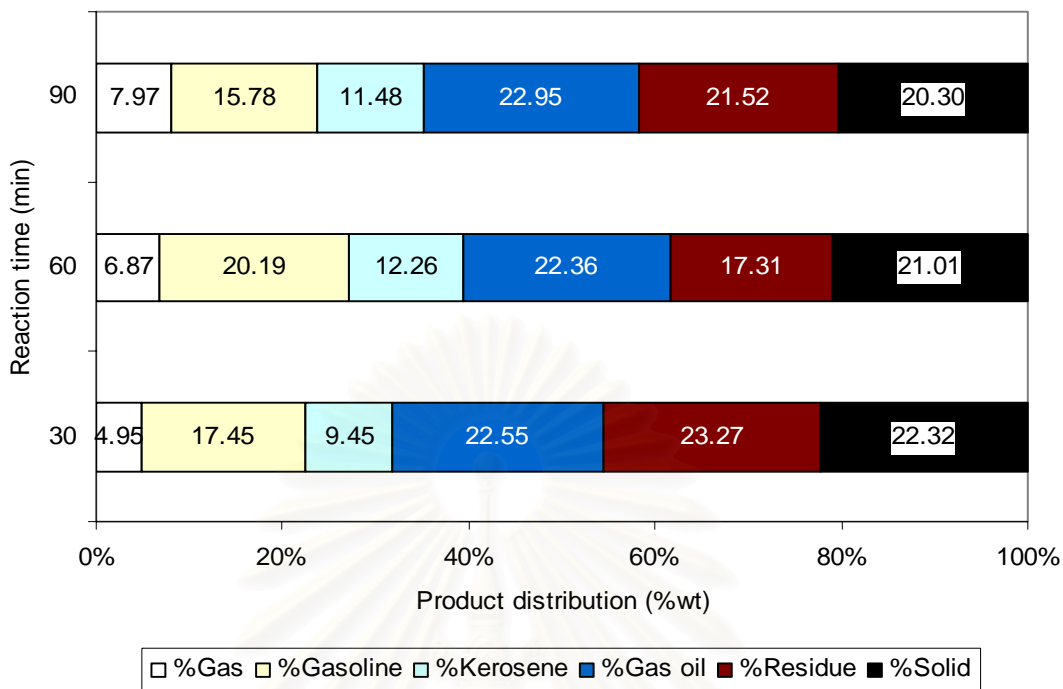


Figure 4.6 Effect of reaction time on the product distribution in coliquefaction. Lignite/NR = 30/70, ZrO_2/SO_4^{2-} = 3 %wt, 375 °C, $P(H_2)$ 40 bar.

4.2.4 Effect of initial pressure of hydrogen pressure on coliquefaction.

Figures 4.7 and 4.8 showed the influence of variation of hydrogen pressure range from 20 to 50 bar on conversion and percentage composition by fixed condition at feed ratio 30:70, 375 °C, 60 min and 3% of catalyst.

When pressure an increased from 20 bar to 50 bar, the result showed that pressure was not significant effect on the total conversion and oils yield because the conversion and oil yield was slightly changed when comparing with the low pressure. When pressure was raised up from 20 bar to 40 bar, the result showed the increasing of percentage of oils yield approximately 1.4%. After the pressure was raised up more than 40 bar, the result showed that oils yield was reduced, whereas gas yields was increased.

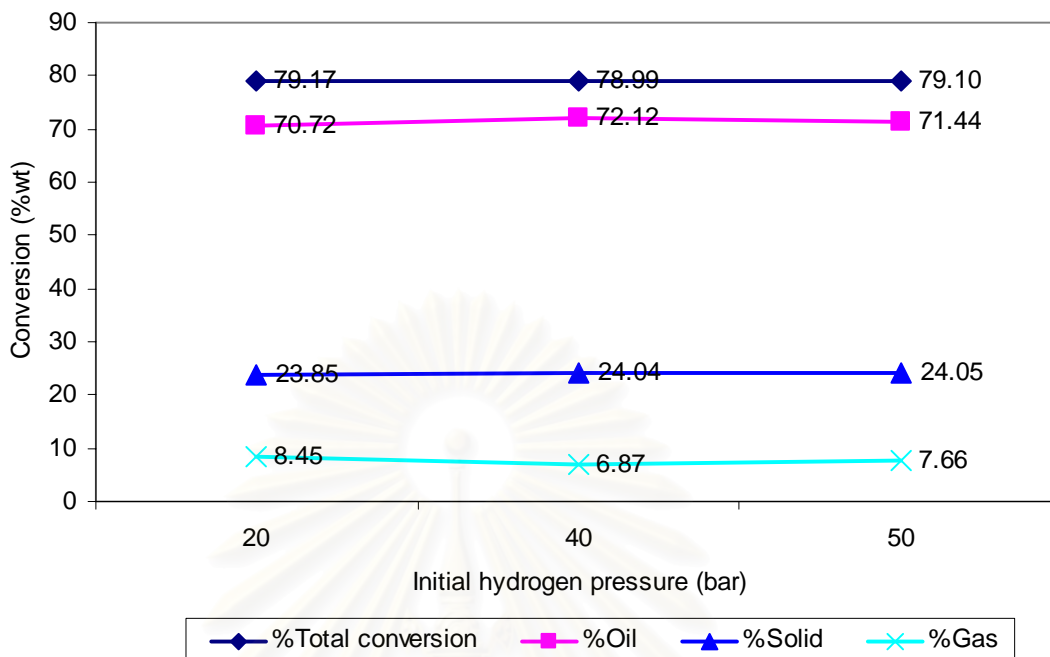


Figure 4.7 Effect of hydrogen pressure on the coliquefaction. Reaction using lignite/NR = 30/70, $\text{ZrO}_2/\text{SO}_4^{-2} = 3$ %wt, 375 °C, 60 min.

The results from Figure 4.8 showed that the increasing of the initial hydrogen pressure from 20 to 50 bar decreased the quality of oil. When pressure was raised up from 20 bar to 40 bar, percentage of gasoline was decreased from 21.92 % to 20.19%.

In fact, coliquefaction of lignite with NR is mainly a thermal process not affected by the reaction atmosphere. Thus, liquefaction can reduce the hydrogen gas cost by reduce hydrogen pressure and added NR to be hydrogen source.

In conclusion in case of initial hydrogen pressure, the suitable pressure is 40 bar because of high oils yield (72.12%). The composition of liquid product was gasoline, kerosene, gas oil and long residues at 20.19, 12.26, 22.36 and 17.31% respectively with gave the best product distribution.

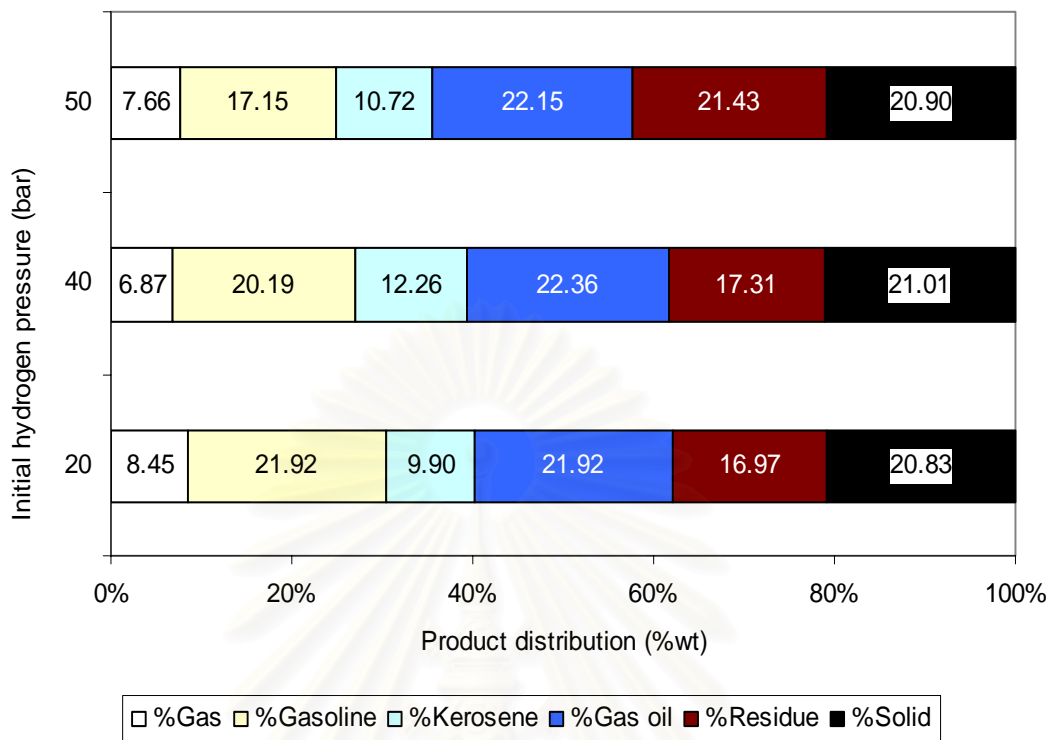


Figure 4.8 Effect of initial pressure of hydrogen on the product distribution in coliquefaction. Lignite/NR = 30/70, ZrO_2/SO_4^{-2} = 3 %wt, 375 °C, 60 min.

4.2.5 Effect of percent of sulfated zirconia on the coliquefaction.

The variation of percentage loading of ZrO_2/SO_4^{-2} catalyst 1, 3 and 5% at fixed condition at C/R ratio = 30:70, H_2 pressure of 40 bar, 375 °C, 60 min and comparing without catalyst were showed in Figure 4.9.

It showed that in the coliquefaction of lignite with NR without catalyst, the oil yield is low (54.68 %). However, in the presence of ZrO_2/SO_4^{-2} catalyst, the conversion and oil yield increased with increased percent of ZrO_2/SO_4^{-2} . The reaction with catalyst gave 78.99% of conversion and 72.12 % of oil yield at 3% of ZrO_2/SO_4^{-2} . This trend was observed which ZrO_2/SO_4^{-2} catalyst was effective for coliquefaction of lignite with NR.

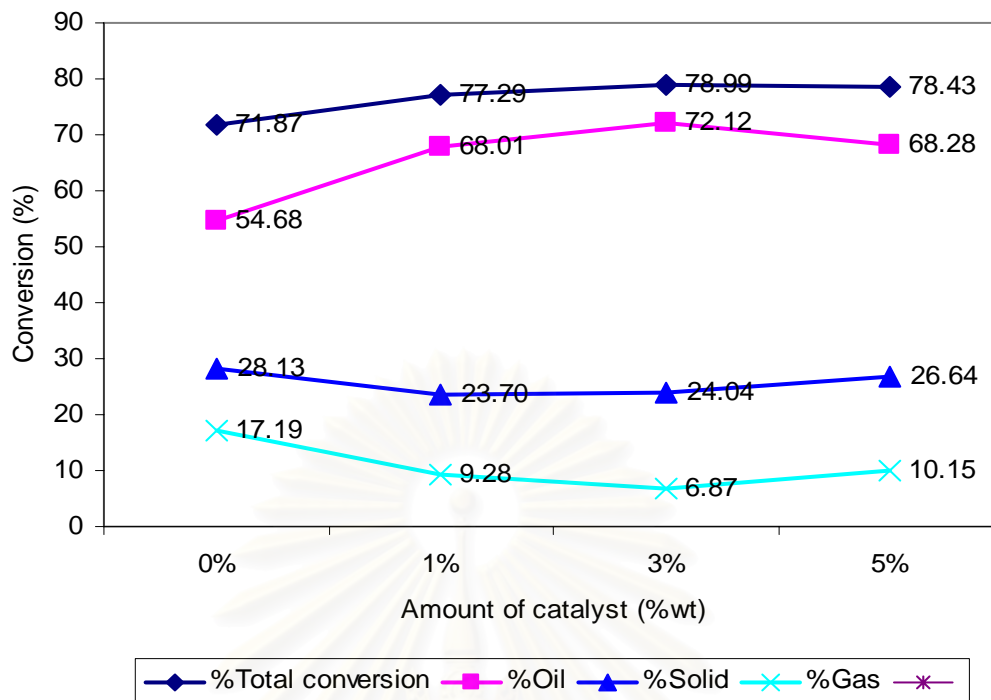


Figure 4.9 Effect of percent of sulfated zirconia on the coliquefaction. Reaction using lignite/NR = 30/70, $\text{ZrO}_2/\text{SO}_4^{-2} = 3$ %wt, 375 °C, 60 min, P (H_2) 40 bar.

Figure 4.10 indicated that the product distribution of liquid product was obtained the higher quality of oil. It was found that an increasing percent of $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst from 0 to 3% increased the gasoline value from 12.03% to 20.19%, kerosene value from 9.84% to 12.26% and gas oil from 19.14% to 22.36%. The value of gas yield was decreased from 17.19% to 6.87%, while amount of solid decreased from 28.13% to 21.01%.

Based on above results, $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst showed high activity as well as selectivity for conversion to small molecules, $\text{ZrO}_2/\text{SO}_4^{-2}$ was solid super acid catalyst which found to be effective hydrogenolysis catalysts in low temperature depolymerization-liquefaction of coal^[34].

Consequently, small amounts of (1-3 %wt) $\text{ZrO}_2/\text{SO}_4^{-2}$ can be convenient in the coliquefaction of lignite with NR.

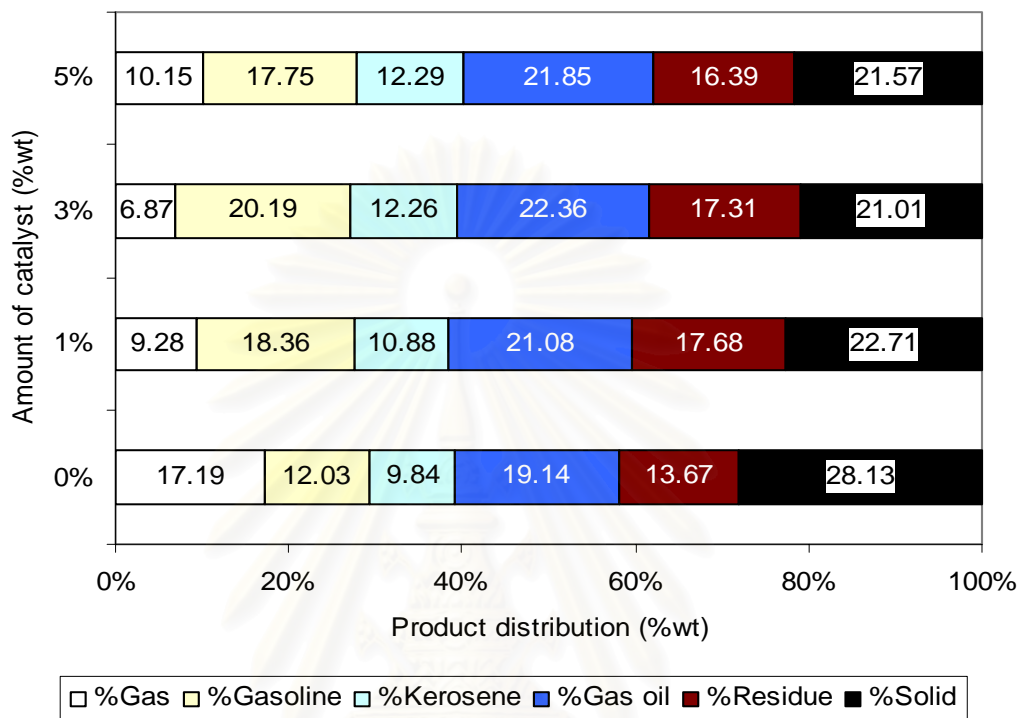


Figure 4.10 Effect of percent of sulfated zirconia on the product distribution in coliquefaction. Lignite/NR = 30/70, 375°C , 60 min, $P(\text{H}_2)$ 40 bar.

4.2.6 Effect of a donor solvent in case of without catalyst.

The effect of tetralin as solvent extraction method (donor solvent) for requiring data about the variation of product yields and product distribution to comparison catalyst method.

Comparison of catalyst, non-catalyst and H-donor solvent (tetralin) in Figure 4.11 showed the highest oil yields produced with $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst were 72.12%. From tetralin, the oil yield decreased to 65.78%. Comparison of

total conversion and gas yields showed in Figure 4.11 also showed that catalytic reaction gave a better total conversion (78.99%) and gas yield slightly higher than tetralin.

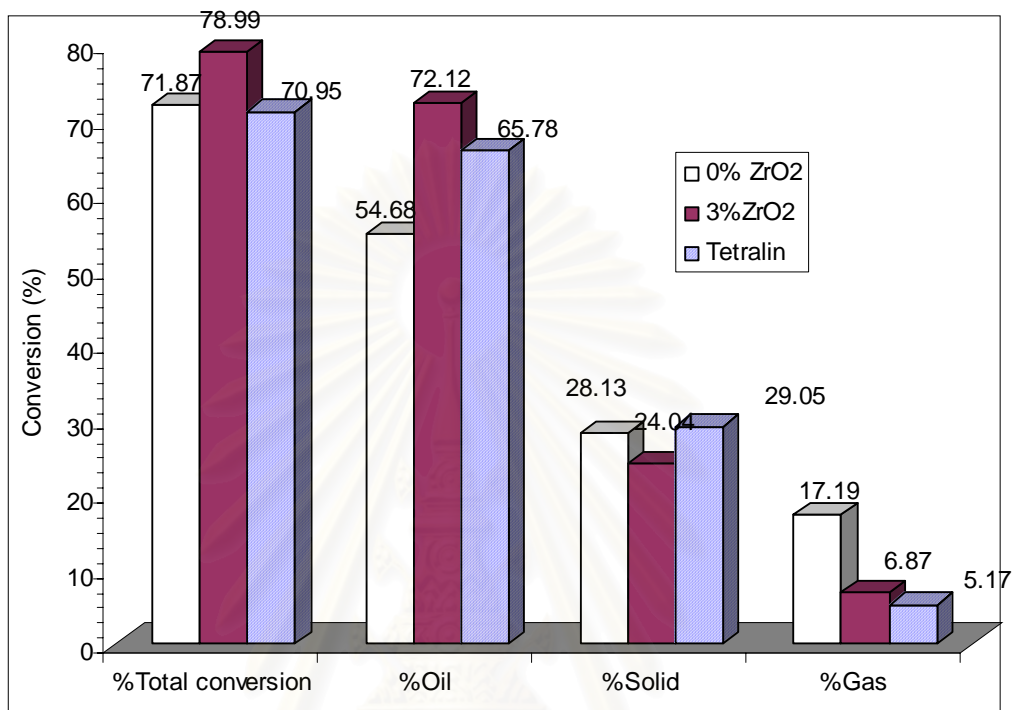


Figure 4.11 Comparison of products yield of coliquefaction of lignite with NR using $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst and tetralin.

The effects of catalyst and tetralin on product distribution were showed on Figure 4.12. Cracking reaction on catalyst process in coliquefaction showed that total conversion and oil yield higher than tetralin, because catalyst presented in coliquefaction had two steps of cracking. The catalytic reaction was simultaneously processed by thermal and catalytic cracking; as a result the product distribution of hydrocarbon molecules was obtained the higher quality of oil, namely, an increase of gasoline from 13.16% to 20.19%, gas oil 19.73% to 22.36%.

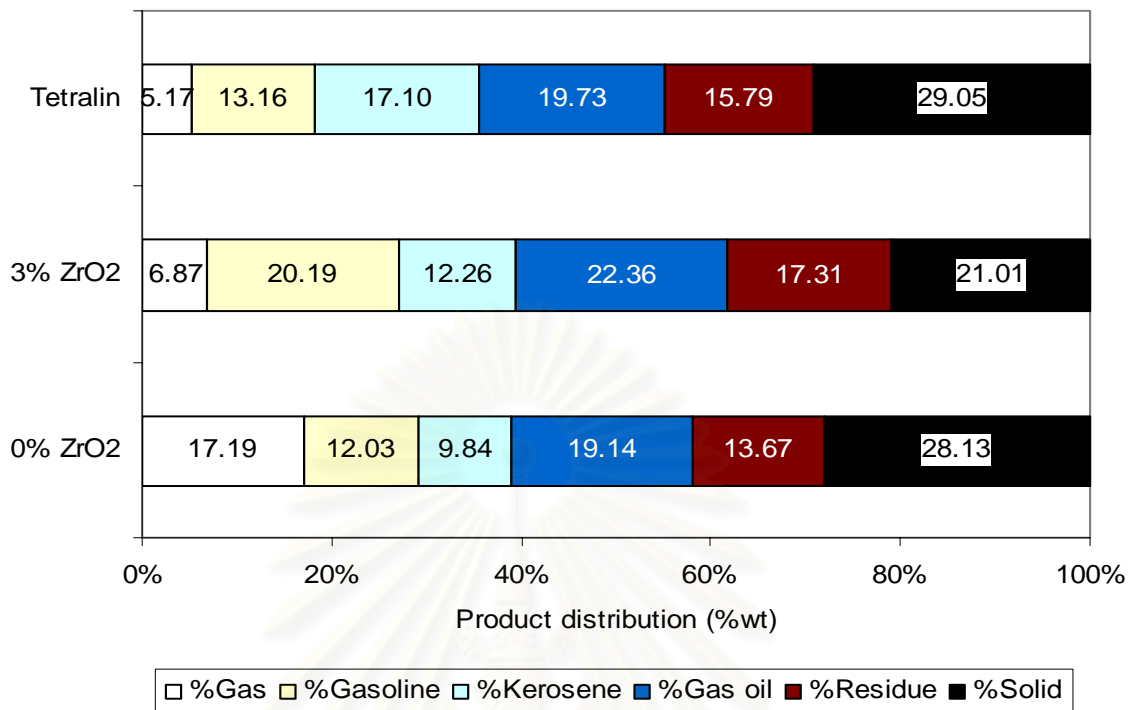


Figure 4.12 Effect of tetralin on the product distribution in coliquefaction. Lignite/NR = 30/70, 375 °C, 60 min, P (H₂) 40 bar.

It was considered that the ZrO_2/SO_4^{-2} as catalyst gave high value product (gasoline) and raises the total conversion and oil yields more than a tetralin solvent, which indicated that the ZrO_2/SO_4^{-2} catalyst showed a higher conversion than solvent extraction in coliquefaction process of lignite with NR.

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4.3 The functional-group of liquid products

The functional group of liquid products was analyzed by fourier transform infrared (FT-IR). The spectra were obtained by absorption mode. Analyses of liquid from lignite and dry rubber were carried out using the following characteristic absorptions ascribed to respective component. The liquid products from coliquefaction exhibited strong C—H vibrations at 2954 cm^{-1} and 2925 cm^{-1} , aromatic C=C in around 1600 cm^{-1} , substituted benzene ring at 876 cm^{-1} and cyclic $-\text{CH}_2-$ in 815 cm^{-1} as showed in Figure 4.13.

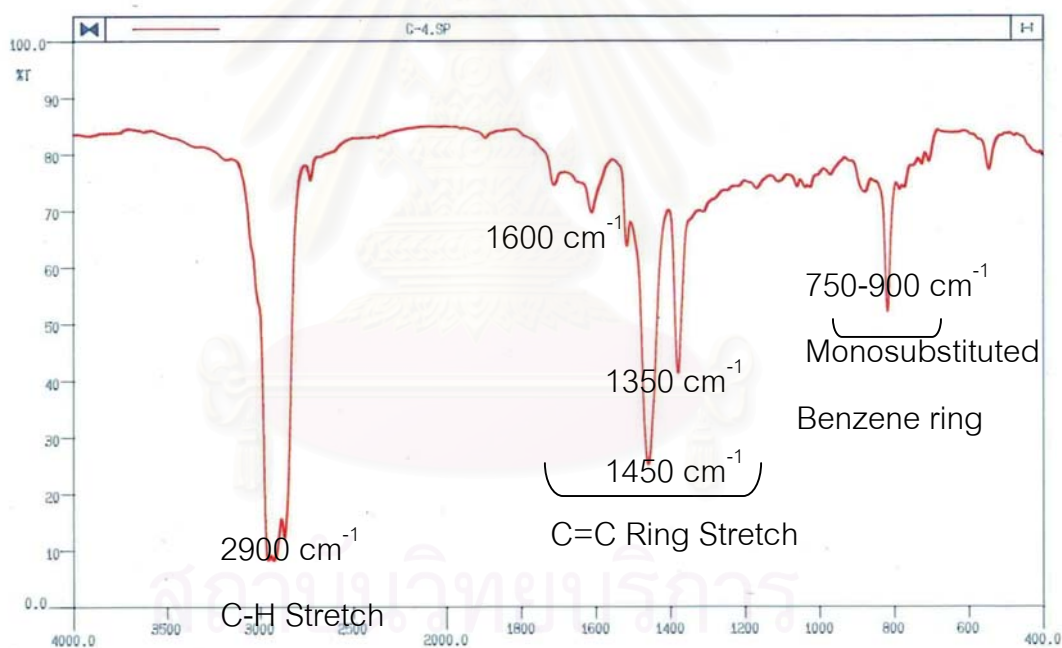


Figure 4.13 FT-IR spectrum of liquid product from liquefaction. Lignite/NR ratio 30/70, $375\text{ }^{\circ}\text{C}$, 40 bar, 60 min. (Perkin Elmer; FTIR 1760x)

4.4 Comparison of the conversion of coal into fuel with another research.

Table 4.3 Comparison of conversion of coal into fuel with another research.

No*.	Catalyst	Feed	Temp (°C)	Pres. (Bar)	Time (min)	Total convers. (Oil+Gas)	Oil (%)
1.	Ni/Mo	Tire/Coal	400	60	60	72.40	52.54
2.	Fe/A.C.	PP/Coal	400	62	30	78.25	53.36
3.	ZrO ₂ /SO ₄ ⁻²	NR/Coal	375	40	60	78.99	72.12

* 1. Thanakorn (2000)^[8], 2. Tharinee (2000)^[9], 3. Chaiyapong (2001)

The conversion of coal into fuel was showed in Table 4.3:

Thanakorn reported a direct liquefaction of lignite and used tires with hydrogen on nickel/molybdenum on alumina as catalysts and found the appropriate condition at 400 °C, 60 min and 60 bar of hydrogen pressure with an 80% tire 20% coal mixture feed, obtaining liquid oil yield 52.54% by weight.

Tharinee studied the conversion processing of polypropylene and lignite using iron on active carbon. The appropriate condition under hight maximum oil yields will be produced at the ratio of polypropylene: lignite was 80:20, 400 °C, 30 min and 62 bar of hydrogen pressure, the highest yield of oil was 53.36% by weight.

The possibility of the coliquefaction of lignite and NR by using ZrO₂/SO₄⁻² catalyst in this experiment gave high oil yield 72.12% at 375 °C, 60 min and 40 bar of hydrogen pressure. The results indicate that the oil yield observed in coliquefaction of lignite with NR using ZrO₂/SO₄⁻² as catalyst were higher than previous research. The results also suggest that ZrO₂/SO₄⁻² could provide a sufficient amount of active species for the liquefaction of lignite and NR.

CHAPTER V

CONCLUSION

This research aimed to study the effects of ZrO_2/SO_4^{-2} catalyst on coliquefaction of lignite with NR in a micro-reactor; the temperature was varied from 325 - 400 °C, 20 - 50 bar of initial hydrogen pressure, 30 - 90 min of reaction time and lignite and NR feed ratio 30:70.

From the experimental, it can be concluded that hydrogen pressure does not significantly affect to coal conversion with NR. The yield of oil and product distribution obtained from ZrO_2/SO_4^{-2} solid super acid catalyst in coliquefaction obtaining the higher than obtained from liquefaction experiments carried out at 375 °C in a tetralin solvent.

The suitable condition for coliquefaction of lignite and NR by ZrO_2/SO_4^{-2} catalyst in this experimental to give oil yield 72.12% are the following:

Ratio of weight lignite/ NR at 30:70

Reaction temperature: 375 °C

Residence time: 60 min

Amount of catalyst: 3 wt%

Initial hydrogen pressure: 40 bar

The liquid product distributions in this condition were consisting of:

Gasoline fraction	=	20.19 wt %
Kerosene fraction	=	12.26 wt %
Gas oil fraction	=	22.36 wt %
Residue fraction	=	17.31 wt %

Suggestion for further work

While the trends observed in this study have been found to be reproducible, it must be note that the present results were in 75 ml micro reactors. They should not be compared on absolute yield basis with the data from large scale tests. Batch system in experiment was difficult in product separation, catalyst recycle, product upgrading and reactor efficiency. Care must be taken when one tries to compare liquefaction data from different sources.



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APPENDICES

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APPENDIX A

Proximate analysis (ASTM D 3172-73)

In this analysis, the pulverized coal is first heated to just above boiling, 104 to 110 °C, to drive off the moisture (*M*), which is weighed by difference, ASTM D 3173-73. Heating then drives off the volatile material (*VM*) to 950 °C for 7 minutes in closed crucible and weighting by difference, ASTM D3175-73. The remainder is then burned in air at 700 to 750 °C, and the remaining ash (*A*) is weighed, ASTM D 3174-73. The balance burned off is the fixed carbon, $FC = 100 - (M + VM + A)$, all quantities in percentages, ASTM D 3172-73.

1. Moisture in the analysis sample coal : ASTM D 3173

Moisture is refers to water in coal and its quantitative determination has been the subject of numerous investigations.

Procedure:

1.1 To bake the aluminum dish with a cover at 105 –110 °C. After

heating for a total of exactly 2 hours, remove the aluminum and cover from oven allow it cool in desiccators. Weigh as soon as cool.

1.2 Weigh 1 g of coal in an aluminum dish, close with cover.

1.3 Insert in the oven, which adjust temperature at 105-110 °C, after

1 hour remove from oven and cool in desiccators. Weigh as soon as cool.

Calculation:

Moisture (M), % = $[(A - B)/A] \times 100$, where:

A = Weight of sample use in gram

B= Weight of sample after heating in gram

2. Ash in the analysis sample coal: ASTM D 3174

Ash is non-combustion residue after burning the coal and coke. Ash obtained differs in composition from mineral and organic matter. Ash can divide into two types:

1.1 *Extraneous or Adventitious* mineral matter composed of clay, shale, pyrite and another chemical from inorganic sulphate, chlorides and fluorides.

1.2 *Inherent Ash* consists of inorganic to combine organic in coal.

Procedure:

2.1 Burn the porcelain crucible in furnace at temperature 700 to

750 °C in 1 hour, remove from furnace and cool in desiccators.

2.2 Weigh crucible with cover; place the sample 1 gram of coal to weighed crucible and coal.

2.3 Place capsule containing sample in a cold furnace and heat

gradually at such a rate the temperature reaches 450 to 500 °C in 1 hour.

2.4 Continue heating so that a temperature of 700 to 750 °C for two hours.

2.5 Remove capsule from the muffle, cool in the desiccators and weigh.

Calculation:

Calculate the ash percent in the analysis sample as follows:

$$\text{Ash in analysis sample (A), \%} = [(A-B)/C] \times 100$$

Where:

A = weight of capsule, cover and ash residue, g

B = weight of empty capsule and cover, g

C = weight of analysis sample used, g

3. Volatile matter in the analysis sample coal: ASTM D 3175

The term “volatile matter” refers to the loss of weight, corrected for moisture, when coal is heated in specified apparatus under standardized conditions. The volatile matter evolved during heating of coals consists mainly of the combustible gas hydrogen, carbon monoxide, methane and another hydrocarbon; tar vapors and incombustible gas. The volatile matter (VM) contents of coals increase with decrease in rank.

Procedure:

3.1 Set the furnace chamber maintained at temperature of 950 ± 20 °C

3.2 Weigh 1 g of coal in weighed nickle crucible, close with a cover with fits closely enough for coals does not burn away from the underside.

3.3 Insert directed into the furnace chamber to the top of furnace, the temperature estimate 300 °C for 3 min.

3.4 The sample shall be given a preliminary gradual heating such that a temperature of 600 ± 50 °C is reached in 6 min.

3.5 Reposition the crucible into the furnace chamber to 950 °C zone, for 6 min.

3.6 Remove the crucible from the furnace and without disturbing the cover allow it to cool. Coke should be cooled in desiccators.

Calculation

Calculation the weight loss percent as follows:

$$\text{Weight loss, \%} = [(A-B)/A] \times 100$$

Where:

A = weight of sample used, gram

B = weight of sample after heating, gram

Volatile matter in analysis sample, (V), % = C – D

Where:

C = weight loss, %

D = moisture, %

4. Fixed carbon

The term “fixed carbon” (FC) refers to the weight loss upon combustion of a devolatilized coal sample.

$$\text{Fixed carbon} = 100 - (\text{moisture} + \text{ash} + \text{volatile matter})$$

APPENDIX B

Table B.1 Product from coliquefaction

No.	Condition					% Product		
	Ratio C/R	Temp. (°C)	Pressure (bar)	Time (min)	Catalyst (Wt %)	% yield of liquid	% yield of gas	% total solid
1	30/70	325	40	60	3	70.45	5.36	27.34
2	30/70	350	40	60	3	70.89	6.41	25.70
3	30/70	375	40	60	3	72.12	6.87	24.04
4	30/70	400	40	60	3	73.33	7.78	21.85
5	30/70	325	40	30	3	*	*	*
6	30/70	350	40	30	3	65.48	5.203	29.32
7	30/70	375	40	30	3	72.73	4.95	25.31
8	30/70	325	20	60	3	*	*	*
9	30/70	350	20	60	3	70.10	5.49	24.41
10	30/70	375	20	60	3	70.72	8.45	23.85
11	30/70	325	20	30	3	*	*	*
12	30/70	350	20	30	3	68.34	5.65	26.00
13	30/70	375	20	30	3	68.89	6.07	25.04
14	30/70	375	50	60	3	71.44	7.66	24.05
15	30/70	375	40	90	3	71.73	7.97	23.46
16	30/70	375	40	60	0	54.68	17.19	28.13
17	30/70	350	40	60	0	26.92	19.56	53.51
18	30/70	325	40	60	0	60.03	8.96	31.01
19	30/70	375	40	60	1	68.01	9.28	23.70
20	30/70	375	40	60	5	68.28	10.15	26.64
21	40/60	325	40	60	3	53.78	13.62	32.60
22	40/60	350	40	60	3	58.81	9.49	31.70
23	40/60	375	40	60	3	61.40	10.92	30.64
24	40/60	325	40	30	3	51.62	15.45	32.92
25	40/60	350	40	30	3	52.44	15.88	31.68

* Product cannot separate

Table B.1 (to continue) Product from coliquefaction

No.	Condition					% Product		
	Ratio C/R	Temp (°C)	Pressure (bar)	Time (Hour)	Catalyst (Wt %)	% yield of liquid	%yield of gas	% total solid
26	40/60	375	40	30	3	56.35	16.48	27.17
27	40/60	325	20	60	3	60.55	6.73	32.72
28	40/60	350	20	60	3	56.10	14.78	29.11
29	40/60	375	20	60	3	60.43	9.41	30.16
30	40/60	325	20	30	3	60.63	6.27	33.10
31	40/60	350	20	30	3	55.98	6.92	37.09
32	40/60	375	20	30	3	61.19	8.12	30.69
33	50/50	325	40	60	3	52.07	8.91	39.02
34	50/50	350	40	60	3	52.22	9.49	38.28
35	50/50	375	40	60	3	52.09	12.08	38.78
36	50/50	325	40	60	3	*	*	*
37	50/50	350	40	30	3	51.36	8.70	39.93
38	50/50	375	40	30	3	53.30	8.83	37.87
39	50/50	325	20	30	3	59.28	8.20	32.52
40	50/50	350	20	60	3	51.72	10.34	37.94
41	50/50	375	20	60	3	52.68	9.35	37.97
42	50/50	325	20	30	3	*	*	*
43	50/50	350	20	30	3	55.72	7.18	37.11
44	50/50	375	20	30	3	51.39	9.48	39.13
45	50/50	375	40	60	1	*	**	*
46	50/50	375	40	60	5	*	13.35	*
46	30/70	375	20	60	5	65.67	7.02	27.31
47	50/50	375	40	60	Tetralin	63.04	6.87	30.09
48	30/70	375	40	60	Tetralin	65.78	5.17	29.05
49	100/0	325	40	60	3	-	-	-
50	100/0	350	40	60	3	-	-	-
51	100/0	375	40	60	3	-	-	-
52	100/0	400	40	60	3	-	-	-
53	100/0	450	40	60	3	-	-	-

Table B.1 (to continue) Product from coliquefaction

No.	Condition					% Product		
	Ratio C/R	Temp (°C)	Pressure (bar)	Time (Hour)	Catalyst (Wt %)	% yield of liquid	%yield of gas	% total solid
54	100/0	375	60	60	3	-	-	-
55	100/0	375	40	90	3	-	-	-

* Product cannot separate

** Gas leak when operating

- No reaction



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APPENDIX C

Table C.1 Product distribution of lignite with natural rubber by using sulfated zirconia catalyst

NO.	Ratio	Temp.	Pressure	Time	Catalyst	Product distribution					
	lignite/rubber	(°C)	Bar	min	wt%	Gasoline	Kerosene	Gas oil	Residue	Solid	Gas
C-2	Blank	375	40	60	0	12.03	9.84	19.14	13.67	28.13	17.19
C-3	Tetralin	375	40	60	0	13.16	17.10	19.73	15.79	29.05	5.17
C-4	30/70	375	40	60	0.3	20.19	12.26	22.36	17.31	21.01	6.87
C-5	30/70	350	40	60	0.3	16.30	8.51	21.27	24.81	22.70	6.41
C-6	30/70	325	40	60	0.3	14.09	7.05	19.73	29.59	24.18	5.36
C-7	40/60	375	40	60	0.3	14.74	11.67	20.88	14.12	27.66	10.94
C-8	50/50	375	40	60	0.3	11.46	12.50	19.80	8.34	35.82	12.08
C-9	30/70	375	20	60	0.3	21.92	9.90	21.92	16.97	20.83	8.45
C-10	30/70	375	50	60	0.3	17.15	10.72	22.15	21.43	20.90	7.66
C-11	30/70	375	40	60	0.5	17.75	12.29	21.85	16.39	21.57	10.15
C-12	30/70	375	40	60	0.1	18.36	10.88	21.08	17.68	22.71	9.28
C-13	30/70	375	40	30	0.3	17.45	9.45	22.55	23.27	22.32	4.95
C-14	30/70	375	40	90	0.3	15.78	11.48	22.95	21.52	20.30	7.97
C-15	30/70	400	40	60	0.3	20.53	13.93	24.20	14.67	18.89	7.78

APPENDIX D

Standard test method for boiling range distribution of petroleum fraction by gas chromatography (ASTM D 2887-93)

1. Scope

This test method covers the determination of the boiling range distribution of petroleum products. The test method is applicable to petroleum products and fractions having a final boiling point 538 °C.

2. Summary of test method

The boiling range distribution determination by distillation is stimulated by gas chromatography. A nonpolar packed or open capillary gas chromatography column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. The column temperature is raised at reproducible linear rate and area under the chromatogram is recorded throughout the analysis. Boiling points are assigned to the time axis from a calibration curve obtained under the same chromatographic conditions by analyzing a mixture of hydrocarbons covering the boiling range expected in the sample.

3. Apparatus

3.1 Chromatography

3.2 Column

3.3 Data Acquisition System: recorder and integrator

4. Sample

Sample to be analyzed must be homogeneous and free for dust or undissolved material.

5. Report

Plot each boiling temperature against its corresponding normalized percent. Draw smooth curve connecting the points.

Liquid product analysis from coliquefaction of lignite with NR by SD-GC, the conditions of G.C. are:

Open tubular columns type capillary column: RTX 2887

Initial temperature 40 °C

Final temperature 350 °C

FID detector

Sample size 0.5 μ L

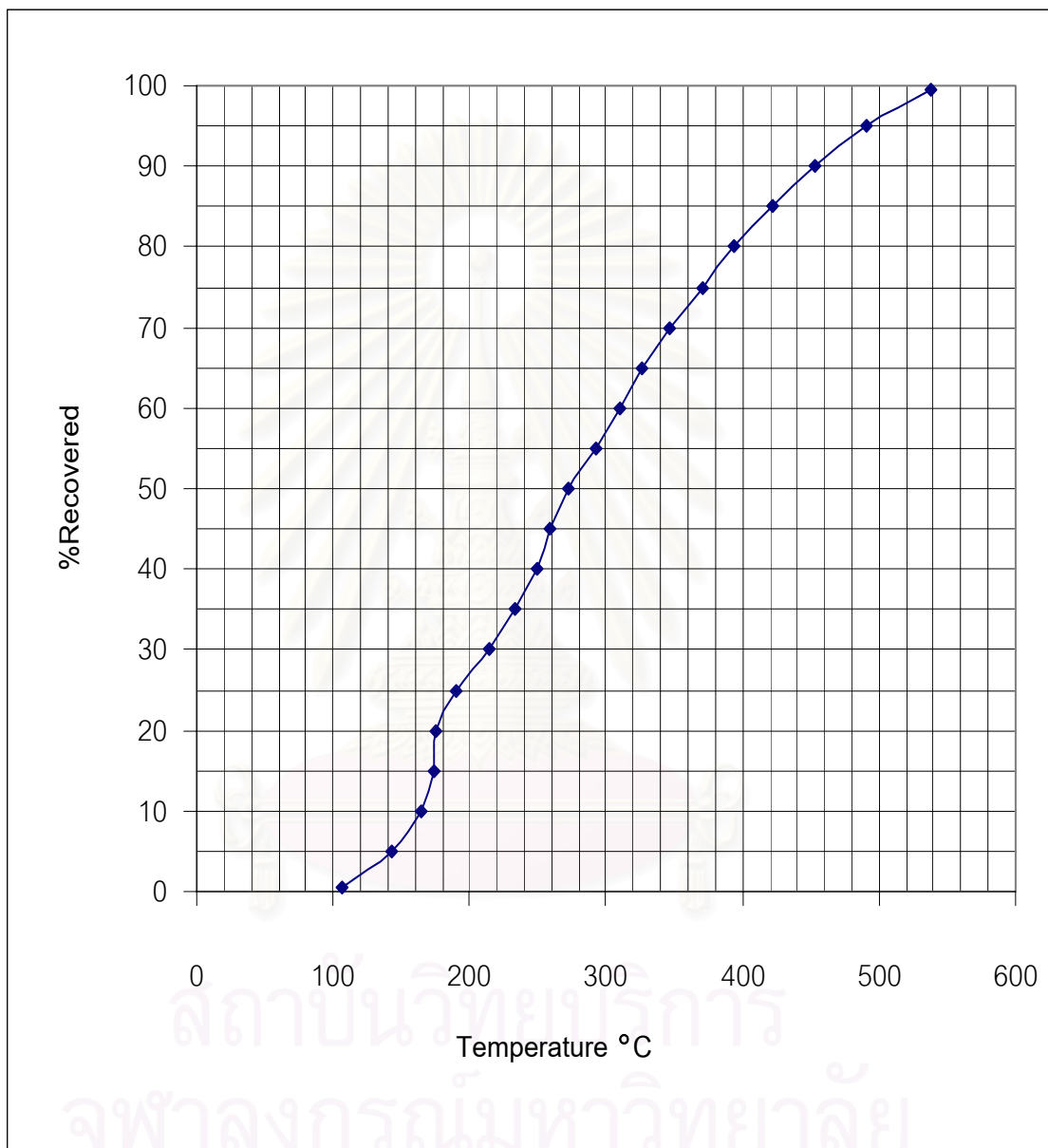
Carrier gas helium

Programming rate 10 °C/min

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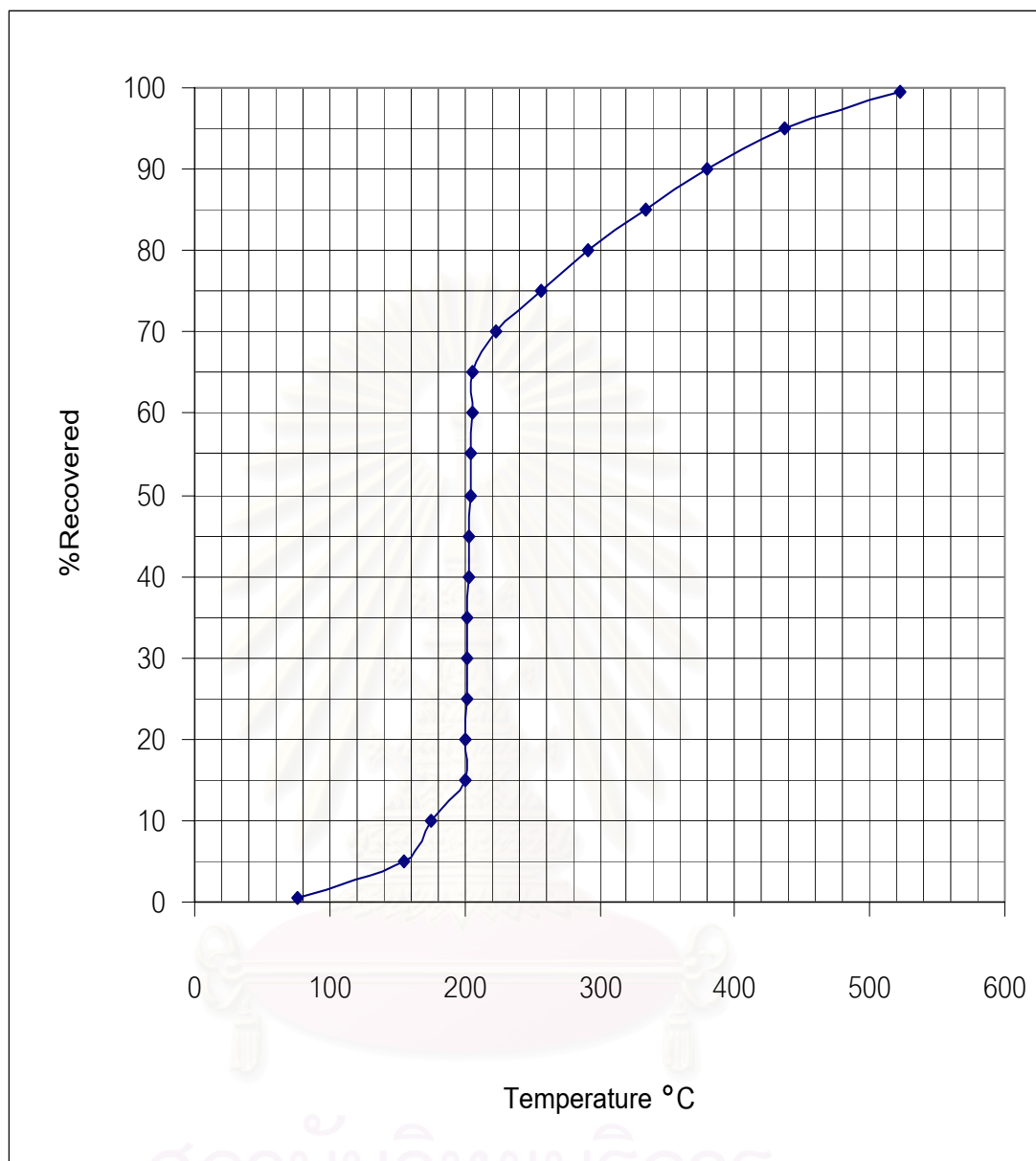
APPENDIX E

Analysis report from gas chromatography (SD-GC)



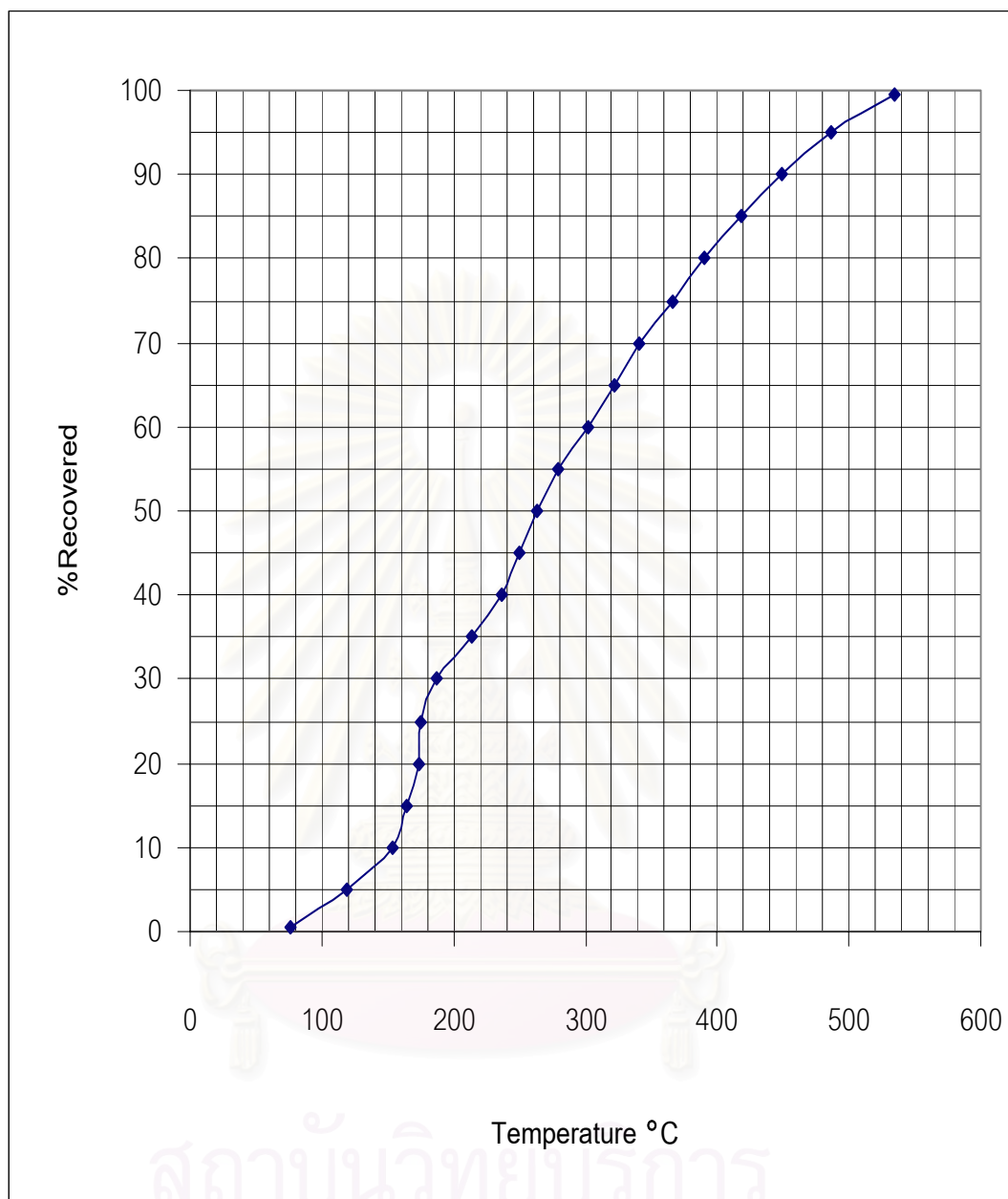
Sample name: C-2

Figure E.1 Boiling range distribution of oil product for non-catalytic coliquefaction reactions without organic solvent of lignite/NR feed ratio 30/70, 375 °C, 60 min, 40 bar by SD-GC.



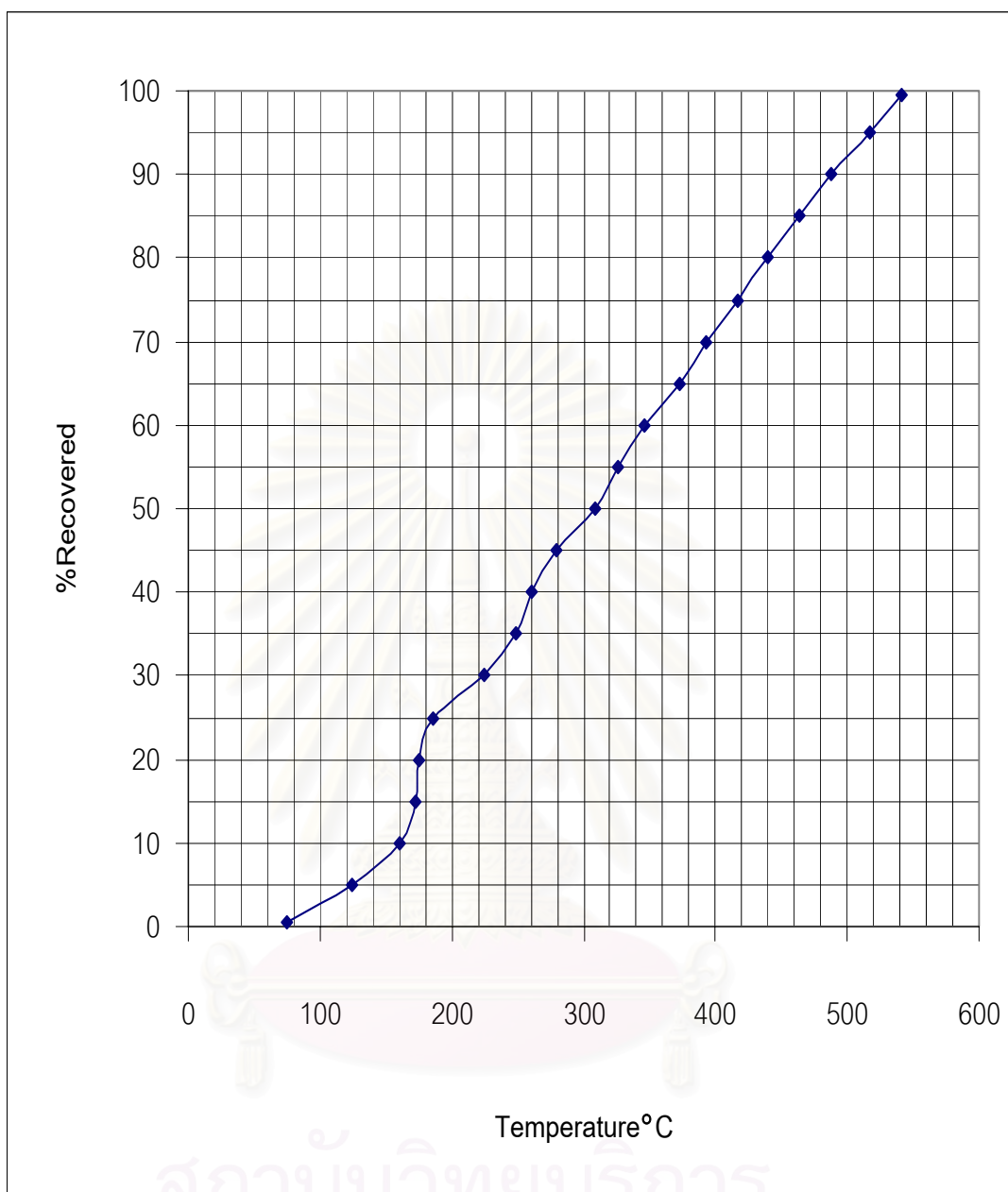
Sample name: C-3

Figure E.2 Boiling range distribution of oil product for non-catalytic coliquefaction reactions with tetralin solvent of lignite/NR feed ratio 30/70, 375 °C, 60 min, 40 bar by SD-GC.



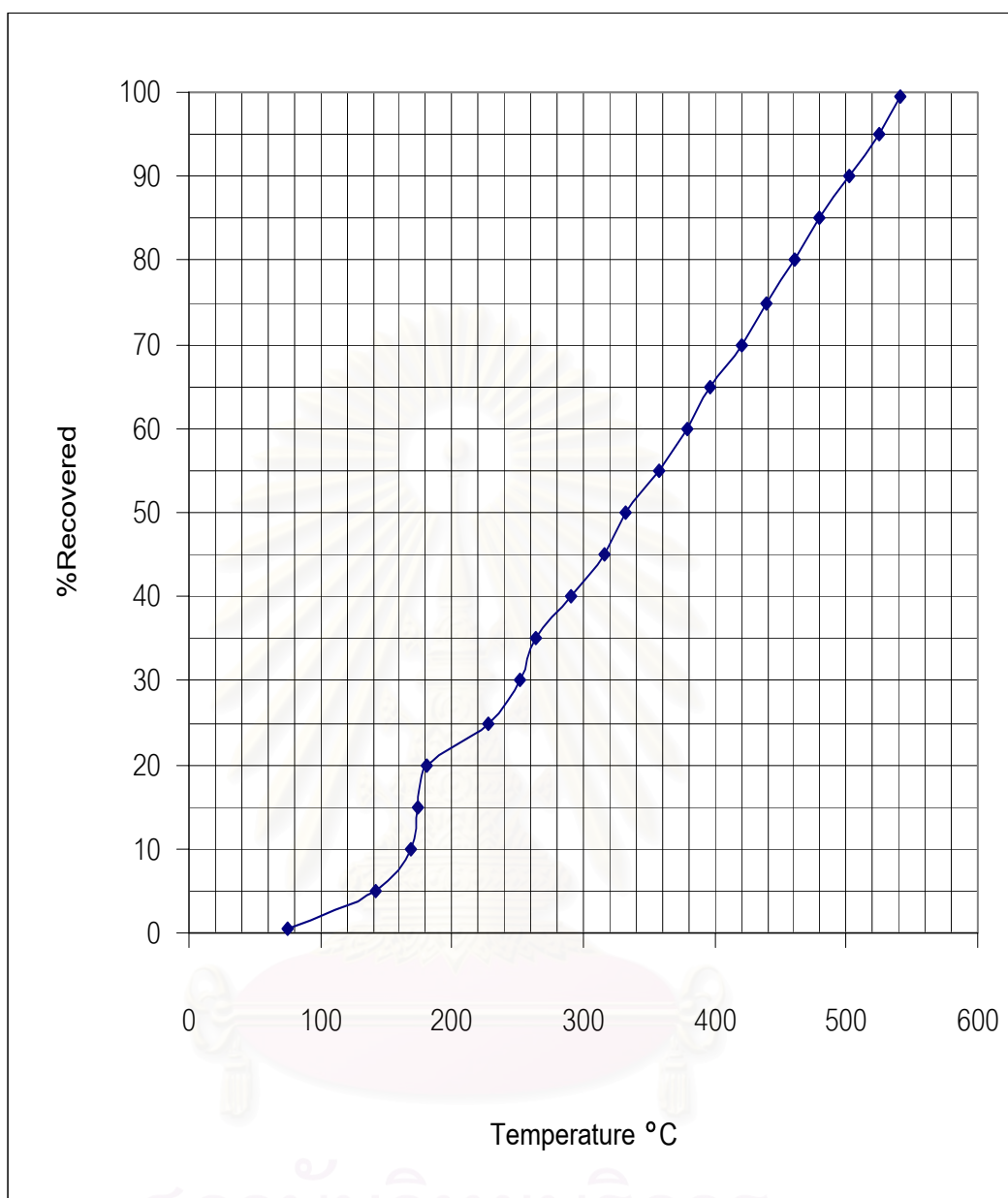
Sample name: C-4

Figure E.3 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 30/70, 375 °C, 60 min, 40 bar and 3 %wt of ZrO_2/SO_4^{-2} catalyst by SD-GC.



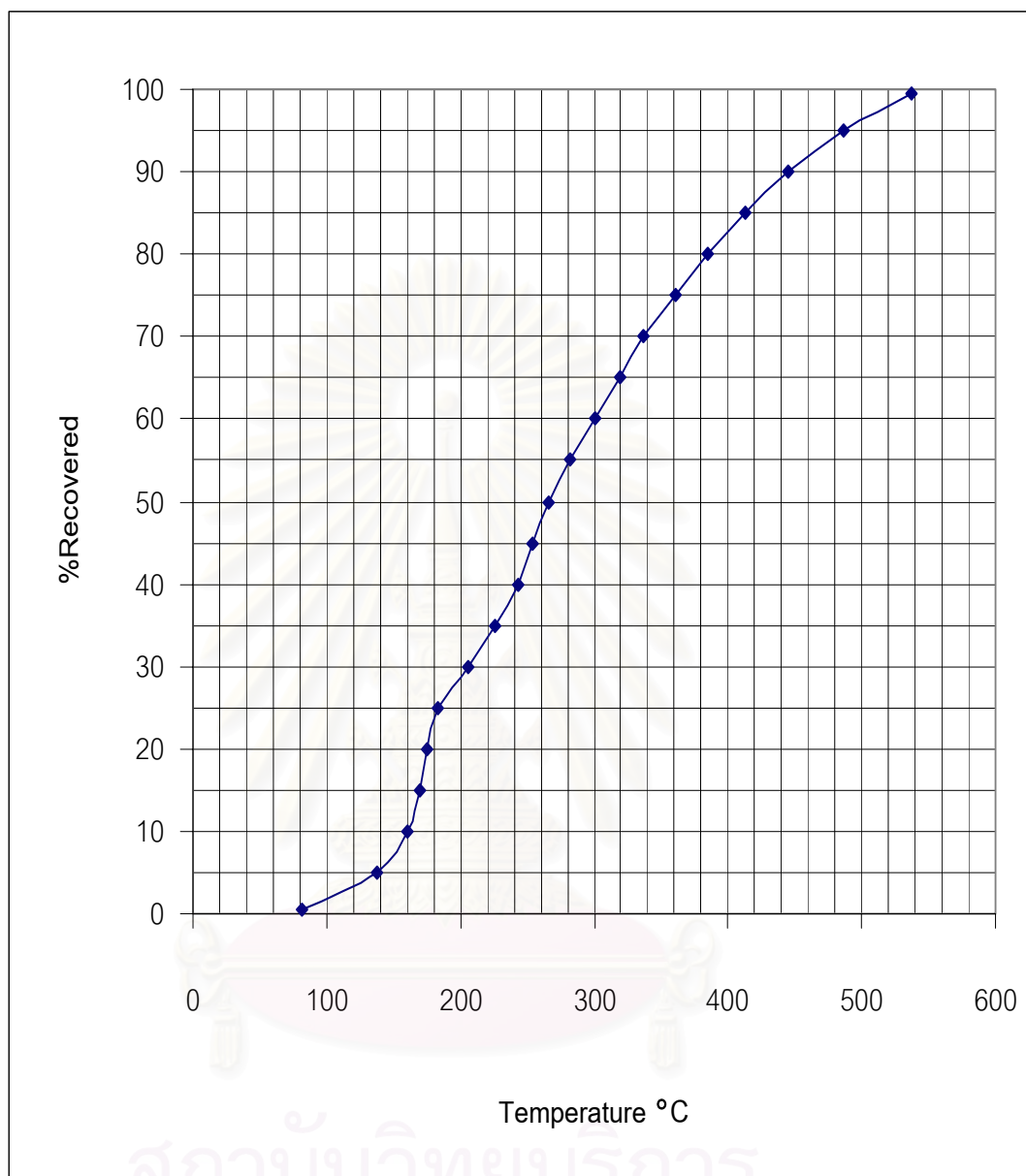
Sample name C-5

Figure E.4 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 30/70, 350 °C, 60 min, 40 bar and 3 %wt of ZrO_2/SO_4^{-2} catalyst by SD-GC



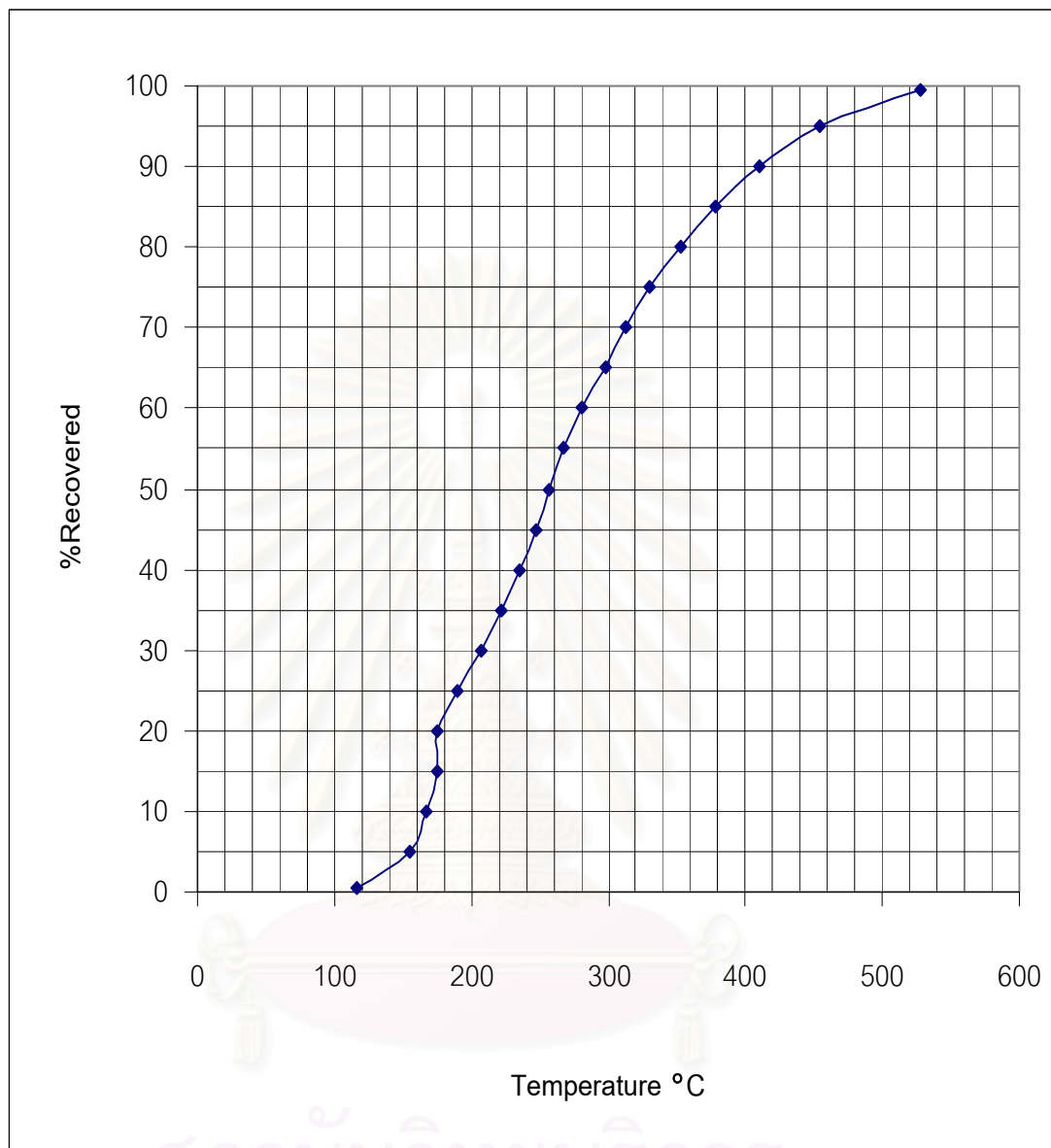
Sample name: C-6

Figure E.5 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 30/70, 325 °C, 60 min, 40 bar and 3 %wt of ZrO_2/SO_4^{2-} catalyst by SD-GC.



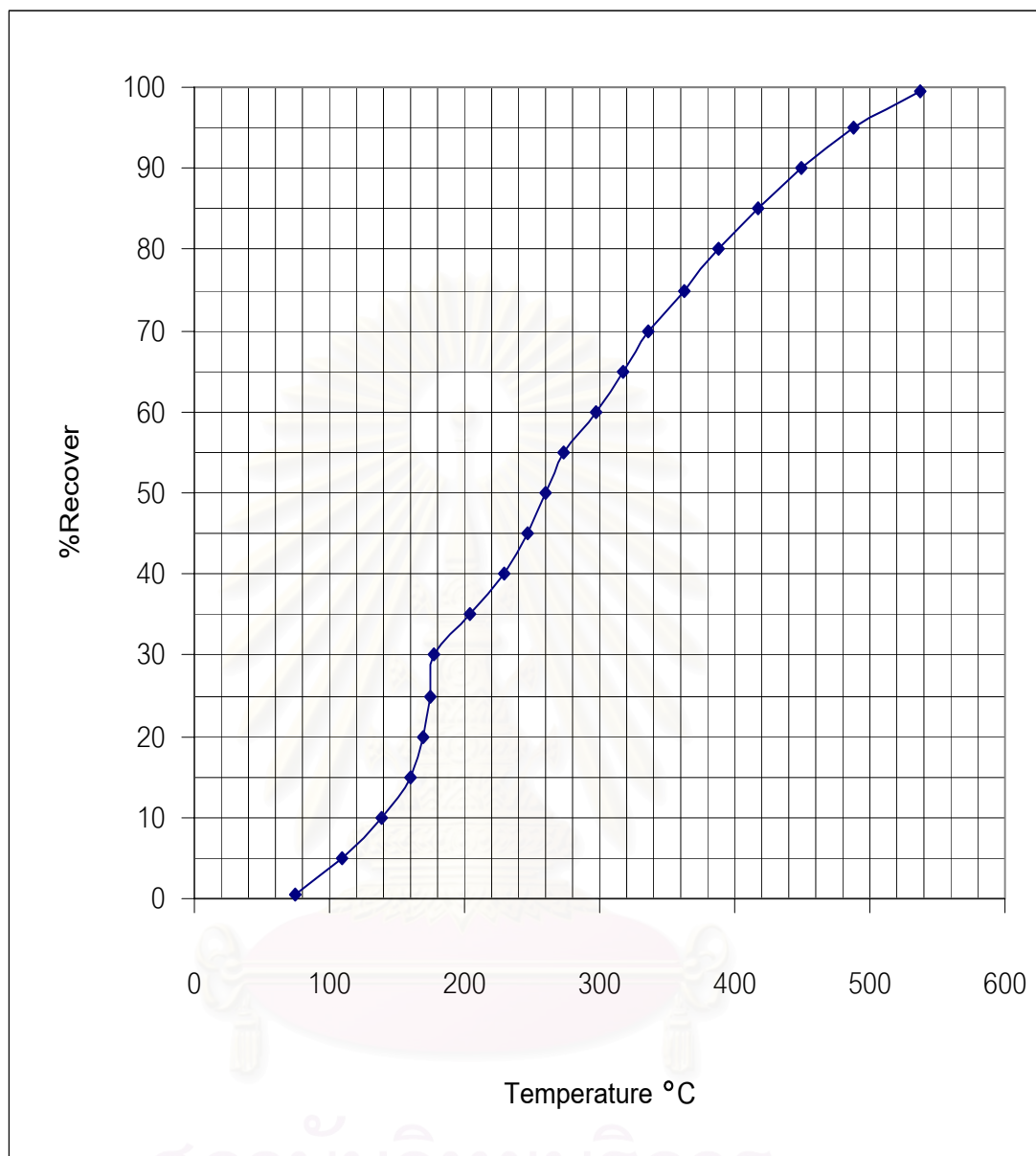
Sample name: C-7

Figure E.6 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 40/60, 375 °C, 60 min, 40 bar and 3 %wt of $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst by SD-GC.



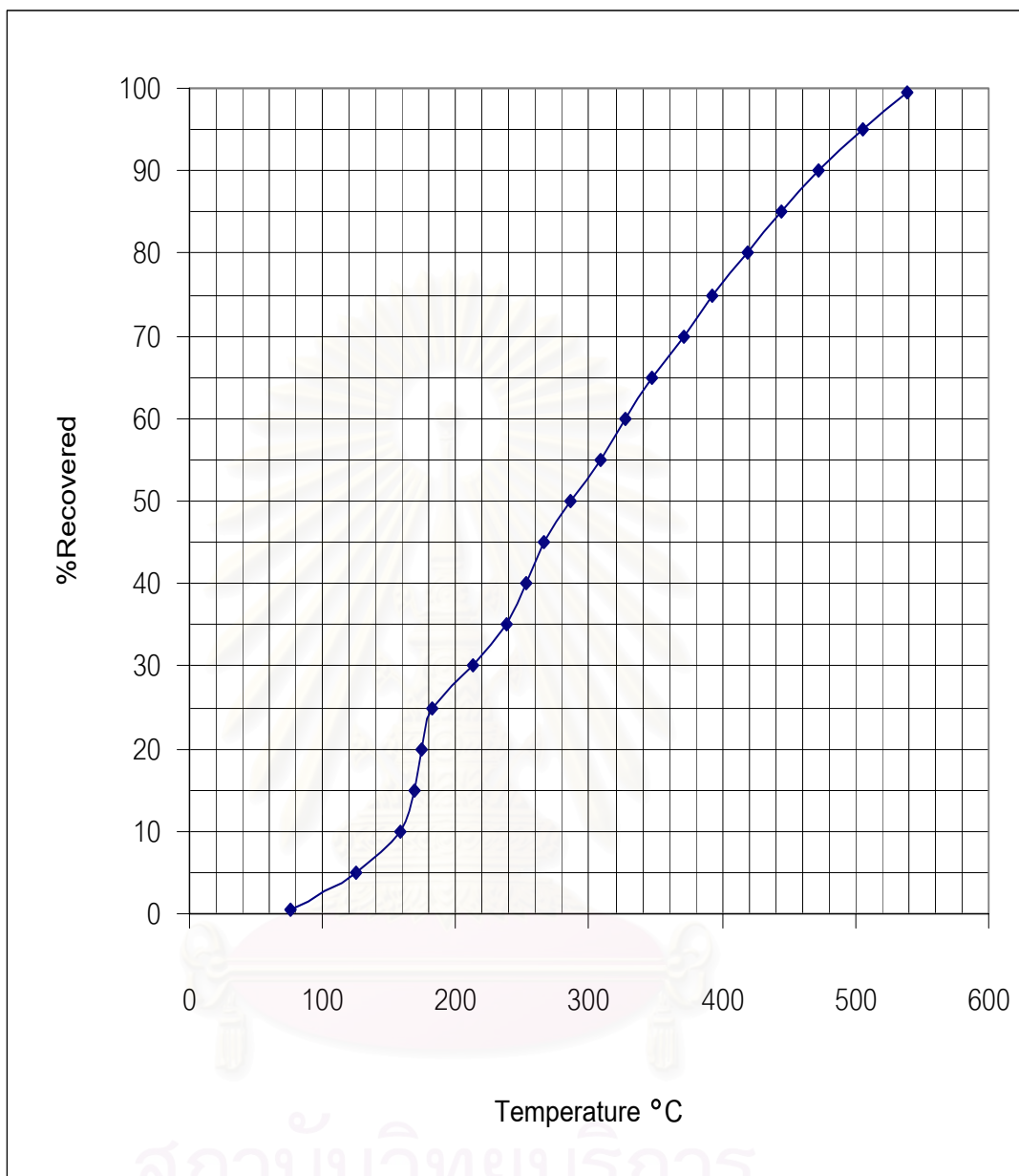
Sample name: C-8

Figure E.7 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/natural rubber feed ratio 50/50, 375 °C, 60 min, 40 bar and 3 %wt of $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst by SD-GC.



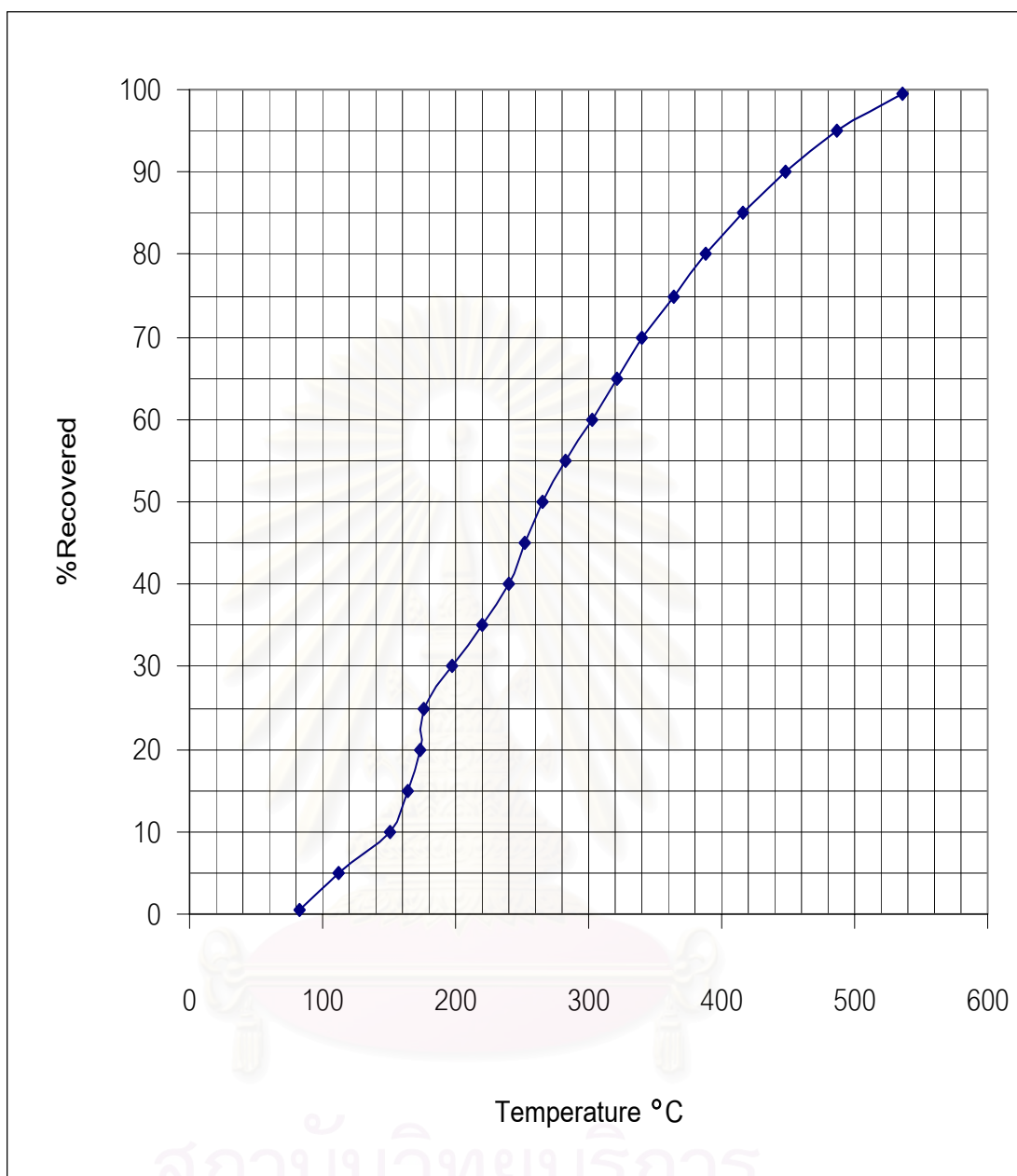
Sample name: C-9

Figure E.8 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/natural rubber feed ratio 30/70, 375 °C, 60 min, 20 bar and 3 %wt of $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst by SD-GC.



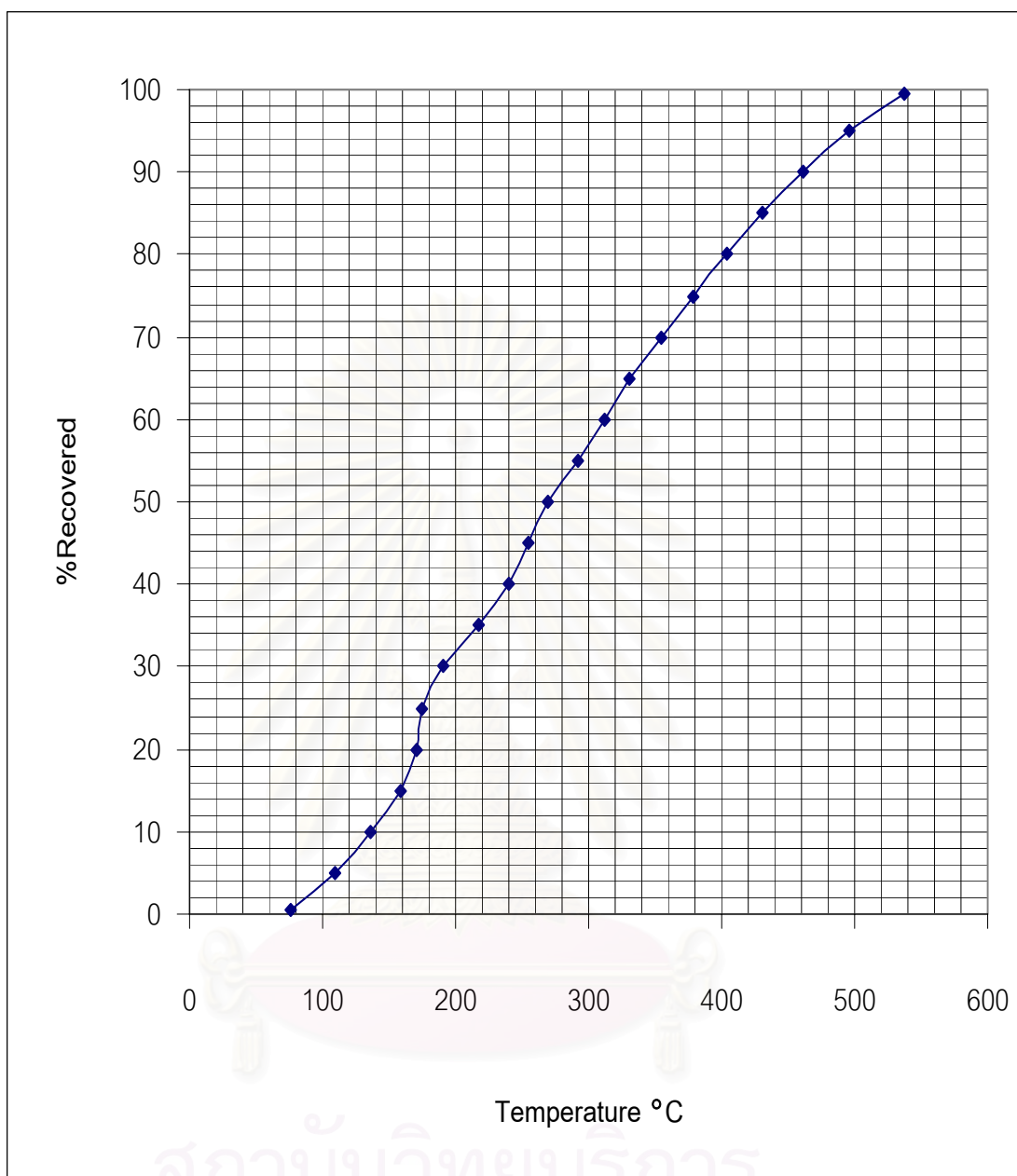
Sample name: C-10

Figure E.9 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 30/70, 375 °C, 60 min, 50 bar and 3 %wt of ZrO_2/SO_4^{2-} catalyst by SD-GC.



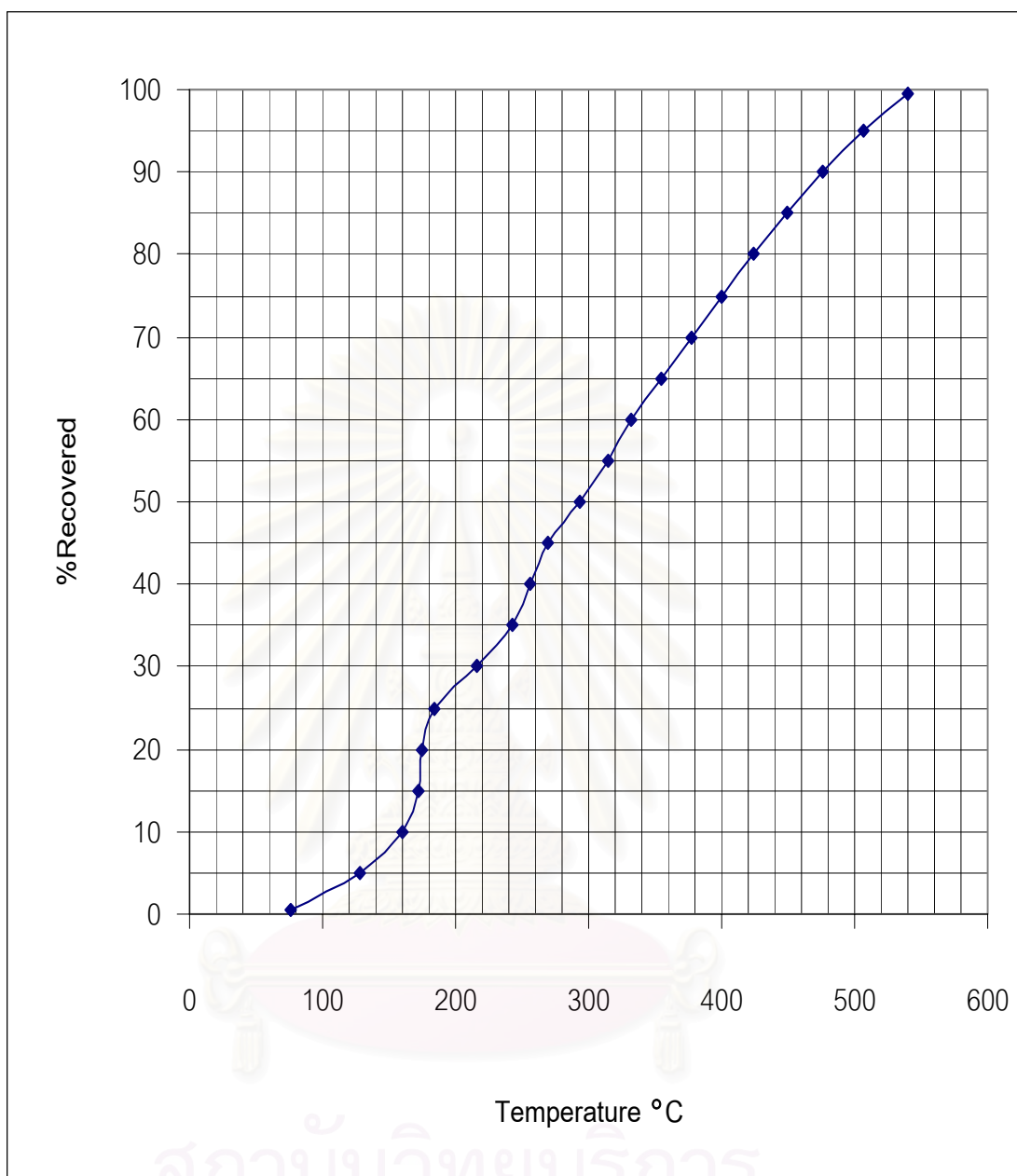
Sample name: C-11

Figure E.10 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 30/70, 375 °C, 60 min, 40 bar and 5 %wt of ZrO_2/SO_4^{2-} catalyst by SD-GC.



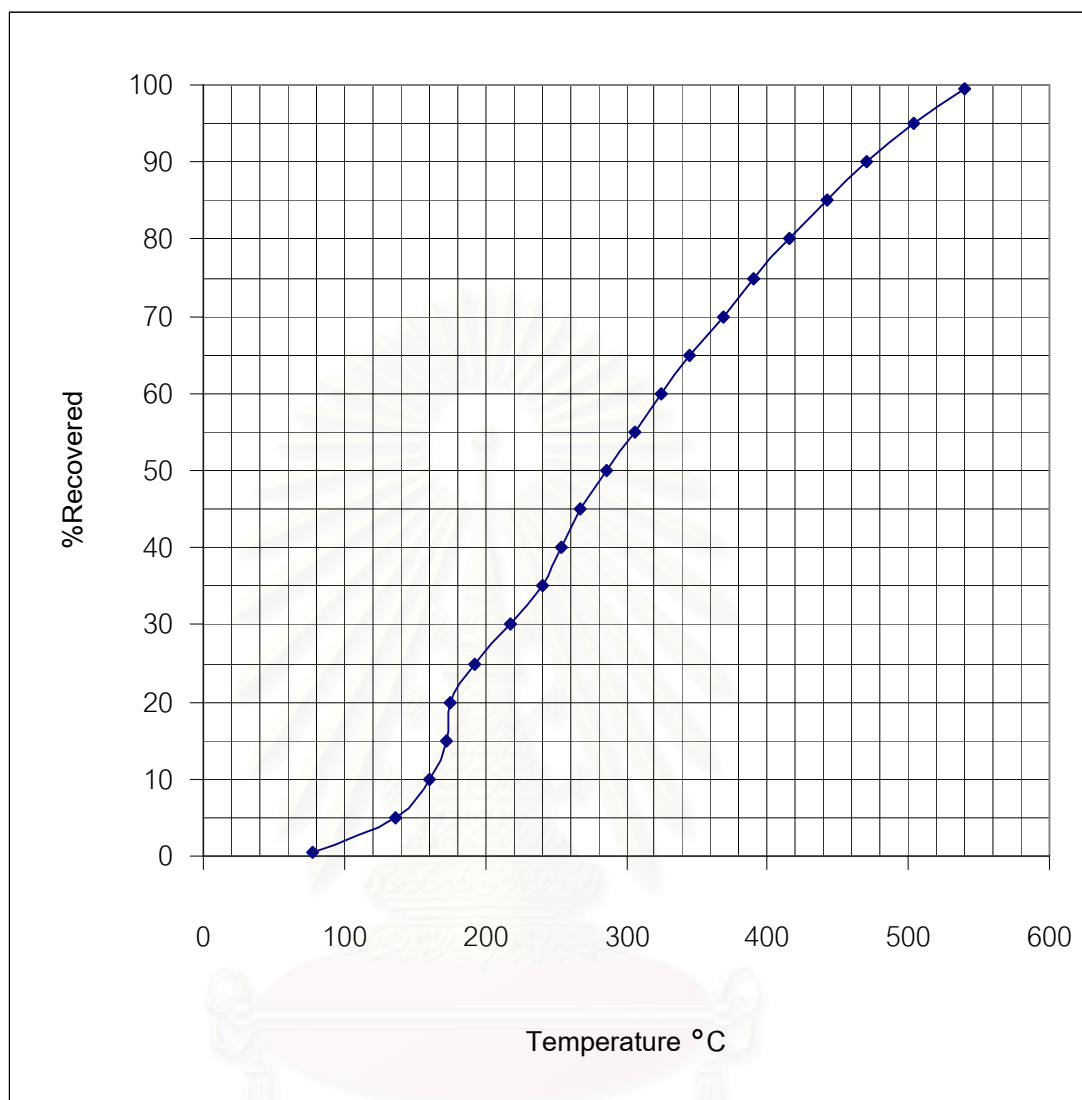
Sample name: C-12

Figure E.11 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 30/70, 375 °C, 60 min, 40 bar and 1 %wt of $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst by SD-GC.



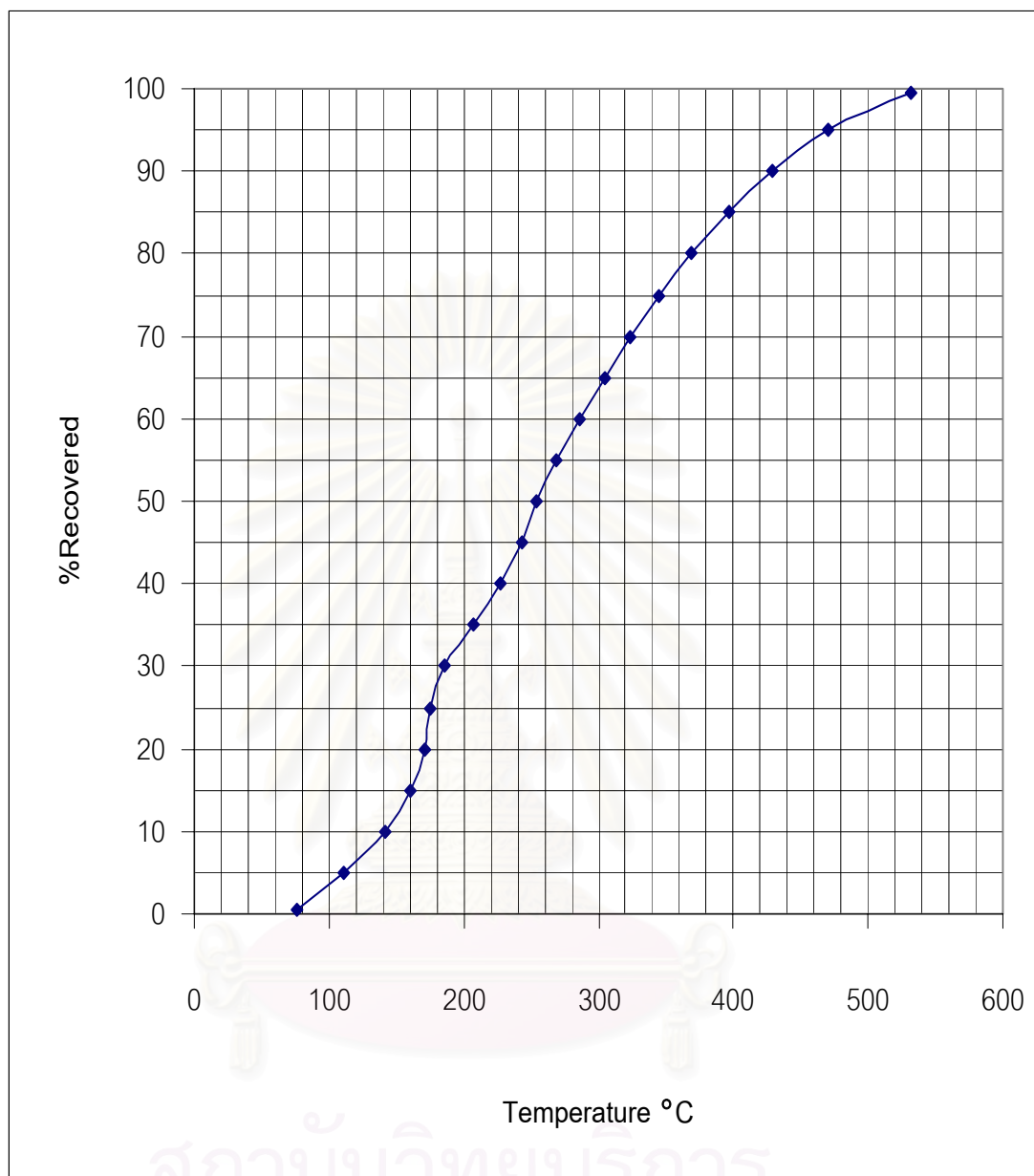
Sample name: C-13

Figure E.12 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/natural rubber feed ratio 30/70, 375 °C, 30 min, 40 bar and 3 %wt of $\text{ZrO}_2/\text{SO}_4^{2-}$ catalyst by SD-GC.



Sample name: C-14

Figure E.13 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 30/70, 375 °C, 90 min, 40 bar and 3 %wt of ZrO_2/SO_4^{-2} catalyst by SD-GC.



Sample name: C-15

Figure E.14 Boiling range distribution of oil product for catalytic coliquefaction reaction of lignite/NR feed ratio 30/70, 400 °C, 60 min, 40 bar and 3 %wt of $\text{ZrO}_2/\text{SO}_4^{-2}$ catalyst by SD-GC.

VITA

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