Liquefaction of wasted high density polyethylene and wasted rubber gloves by supercritical toluene

BY

Miss Nuchrawee Jamjumrus
Miss Papaphan Surmpanich

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF
BECHELOR OF SCIENCE PROGRAM IN PRETROCHEMICAL TECHNOLOGY
FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
2003

Special Project Title : **Liquefaction of wasted high density polyethylene and wasted rubber gloves by supercritical toluene**

Name : **Miss Nuchrawee Jamjumrus**
Miss Papaphan Surmpanich

Faculty : **Science**

Department : **Petrochemical Technology (International)**

Academic Year : **2003**

Special Project Advisor : **Assoc.Prof.Dr Somsak Woramongkolchai**

Special Project co-advisor : **Assist.Prof.Dr Kejvalee Pruksathorn**

ABSTRACT

Hydrocarbon oils were obtained from wasted rubber gloves (WRG) and wasted high density polyethylene (WHDPE) by using supercritical toluene as solvent. The pressure and temperature were varied to 5, 10 and 15 MPa and 400 and 450 °C, respectively. The scraped sample (approximately 10 grams) of WRG and WHDPE were run in batch reactor for 1 hour with the ratio of WRG and WHDPE as 10:0, 8:2, 6:4, 4:6, 2:8 and 0:10. By using toluene as a supercritical solvent, 10 grams of scraped sample (the ratio of WRG and WHDPE) decomposed to be liquid oil. Then the gas chromatography was applied to determine the quantity of hydrocarbon compound.

It was found that the ratio of WRG and WHDPE, operating temperature and pressure were so significant to liquid oil conversion. The optimum yield was 77.91% as the ratio of WRG and WHDPE of 8 to 2, temperature of 400 °C and pressure of 5 MPa.

Key words: High Density Polyethylene, Natural Rubber, Supercritical Toluene, Liquefaction Process.

หัวข้อวิทยานิพนธ์ : **การสกัดน้ำมันเหลวจากพอลิเอทิลีนที่มีความหนาแน่นสูงและถุงมือยางที่ไม่ใช้แล้ว โดยใช้โทลูอีนสภาวะเหนือวิกฤตเป็นตัวทำละลาย**
นักศึกษา : **นางสาว นุชระวี แจ่มจำรัส**
นางสาว ปภาพรรณ เสริมพานิช
ภาควิชา : **เคมี คณะวิทยาศาสตร์**
สาขาวิชา : **เทคโนโลยี ปิโตรเคมี (นานาชาติ)**
พุทธศักราช : **2546**
อาจารย์ที่ปรึกษา : **รศ.ดร. สมศักดิ์ วรมงคลชัย**
อาจารย์ที่ปรึกษาร่วม : **ผศ.ดร. เก็จวลี พฤกษาทร**

บทคัดย่อ

ในงานวิจัยนี้ สารประกอบไฮโดรคาร์บอน ได้มาจากถุงมือยาง (waste rubber gloves) และขวดพลาสติก (high density polyethylene) ที่ไม่ใช้แล้ว โดยใช้ โทลูอีนสภาวะเหนือวิกฤตเป็นตัวทำละลาย ที่อุณหภูมิ 400 และ 450 องศาเซลเซียส และ ที่ความดัน 5 10 และ 15 MPa ในการทดลอง นำถุงมือยางและขวดพลาสติกที่ตัดเป็นชิ้นเล็กๆแล้ว ประมาณ 10 กรัม ใส่ลงไปใน batch reactor เป็นเวลา 1 ชั่วโมง โดยทำการทดลองที่แต่ละอัตราส่วนระหว่างถุงมือยาง และขวดพลาสติก คือ 10:0 8:2 6:4 4:6 2:8 และที่ 0:10 โดยใช้โทลูอีนสภาวะเหนือวิกฤตเป็นตัวทำละลาย เพื่อต้องการให้เกิดกระบวนการเปลี่ยนรูปกลายเป็นน้ำมันเหลว จากนั้นใช้ก๊าซโครมาโตกราฟีในการหาปริมาณของสารประกอบไฮโดรคาร์บอน จากการทดลองพบว่าแต่ละอัตราส่วนของถุงมือยาง และขวดพลาสติก รวมทั้ง อุณหภูมิ และความดัน ล้วนมีผลต่อกระบวนการแปรรูปเป็นของเหลวทั้งสิ้นโดยผลที่ดีที่สุดจากการเปลี่ยนรูปเป็นน้ำมันเหลวของถุงมือยางและขวดพลาสติก อยู่ที่ 77.91 % โดยมีอัตราส่วนระหว่างถุงมือยางกับขวดพลาสติกเท่ากับ 8:2 ที่อุณหภูมิ 400 องศาเซลเซียส และ ความดัน 5 MPa

ACKNOWLEDGEMENT

We wish to express our profound gratitude to our advisors, Assoc. Prof. Dr. Somsak Woramongkolchai and Asst. Prof. Dr. Kejvalee Pruksathorn for content guidance, advice and encouragement throughout this project. We would like to thanks Ms. Ratchanee Saeoung at Chemistry Technical Laboratory for her help in gas chromatography determination and Mr.Kittichai Suprawat; technician of Chemistry Technical Operation, Chulalongkorn University for his assistant to success work.

At last, we would like to express my faithful thanks to our parents and friends for their kindness and encouragement throughout this project.

Nuchrawee Jamjumrus
Papaphan Surmpanich

TABLE OF CONTENTS

Page

LIST OF TABLES

Table page

LIST OF FIGURES

Figure **Page**

CHAPTER 1

Introduction

1.1 Motivation

At present, the increasing price of petroleum oil affects directly to many industries as the need of energy using raises up continuously. Thailand has an impact to this crisis because Thailand must import petroleum oil from foreign countries. We hope that in the future Thailand can find new source of energy to replace for petroleum oil. Liquefaction is an interesting process because it can change wasted plastics or rubbers to be a liquid fuel. The liquid fuel is a high quality product which can be further extracted to fuel.

Nowadays, plastics and rubbers are using quite a lot, they can cause the unavoid problem to environment due to taking time for decomposition. One way to solve this problem is to convert wasted plastics and rubbers to liquid oil by liquefaction process. The most product from this process is liquid petroleum oil which is easier to transport and can be used in various tasks.

This project is interested in wasted high density polyethylene (WHDPE) and waste rubber gloves (WRG), which are out of specification from export. Most of them are hydrocarbon compounds which have higher ratio of hydrocarbon and carbon comparing to coal. The liquefaction is a process to convert these wasted materials to liquid oil by using supercritical toluene as a solvent. Supercritical toluene uses as a solvent because viscosity is quite low and diffusion coefficient is rather high. That why it can penetrate into matrix easily. Under supercritical condition (higher temperature and pressure), toluene can penetrate into matrix of WHDPE and WRG helping them to swell. Then the existed water in the system doses the reaction with carbon and gives water out hydrogen which will further react to polymer chains of WHDPE and WRG until short fragment molecules as solids are occurred. The products are liquid and gas. The quantity of product depends on condition such as temperature, pressure, time and ratio of WHDPE and WRG. Gas chromatography is a good tool to check or determine hydrocarbon compounds in the liquid product.

1.2 Objectives:

1. To investigate the possibility of converting wasted high density polyethylene (WHDPE) and wasted rubber gloves (WRG) to liquid fuel with liquefaction process by using toluene as a supercritical solvent.
2. To study the effects of liquefaction process conditions (temperature, pressure and ratio of WHDPE and WRG) by using toluene as supercritical solvent.

1.3 Scope of study:

1. To design and set up experimental conditions.
2. To study the effects of liquefaction process conditions
3. To investigate the liquefaction parameters by gas chromatography.

1.4 Expected Results:

1. To convert WHDPE and WRG to liquid fuel by liquefaction process.
2. To reduce pollution and protect environment by converting wasted materials to benefit products.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Literature Review

Ding, W., Liang, J. and Anderson, L.L. [1] studied the way to synthesis liquid for using as a automobile fuel from wasted plastics at temperature 480°C and 525°C for 5 min and 10 min. They also studied the effect of each type of catalysts consists of NiMo/Al_2O_3, NiMo/(HZSM-5+SiO-Al_2O_3) and KC-2600, which gave high percentage of compound and could be used as a fuel. They found that the reaction in the catalyst system was easier to do the liquefaction reaction and the pressure and temperature condition were quite low.

Feng, Z., Zhao, J., Roclewell, J., Bailey, D. and Huffman, G. [2] studied the liquefaction reaction of waste plastic high density polyethylene group , medium density polyethylene and polypropylene and coal mixed with plastic. They found that waste oil solvency reagent helped in increasing volume of liquid product when compared with the tetralin solvent. They also found that liquid polypropylene gave the best product at temperature 420°C. Mixed plastic gave high product at temperature 445-460°C. They found that volume of oil and liquid product which got from polyethylene and mixed plastics slightly decreased when hydrogen pressure decreased. In this experimental, they took polyethylene and mixed plastics to mix with coal in ratio 50:50, this experimental gave the best result when added up tetralin solvent. Added only waste oil or no adding any solvent they got the low products. When used catalyst HZSM-5 or Al_2O_3-SiO_2-ferrihydrite at 460°C, it was found that products from polypropylene mixed with coal were higher than polyethylene mixed with coal.

Taghlei, M.M., Feng, Z., Huggins, F.E. Huffman, G.P. [3] compared each type of plastics such as polyethylene (PE), polypropylene(PP), polyethylene terephthalate (PET) and mixed of PE, PP and PET with coal to liquefy conversion temperature under 420-450°C for 60 min at pressure

800 lbs/in^2 by using two catalysts based on iron and HZSM-5 zeolite catalyst. The results were shown that synthesis using only plastic temperature under 430-450°C on the HZSM-5 zeolite catalyst gave the percent yield oil was up to 80-98% and the percentage of conversion was up to 90-100. When used Iron-based catalyst, it also gave high conversion but the temperature was too high. For experimental of mixed coal and plastic ratio 1:1by using HZSM-5 zeolite and Iron-based as catalysts. It was given the oil product higher to 60-80 and the conversion was up to 90%.

Huffman, G.D., Feng,Z., Huggins,F.E. and Mahajan,V. [4] studied the liquefied synthesis from waste plastic and mixed with coal. Each type of plastics was mixed with sub-bituminus coal ratio 1:1 at temperature 430°C and pressure 800 lbs/in^2 with existing of hydrogen gas by using HZSM-5 zeolite as a catalyst. They found that mixing of polypropylene and bituminus coal gave higher percentage of conversion than polyethylene mixed with bituminus coal at the same condition. The effects of two solvents were also studied. They were tetralin and lubricant oil. It was found that adding lubricant oil gave higher oil product, but when added tetralin solvent in the process, it made plastics convert to liquid. The different type of catalyst was another effect. When added tetralin solvent into liquid synthesis from coal and plastic it should gave higher liquid conversion. They also found that SiAl catalyst indicated higher conversion than HZSM-5-Zeolite.

Anderson, L.L.,Tuntawiroon, W.and Ding,W.B. [5] studied the liquefied synthesis from waste plastic such as polyethylene, polypropylene, polystyrene and polyethylene teraphthalate and sub-bituminus coal and sub- bimitunus mixed with plastics. By using $TiCl_3$ 5% as a catalyst at temperature 400, 420 and 430°C. They found that at temperature 420°C indicated percentage of conversion of high density polyethylene almost 100% and gave higher liquefy conversion up to 80% when temperature was increased. They also found that suitable condition of high density polyethylene was 430°C under hydrogen pressure 100 psig with 5% of $TiCl_3$ as a catalyst. In case of sub-bimitunus mixed with plastic pointed out liquefy conversion to 50%.

Shishido, M., Mashiko, T. and Arai, K. [6] studied the resulting of combination solvents of tetralin and ethanol for coal extraction by supercritical toluene. In the experimental took the coals sample from eleven places and extraction with three different types of solvent; toluene, toluene-tetralin and toluene-ethanol. It was found that added tetralin or ethanol into toluene made the percent yield of conversion for each coal higher. This was due to occurring of free radicals. The transformation of tetralin stopped to assemble of free radicals with coals and help to increasing of conversion.

Ding, W.B., Tuntawiroon, W., Liang, J. and Anderson,L.L. [7] studied the hydrogenation-hydrocracking in liquefaction of coal combined with polyethylene and mixed plastics. This project interested in temperature under 430°C and atmospheric pressure of hydrogen 2000 lbs/in^2(psi) for 1 hour. Silica-Alumina was an impregnated support with different types of metals such as platinum (Pt), nickel (Ni), iron (Fe), and palladium (Pd). They found that these metals helped to increasing the reaction. Hydrogenation operated at metals surface as hydrocracking operated at silica-alumina surface. In addition, catalyst with operated two roles Ni/Al_2O_3 -SiO_2, Fe/ Al_2O_3-SiO_2 and Pd/Ni/ Al_2O_3 -SiO_2, were better than Pt/ Al_2O_3 -SiO_2 thermal and Al_2O_3-SiO_2 because they indicated high percent yield of oil conversion.

Ruthai Leesuksan [8] studied the conversion waste of polyethylene to be liquid by using gasoline oil. This project studied the hydrocracking of waste polyethylene by using two roles catalysts as Pt/F on alumina, Pt/Sn/Cl/F on alumina, Ni/Sn/Cl/F on alumina, and Co/Sn/Si/F on alumina. The percentage of liquid conversion was up to 99.8% by weight, when only used 40% by weight of catalysts at temperature 400°C and pressure 600 lbs/in^2 for 12 hr.

Wannipa Amarttayakul [9], studied the liquefaction of natural rubber mixed with liqnite by using supercritical carbon dioxide at temperature 300-375°C for 30 min. The quantity of raw material coal was varied to 0-75% and used iron oxide (FeO) and zinc oxide (ZnO) as catalysts in four liters agitation tank. It was shown that at temperature of 340-375°C gave the high quantity of liquid conversion and the lowest viscosity at 40°C. The 25% quantity of coal as starting raw material pointed out the high percent yield up to 56%, and the catalyst was also used to decrease viscosity of product.

Sarit Sangon [10],studied supercritical extraction of Banpoo coal. He used toluene and its cosolvent (tetralin and ethanol) at 370-490°C, 5-12.2 MPa and 60-90 min. in semi continuous apparatus. A two-level factorial experimental design was applied to study the main effect on coal conversion and liquid yield. The parameters for investigation were temperature, pressure and time. The measured response for the experimental design was coal conversion and liquid yields. The results indicated that two variables of temperature and pressure had significant effects on the coal conversion and liquid yield. The result was also indicated that extraction conditions affected conversion, liquid yields, hydrocarbon group of coal liquid and their residues. The yield of coal liquid at 490°C, 10 MPa and 90 min with toluene/tetralin reached a maximum 33 wt% (in daf coal) which composed of included saturated hydrocarbon 7 wt%, aromatic 13 wt%, resin 13 wt%, asphaltene 64 wt%. For toluene/ethanal at 450°C,12.2 MPa and 90 min reached a maximum 26 wt% (in daf coal) which composed of saturated hydrocarbon 8 wt%, aromatic 1 wt%, resin 24 wt% asphaltene 67 wt%. The compositions of saturated hydrocarbon and aromatics fractions of coal liquid were determined by GC/MS spectroscopy.

2.2 High density polyethylene (HDPE) [11]

Polyethylene is the one kind of polyolefin, which is the highest amount of production when compares with thermoplastic. Polyethylene prepares from the addition of polymerization as shown in figure 2.1

$$n(-CH_2{=}CH_2-) \xrightarrow[(-CH_2-CH_2-)_n]{\text{polymerisation}} (-CH_2CH_2-)_n$$

Figure2.1 Structure of Polyethylene [11]

Polyethylene's structure contain with repeating unit of ethylene monomer. Name of polyethylene is called follow the IUPAC name.

Polyethylene can be divided into several types. Each types of polyethylene are different in structure, behavior and used.

- Low density polyethylene (LDPE) 0.915 – 0.935 g/cm^3
- High density polyethylene (HDPE) 0.941 - 0.967g/cm^3
- Linear low density polyethylene (LLDPE) 0.910 – 0.925 g/cm^3
- Very low density polyethylene (VLDPE) 0.880 – 0.912 g/cm^3
- High molecular weight polyethylene (HMWPE) 200,000 – 500,000
- Upper high molecular weight polyethylene (UHMWPE) 100,000– 300,000

High density polyethylene may be called as linear polyethylene, because the structure of polymer is almost straight chain but contain with some branches. In the other hand, high density polyethylene called as low pressure polyethylene because the preparation of high density polyethylene uses lower pressure than low density polyethylene. High density polyethylene was produced as commercial trading since 1955 until the present with the improvement of production.

2.2.1 Process of production and activation

There are four methods to producing high density polyethylene [11].

(1) Ziegler process

This process is polymerization by catalyst – monomer coordinate complex mechanism coordinate catalyst is the complex compound by occur the reaction between (1) transition metal compound in group 4-8 from periodic (use to be an activated) with (2) organometallic compounds in group 1-3 of metal (coordinate activation). The catalyst of reaction normally use titanium tetra chloride aluminum alkyl (Ziegler – Natta catalyst).

Polymerization reaction keeps continuously in containers, which contains with liquid hydrocarbon as diesel oil or toluene, use very low pressure about 2-4 atm at 50-75 °C, at this state polymer will not melt but polymer will turn to be slurry. When polymerization reaction was ended the catalyst will stop by adding alcohol like a methanol, ethanol and propanol, (except polymer). Then it was extracted by hydrochloric acid (HCl) in alcohol. After the polymer was separated centrifugation method, it was dried.

In this process molecular weight of polymer will be controlled by temperature, which at uses in the polymerization reaction. Normally the ratio of aluminum- titanium in catalyst is used to help substance to proceed chain transfer agent, usually hydrogen. Polymer's structure obtains 5-7 ethyl groups per 1000 atom of carbons, neither occurring of butyl branches by density of polymer 0.945 g/cm^3.

(2) Phillip process

Phillip process is concerned with transition metal compound such as chromium oxide is activated by silica or silica-alumina (Si 75-90%).

There are two important things that changed in the system. The first one is the process of solution or slurry process, it depends on temperature. Temperature is a significant importance used to control molecular weight of polyethylene. In solution process, do the reaction at the range of temperature between 130-160°, which is higher than melting point of polyethylene, so polymer can melt by using liquid hydrocarbon such as cyclohexane as a solvent. In slurry process, do the reaction at 90-100 $^{\circ}$c, which is lower than melting point of polyethylene, so the ability of melting will decrease.

Normally, use the pressure at 14-35 atm, which is between high pressure process and Ziegler process. The density of high density polyethylene (HDPE) is 0.96 g/cm^3 and HDPE has almost complete linear structure, meaning that there are three methyl groups per 1000 of carbon atom, no existing of ethyl group and butyl group.

(3) Standard oil company (Indiana) process

Standard oil process is similar to Phillips process. This process is solution process by using metal oxide as a catalyst such as molybdenum trioxide and using gum as a supporter at 200-300°C, pressure at 40-100 atm. The density of obtained polymer is 0.96 g/cm$^{3.}$ It has almost complete linear structure same as Phillips process.

(4) Union carbide gas phase process.

High density polyethylene (HDPE) which is produced by gas phase, ethylene and fluidized gas are given to the process at the same time, use the temperature at 75-100°C and 7-20 atm, by using high efficiency transition metal such as chromium oxide or titanium to be catalyst. The grain of polyethylene will exist on particle, which is in fluidized bed. The density polyethylene that obtained in this process is 0.94-0.96 g/cm^3

(5) Metallocene – based process

Metallocene-based process uses the newest catalyst, the unusual of this process is the accuracy to control the similar structure of length, chain's degree and stereo regularity of polymer. Metallocene-based is a high efficiency process, the amount of product is obtained one ton of polymer gram of catalyst per hour. Metalloce ne's formula is $L_2 ML_{2.}$ by M is transition metal in group four as titanium X is halogen group or alkyl, phenyl, benzyl and L is ligand.

There are two types of complex metallocene, which are bicomponent system and single component system. In bicomponent system, the highest product is between 0-40°C but it has high molecular weight at low temperature, then has to use hydrogen to control molecular weight. In single component system the suitable temperature is between 15-20°C.

2.2.2 Properties of HDPE [11]

(1) Mechanic and thermal properties.

The important condition of structure to identified the properties of polyethylene long chain's degree or polyethylene short chain degree, average molecular weight and scattering of polymer.

An essentiality that uses to identify the appearance and properties of polyethylene in the different grade is branches of ligand. The amount and the length of branches are controlled by differential variables in polymerization process (temperature, pressure, catalyst or initiator and transfer agent) polymer's chain from order compressing is blocked by branches of ligand, this can effect to density of polyethylene. The density of polyethylene first considers at chain's degree of polymer. The low density varies with high chain's degree.

In case of, there are branches in the structure, it can interfere the ability of polymer's crystal, Crystal's degree of low density polyethylene is 55-70% compared with 75-90% of high density polyethylene. The T_m's range of polyethylene is between 108-136°C with depending on crystal's degree. Therefore, low melting point is the specific characteristic of C-C bonding, which is elastic and no existing of force between strong molecule, T_g is the relationship on flowing of long part in amorphous.

Heat capacity (Cp) of polyethylene is higher than thermo-plastics and Cp depend on temperature. At room temperature, Cp is 2.3 $J/_g$ and at 120-140°C, Cp is 2.9 $J/_g$ Both of these values are for low density polyethylene (LDPE),

Polyethylene is non-polarhydrocarbon and the degree of crystalline is proportional to temperature. The temperature dissolving of low density polyethylene (LDPE) is 60°C and 80-90°C for high density polyethylene (HDPE).

(2) Structure of High density polyethylene

High density polyethylene is high crystallization, because it has straight-run chain and a few amount of branches, non polar. High chemical resistance does not absorb the mixture. HDPE can prevent the water vapor barrier, can use this property for applying about container and package. It is good for electric insulator and HDPE has molecular weight between middle to high, so it good for endure to high bump against. Due to HDPE is almost straight-run chain, then chain of polymer is in order so it affects to crystallization of HDPE (>90% of crystalline). The density and melting point are higher than high pressure polyethylene. The density of HDPE is 0.95-0.97 g/cm^3 and melting point is 135°C HDPE is stronger than low density polyethylene, high attractive resistance but the length, the elasticity and cleanliness are lower than low density polyethylene.

2.2.3 Physical properties

Optical properties: Due to, HDPE has high crystallization, so the thin film of HDPE is translucent Meanwhile the thin film of low density polyethylene(LDPE) is transparent.

2.2.4 Chemical properties

Melting: At room temperature HDPE will not melt in solvent, even if HDPE is swollen. but HDPE will melt in mixture solvent between two types of solvent at lower temperature than 30-40°C.

Degradation: HDPE is rather stable when receive heat but can do the react at high temperature in atmospheric, HDPE will breaking and linking between polymer's chain. This reaction can see obviously at 290-300°C.

Flowing of liquid HDPE: It has molecular weight over than 1,000. At temperature 140-200°C is non-Newtonian liquid, slurry or sticky. It will be decreased when the velocity of liquid HDPE is increase and has low shear rate. At temperature 300°C, HDPE is Newtonian liquid.

2.2.5 Applying process

HDPE is mostly moulding by blowing about 40% As a bottle, package and container which is use high resistance and can endure for squeezing such as acid-base container and chemical substance package.

For moulding by injection about 20%, this can use for making toys, and utensil things. Besides that, it can apply for film making, rope, electric insulator and cable wire. Others HDPE transform such as film-making, injection moulding, blow moulding, pipe extrusion, sheet extrusion, coating etc.

2.3 Natural Rubber [12]

By the end of the nineteenth century, there were 2500 hectares (ha) of land under rubber cultivation in Southeast Asia. The start of the automotive era shortly afterward caused a rocketing demand for rubber, and by 1910 there were 500,000 hectares of rubber planted and the countries of Southeast Asia had become the main suppliers of natural rubber worldwide.

It is thought that only 24 seedlings survived the original journey to Malaysia, and such a small number, coupled with selective breeding for high yield, has produced a narrow genetic base. In order to widen the base, the International Rubber Research and Development Board, in collaboration with Brazilian authorities, carried out a germplasm projections in the Brazilian jungles in 1981.

2.3.1 Rubber production

Dry rubber: On commercial grades of dry rubber arise from the organization of tapping and tappers and from the method of coagulation and processing. Rubber production is generally manage in three ways: the tapper can be a smallholder with 2-20 ha who will sell the crop, either in latex or semiprocessed from; the tapper can be employee of a self-contain estate or plantation of several thousand hectares with the whole operation of dry rubber production managed by the estate; or the tapper can be part of a government-sponsored cooperative and will deliver the crop to central manufacturing stations.

The first cultivated rubber trees produced 500 kg/ha of rubber selective breeding over the years has resulted in yields during the mid-1990s as high as 3000 kg/ha. However, average yields in the principal producing countries can vary from 400-1200 kg/ha. In Malaysia the smallholder sector produces about 850 kg/ha, whereas the estate plantations can produce about 1200 kg/ha

Latex and its Collection. The latex from the Hevea brasiliensis tree is a colloidal dispersion consisting of nonrubber substances and rubber particles in an aqueous serum phase. The rubber hydrocarbon constituted 30-45% of the whole latex; the nonrubber substances account for 3-5%. Rubber particles vary in size from 0.15-3 μm and contain 90-95% natural rubber, i.e., cis-1, 4-polyisoprene, with a molecular weight distribution of 10^5-10^7 g/mol. The shape of the molecular weight distribution curve, which varies from a skewed unimodal to a bimodal distribution and the molecular weight rubber, is determined by clone. In natural rubber, latex coagulation takes place under acid condition at about pH 5. Coagulation can either be induced by the deliberate addition of acid or occurs naturally in the tapping cup by reaction with acids produced by bacterial action, i.e., auto coagulation.

Rubber latex is formed and stored in rings of latex vessels found in the soft bark region of the tree, high lies between the inner cambium tissue and the outer hard bark layers. The physiological role of latex in the rubber tree is undetermined, as of 1996; however, the mechanism of production and methods of tapping are well understood. Latex is collected from the rubber tree by tapping once every two or three days. A tree is tapped by carefully cutting into the trunk with a special knife that removes a thin slice of bark and severs the latex vessels without affecting the normal sap circulatory system. The cut is made at an angle of 25-30° halfway around the circumference of the trunk, and at the lowest point a short metal spout is inserted, from which latex flows into cups and is collected four to five hours later. It is also possible to apply a stimulant such as Ethephon, the active ingredient of which is 2-chloroethanephosphonic acid; the later release ethylene gas to increase the time during which latex flows and thus increase yield with a reduced tapping frequency. Unless the latex is to be processed immediately, a small amount of preservative, e.g., ammonia, is added to prevent premature coagulation before the latexin brought to a factory or smallholder processing center. Rubber collected in this manner is known as field latex.

Latex continues to drip after the initial collection and coagulates naturally in the cup to form cup lump. Coagulum which forms as a film of latex on the tapped cut, called tree lace, or from latex that has dripped onto the ground, called earth scrap, is collected the next day along with the cup lump. Some smallholders may not collect the latex at all, but allow it to coagulate in the cup and collect it as cup lump. All these methods produce rubber known as filed coagulum.

2.3.2 Properties of Natural Rubber[13]

Crystallization : Raw natural rubber may freeze or crystallize during transit or prolonged storage, particularly at subzero temperatures. The rubber then becomes hard, inelastic, and usually much paler in color. This phenomenon is reversible and must be differentiated from storage hardening. The rate of crystallization is temperature-dependent and is most rapid at -26°C. Once at this temperature, natural rubber attains its maximum crystallinity within hours, and this maximum is no more than 30% of the total rubber.

During crystallization, rubber molecules associate into a crystal array. As the storage temperature is increased, thermal motion of the molecules restricts crystallization until, at temperatures above 20°C, the rate is near zero. Observed melting temperatures of natural rubber depend markedly on the temperature at which crystallization occurs. Figure 2.2 shows a general trend in which the higher crystallization temperatures result in higher crystal melting temperature. The wide range of melting temperatures exhibited by rubber crystallized at low temperature is a reflection of a polycrystalline texture that contains a large number of small crystals. The generally accepted crystal melting temperature of natural rubber is 30°C. Crystals with high melting temperature are fewer and larger than those formed at lower temperatures and take a relatively long time to form.

Frozen rubber is normally thawed by storing in a hot room at 40-50°C. Because rubber is a relatively poor thermal conductor, melting is governed by the slow conduction of heat through the bale. As the rubber melts, distinct regions of thawed and frozen rubber become apparent and a sharp boundary can be distinguished between the two. Palletized frozen rubber can take a considerable time to thaw; in a hot room at 50°C it takes about two weeks for the center of the pallet to reach 30°C. Dismantling frozen pallets and thawing bales singly or in well-spaced stakes obviously helps, but this can be a costly operation. Methods of dealing with frozen rubber vary from factory to factory, and consumer experience determines conductions appropriate to particular needs or limitations.

Storage Hardening : Storage hardening is a slow, irreversible increase in the Mooney viscosity of natural rubber that occurs during storage and transport; an increase of some 30 Mooney units is typical for nonviscosity stabilized grades. Hardening is thought to result from the interaction between the nonisoprenic groups, such as aldehydes, present on the rubber molecule to form cross-links, and as the rubber hardens, the extent of long-chain branching and gel increases. Storage hardening is also accelerated by high temperature and low humidity.

Many mechanism of storage hardening are proposed and all have been reviewed. One of the most favored is the bimolecular alder reaction between rubber aldehyde groups. Nevertheless, the involvement of rubbber-bound epoxide groups has also been postulated in cross-link formation, though this was later refuted. The hardening mechanism is certainly catalyzed by the presence of amino acids in the latex however, the question of what constitutes a definitive mechanism for storage hardening has yet to be resolved.

Nevertheless, storage hardening can be effectively inhibited by the addition of a reagent such as hydroxylamine, which produces an oxime via a condensation reaction and thus blocks the cross-linking process. For viscosity-stabilized grades (CV) produced in this way, the viscosity increase during transit and storage is negligible.

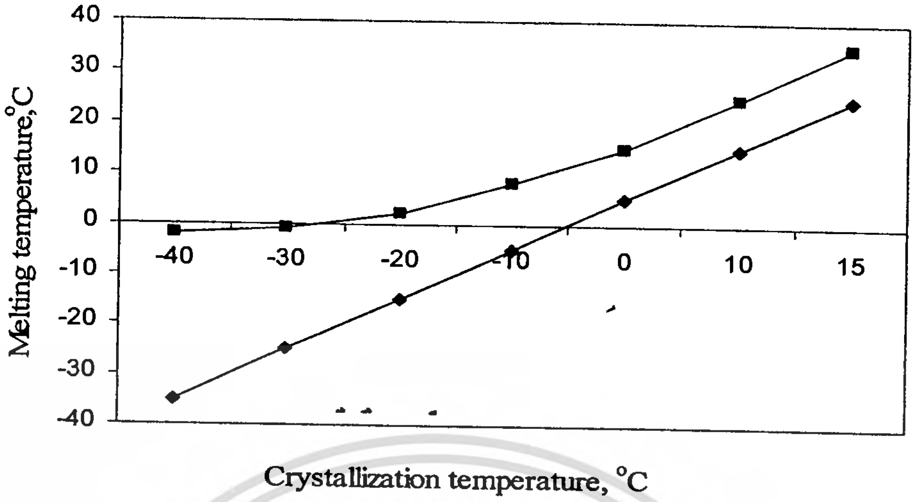


Figure 2.2 . Relation between crystallization temperature and melting temperature for natural rubber. [12]

Cure Characteristics : Methods of natural rubber production and raw material properties vary from factory to factory and area to area. Consequently, the cure characteristics of natural rubber can vary, even within a particular grade. Factors such as maturation, method and pH of coagulation, preservatives dry rubber content and viscosity-stabilizing agents, e.g., hydroxylamine-neutral sulfate, influence the cure characteristics of natural rubber. Therefore the consistency of cure for different grades of rubber is determined from compounds mixed to the ACS1 formulation. The ACS1 formulation is as follows: natural rubber,100; stearic acid, 0.5; zinc oxide, 6.0; sulfur, 3.5; and 2-mercaptobenzothiazole (MBT), 0.5. This is an activator-starved formulation and so is highly sensitive to the presence of nonrubbers that are capable of activating or accelerating vulcanization, and Table 2.1 illustrates the cure behavior of different grades of SMR. Cup lump grades show the highest state of cure and fastest rate of cure, whereas the stabilized grade, SMR CV, shows the lowest state of cure and slowest cure rate. Although filled systems are not as sensitive to variations in this type of cure behavior, certain correlations can be made with practical vulcanizing systems.

Plasticity Retention Index : The oxidation behavior of natural rubber may affect both the processing characteristics and final vulcanizate performance, and the plasticity retention index(PRI) test can be used to give an indication of both. Natural antioxidants present in natural rubber give some protection and a measure of the efficacy of protection is given by PRI. PRI% = $P_{30}/P_0 \times 100$, Where P_0 is the initial plasticity and P_{30} is the plasticity after aging in an oven at 140°C for 30 min. During mastication, rubber with high values of PRI tends to break down less rapidly than rubber with a low value; normally.There is little significant difference between rubbers with a PRI above a value of 60%. PRI can also be correlated with the aging performance of natural rubber vulcanizates. For example, raw rubber with a large PRI value gives better high temperature aging resistance, even in a formulation containing two parts of p-phenylenediamine antioxidant.

Table 2.1. Cure Characteristics of SMR Grades Mixed to the ACS1 Formulation. [12]

Grade	Monsanto rheometer,[a] 160°C, ±3° arc		
	MHR-ML,[b] J·cm^2	[c]T_{S2} , min	[d]T_{90}, min
SMR CV	29.4	2.2	11.6
SMR L	33.9	1.8	9.7
SMR 5	37.2	1.5	7.8
SMR 10	40.0	1.3	6.8
SMR 20	41.1	1.2	6.8

[a]See RHEOLOGICAL MEASUREMENTS.

[b]MRH = maximum stiffness during cure, and ML = minimum stiffness, both in a rheometer. To convert J/cm^2 to lbf · in ., divide by 0.0175.

[c]T_{S2} = Scorch time.

[d]T_{90} = Fractional modulus (90% of MHR-ML)

2.3.3 Chemistry and Technology[13]

Natural rubber as obtained from Hevea brasiliensis is cis-1,4-polyisoprene with small amounts of non-rubber produced by the tree. Although the double-bond structure is useful for chemical modification purposes, it does not benefit natural rubber's heat resistance. Natural rubber is relatively unstable compared to the more modern almost fully saturated elastomers, such as EPDM rubber. In terms of physical properties, the strain crystallizing nature of natural rubber gives if high tensile and tear strengths and it exhibits both low heat buildup and low rolling resistance. These latter two features make it especially attractive for tire manufacture. However, unless modified, it shows extensive swelling in oils, is relatively permeable to gases, and is not generally suitable for damping applications.

In the majority of applications, natural rubber is used in blends and, until fairly recently, remarkably little was known about the distribution of cross-links in such blends. Modern techniques have been adapted to look into this subject, with a consequent improvement in properties brought about by achieving a better balance of cross-links in the blend. In latex applications, a large proportion of the industry has moved out to the Far East, for example to Malaysia, if only because it is logical to ship the final product to the end user country rather than the latex, which contains 40% water. In general terms, the proportion of natural rubber in the total rubber market is slowly increasing (ca 1996), partly because it is technically necessary in tires for radical sidewalls, low rolling resistance, and low temperature behavior, and partly because the rubber industry is moving to the Far East, where the bulk of natural rubber is grown and is more easily available.

Vulcanization: Natural rubber is general vulcanized with a sulfur-based system, the mechanism of which is extremely complex and has been studied for many years by a number of workers. Basically, high sulfur, low accelerator (2.5 parts phr of sulfur and 0.5 part of sulfonamide) system results in the mainly polysulfidic cross-linked rubber that has a high tensile strength and exhibits good dynamic performance, but has relatively poor aging characteristics, even with an antidegradant present. On the other hand, an efficient vulcanizing(EV) system based on low sulfur and high accelerator levels leads to a mainly monosulfidic cross-linked network with consequent improvement in compression set and aging characteristics, but less good tensile and tear properties and inferior dynamic performance. Between them there are a multitude of semi-EV systems that fall between the high sulfur-low accelerator and low sulfur-high accelerator recipes and give a compromise in properties. For maximum heat resistance, as distinct from oxidative aging, there are also the Peroxide and Novor systems. The peroxide vulcanizing agent, e.g., dicumyl peroxide, gives direct carbon-carbon cross-links for extreme thermal stability. However, such systems have little or no scorch safety, unless a free-radical trap is incorporated, and they tend to require very long cure times. For example, about six times the half-life of the peroxide is needed to ensure complete decomposition; otherwise, aging performance is reduced.

Protective systems: As in the case of sulfur vulcanization, there have been many research workers in the field of natural rubber oxidation and its protective. The principal problem has always been to find and antioxidant that provide protective against flex-cracking, and yet does not stain. None has been found as of the mid-1990s; hence it is best to categorize the various types according to their capabilities.

The principal category of protective agents is the staining antidegradenes, which protect against oxygen, ozone, and flex-cracking. By far the most effective are the p-phenylenediamines. These are the N-alkyl-N′-phenyl,N,N′-dialkyl, and N,N′-diaryl compounds. As a general rule, those with the lowest molecular weight are the most reactive, but also the most volatile, most easily extracted, and the worst staining. The second category is staining antioxidants with antiflex cracking capability only. Example of these is diphenylamineaceton condensates and naphthylamine derivatives. There are good antiflex cracking agents, but not as effective as the p-phenylenediamines. The condensates are good as general purpose antidegradants and are used in tire compounds. The third type is made up of the low staining amine antioxidants, which include polymerized 2,2,4-trimethyl-1,2-dihydroquinoline,di-ß-naphthyl-penylenediamine and alkylated or aralkylated diphenylamines. These impart good protective against heat and oxygen, and the p-phenylenediamine is also effective as a metal deactivator. All stain less than most of the other amine antioxidants. Among non-staining antioxidants, the least staining and discoloration is given by the phenolic antioxidants, such as the phenol-alkanes, hindered phenols, hydroquinones. These give reasonably good antioxidant protection, but some are susceptible to pinking on exposure to light. For nonstaining protection against ozone attack under static conditions, waxes are used. The type of wax is determined by the service condition involved and the temperature. In general, the melting temperature of the wax should not be less than 20°C above the maximum temperature that the surface of the product is likely to reach. The wax must bloom to the surface and form a coherent layer to work satisfactorily. Finally, it is well known that traces of certain metals such as copper, manganese, and iron act as catalysts in the oxidation of natural rubber vulcanizates. Many amines and some phenolics are effective inhibitors of metalcatalyzed oxidation. Here again, p-phenylenediamines are particularly effective, providing their staining can be tolerated. Blends of antioxidants are also used and 2-mercaptobenzimidazole or its zinc salt have been found to be very effective.

2.3.4 Applications [14]

In the same way that natural rubber is predominantly used in blends, it is also predominantly used in tire manufacture. Its excellent building tack, low heat buildup, low rolling resistance, and good low temperature performance make it the polymer of choice for many parts of tire construction, for both passenger and truck vehicles. The effects of radialization and demand for low rolling resistance and good low temperature performance have all tended to benefit natural rubber, especially in truck tire construction, as shown in Table 2.2.

A large proportion of the about 3.7×10^6 t/yr of natural rubber used in tire is consumed in truck tires, off-the-road tires, and aircraft tires, all of which demand a low heat buildup performance. The retreating of truck tires was also the province of natural rubber until the precured process was developed. Prior to the advent of this technique, the tack of natural rubber was essential for the unvulcanized rubber to adhere onto the buffed carcass, and the thickness of the shoulder region was such that the low heat buildup of natural rubber was essential to ensure that no failure occurred in service. With the precured tread process neither of these attributes was necessary and, synthetic rubber, which was and continues to be used, was found to give particularly good wear performance under low severity conditions, especially in the United States. However, work [67] has shown that natural rubber-based formulations can be developed which give a similar order of wear performance to the all-synthetic rubber tread, but with the additional benefit of lower rolling resistance, and hence better fuel economy.

Natural rubber was also used extensively in its oil-extended form in winter tires in the 1970s. Use of oil-extended natural rubber treads, found to have exellunt traction on ice and snow and superseded studded synthetic rubber treads when studs were banned in certain countries and states owing to the damage they cause to partially cleared roads. This concept has been extended into all-season tires, which account for over 75% of original equipment and replacement tires in the United States. It has been shown that part replacement of styrene-butadiene rubber (SBR) in formulation of all-season tire tread compounds with oil-extended natural rubber increase ice and snow traction, reduces rolling resistance, and has no effect on normal wet grip. Also, there is only a minor trade-off in wear performance, because below a tire surface temperature of approximately 32°C, the wear of natural rubber is superior to SBR, whereas above this temperature the reverse is true. Thus, wear of an all-season tire ultimately depends on the surface temperature of the tread over its annual cycle of temperatures.

Table 2.2. Average polymer composition of truck tire components,[a] %. [14].

Year	Tread			Sidewall			Ply/belt		
	NR	SBR	BR	NR	SBR	BR	NR	SBR	BR
1974	45	21	34	48	37	15	71	20	9
1981	60	12	28	44	19	37	84	11	4
1983	77	7	16	58	6	36	100		
1985	86	5	9	62		38	100		
1990	86	5	9	75		25	100		
1994	100			60		40	100		

[a] NR = natural rubber, SBR = styrene-butadiene rubber, and BR = butadiene rubber.

Other than tire use, there are few other significantly large application areas for natural rubber that can be identified, as indicated in Table 2.3. The use of natural rubber in latex products covers items such as gloves, condoms, balloons, catheters and other dipped goods, latex thread, foam and carpet backing, and rubberized coir and hair. In total, latex goods consume about 11% of world rubber production. Thereafter, there are four categories: footwear, nonautomotive engineering, belting and hose, and nontire automotive applications, which consume 1.5-4% each. Footwear is self-explanatory, with the market for athletic shoes, especially those made is the Far-East, tending to keep natural rubber in this market. Nonautomotive engineering applications cover the use of natural rubber in civil engineering products such as bridge bearings, off-shore oil field equipment, and the growing market for rubber-metal-laminated bearings to protect buildings against earthquakes. This relatively new application was born out of the early work on metal-laminated natural rubber bearings for bridges, which later spawned the used of natural rubber bearing to protect buildings against ground-borne vibrations,eg, from the London Underground. This in turn developed in the 1980s into natural rubber bearings to protect buildings against earthquakes, a technique fast developing around the world in earthquake-prone areas, notably Japan, New Zealand, Italy, and the state of California in the United States. Another significant use of natural rubber is in belting and hose, where natural rubber's high strength, resilience, and fatigue performance still help to maintain its use as a premium rubber for these applications.

The nontire automotive sector includes engine mounts, where natural rubber is still regarded as the preferred polymer, and the many other rubber bearings, seals, grommets, washers, and boots used in the automotive industry for which oil-resistance is not required. It is likely that some of these items will change to thermoplastic materials, including thermoplastic natural rubber, in coming years as the demand for total recyclability of automobiles takes hold. The wire and cable industry has continued to use less natural rubber over the years because of its poor durability as compared to PVC and ethylene-propylene rubbers. However, improvements in blend technology may well reverse this trend if natural rubber/ethylene-propylene rubber blend properties can be optimized for the cable market.

The other miscellaneous uses of natural rubber cover a multitude of applications, none of which of themselves consume a large tonnage. Many of these are traditional uses such as pipe seals, medical closures, rollers, small solid tires, mountings for a whole range of domestic and commercial appliances, rubber balls and tubing, milking inflations, and other agricultural-based applications. In total these make up approximately another 7% of natural rubber usage, which for 1993 had a total market share of some 5.33×10^6 t.

Table 2.3. End Uses of Natural Rubber. [14]

Use	Amount, 10^3 t	Percent of total
Tires and related products	3800	71
Latex products	585	11
Footwear	210	4
Non-automotive engineering	200	4
Belting and hose	80	1.5
Automotive (non-tire)	80	1.5
Wire and cable	15	<1
Other	360	7
Total world natural rubber consumption	5330	100

2.4 Liquefaction process [15]

Liquefied gases are in common use for variety of purposes. For example, liquid propane in cylinders serves as a domestic fuel, liquid oxygen is carried in rockets, natural gas is liquefied for ocean transport, and liquid nitrogen is used for low temperature refrigeration. In addition, gas mixtures (e.g., air) are liquefied for separation into their component species by fractionation.

Liquefaction results when a gas is cooled to a temperature in the two phase region. This may be accomplished in several ways:

1. By heat exchange at constant pressure.
2. By expansion in a turbine from which work is obtained.
3. By a throttling process.

The first method requires heat sink at a temperature lower than that to which the gas is cooled, and is most commonly used to pre-cool a gas prior to its liquefaction by the other two methods. As external refrigerator is required for a gas temperature below that of the surroundings.

The three methods are illustrated in Figure 2.3 .The constant pressure process approaches the two phase region (and liquefaction) most closely for a given drop in temperature [16]. The throttling process does not result in liquefaction unless the initial state is at a high enough pressure and low enough temperature for the constant enthalpy process to cut into the two phase region. This does not occur when the initial state is at A. If the initial state is at A′, where the temperature is the same but the pressure is higher than at A, then isenthalpic expansion by process does result in the formation of liquid. The change of state from A to A′ is most easily accomplished by compression of the gas to the final pressure at B, followed by constant pressure cooling to A′. Liquefaction by isentropic expansion along process may be accomplished from lower pressures (for given temperature) than by throttling. For example, continuation of process from initial state A ultimately results in liquefaction.

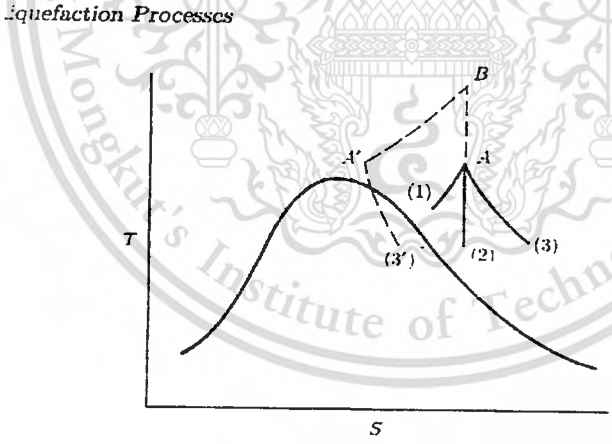


Figure 2.3. Cooling processes on a TS diagram. [16]

The throttling process is the one commonly employed in small-scale commercial liquefaction plants. The temperature of the gas must of course decrease during expansion. This is indeed what happens with most gases at usual condition of temperature and pressure. The exceptions are hydrogen and helium, which increase in temperature upon throttling unless the initial temperature is below about 100 K for hydrogen and 20 K for helium. Liquefaction of these gases by throttling requires initial reduction of the temperature to lower values by method 1 or 2.

As already mentioned, the temperature must be low enough and the pressure high enough prior to throttling that the constant-enthalpy path cuts into two phase region. For example, reference to a TS diagram for air[6] shows that at a pressure of 100 (atm) the temperature must be less than 305(R), it can be partly liquefied by throttling. The most economical way to cool the air is by countercurrent heat exchange with the un-liquefied portion of the air from the expansion process.

This simplest kind of liquefaction system, known as the Line process, is show in Figure2.4. After compression, the gas is pre-cool to ambient temperature. It may even be further cooled by refrigeration. The lower the temperature of the gas entering the throttle value, the greater the fraction of gas that is liquefied. For example, evaporating a refrigerant in the pre-cooler at -40(°F) gives a lower temperature into the valve than if water at 70(°F) is the cooling medium.

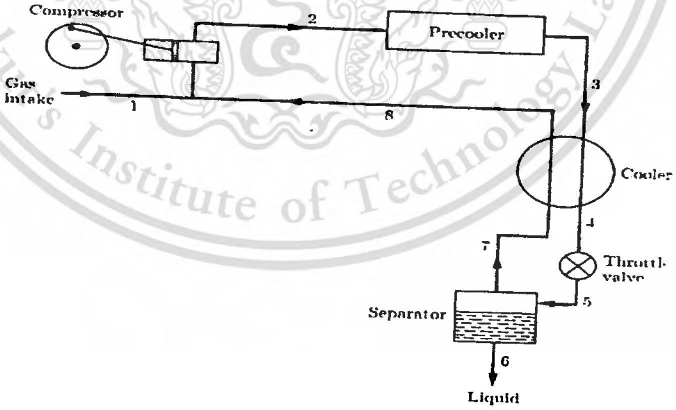


Figure 2.4 . Liquefaction process line. [16]

Under steady-state conditions, an energy balance around the separator, valve, and cooler gives $\Delta(mH)_{fs} = 0$, or [17]

$$H_6z + H_8(1\text{-}z) = H_3 \qquad (2.1)$$

Where the enthalpies are for a unit mass of fluid at the positions indicated in Eq. 2.1. Knowledge of the enthalpies allows solution of Eq. (2.1) for z, the fraction of the gas that is liquefied.

The flow diagram for the Claude process, shown by Figure 2.5, is the same as for the Line process, except that an expansion engine or turbine replaces the throttle valve.

The energy balance here becomes

$$H_6z + H_8(1\text{-}z) - W_8 = H_3 \qquad (2.2)$$

Where W_8 is the work of the expansion engine on the basis of a unit mass of fluid entering the cooler at point 3. If the engine operates adiabatically, this here becomes

$$W_8 = (H_5 - H_4) \qquad (2.3)$$

Equations (2.1) through (2.2) suppose that no heat leaks into the apparatus from the surroundings. This can never be exactly true, and heat leakage may be significant when temperatures are very low, even with well-insulated equipment.

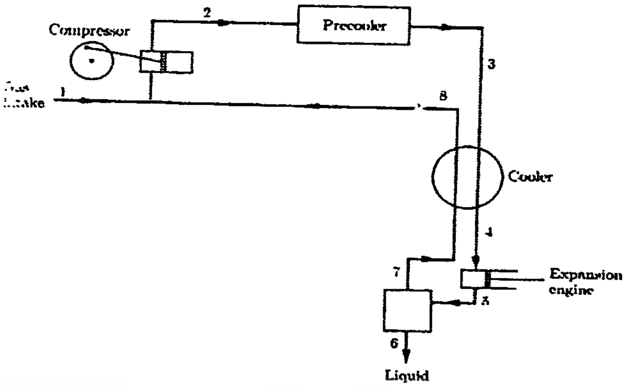


Figure 2.5. Claude liquefaction process. [17]

2.5 Supercritical fluid [18]

Supercritical fluid (SCF) means existence of any substances which can not classify as a liquid or gas. This existence cans explain from pressure-temperature phase diagram of pure substance (Fig 2.6). The figure is shown the area of substance in solid state, liquid phase and gas phase. Sublimation exists between solid phase and gas phase. Fusion line exists between solid phase and liquid phase. Vapor Pressure Line (Boiling Line) exists between solid phase and liquid phase. The point that exists between 3 phases called Triple Point (Tp). When consider with the gas that can change to be liquid phase by two ways. The first one is increasing the pressure and the second one is decreasing temperature to reduce the kinetic energy, which is can make the distance between each other decrease to cause the condensation turn to be liquid. Nevertheless as temperature is higher than one point gas's molecule has high kinetic energy (even though give any value of pressure), gas is cannot to condensation to be a liquid. At high temperature gas condense to be liquid called critical temperature Tc , the pressure called critical pressure, P_c. The point that has temperature as same as critical temperature and pressure point as same as critical pressure called critical, Cp.

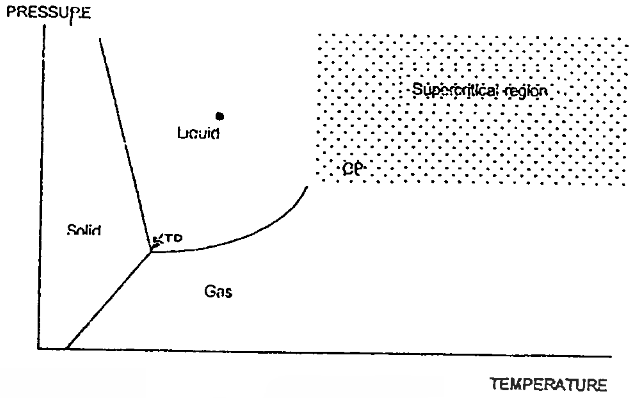


Figure.2.6. Diagram of supercritical fluid. [18]

At higher temperature than critical temperature and higher pressure than critical pressure, the substances cannot classification as liquid or gas, called this status as super critical fluid, by following value of temperature and pressure as Table 2.4.

Table 2.4. Status as supercritical fluid of each substance. [18]

Substance	Critical Temperature (K)	Critical Pressure (MPa)	Critical Density (g/cm^3)
Methane	190.6	4.60	0.162
Ethylene	282.4	5.03	0.218
Chlorotrifluoromethane	302.0	3.92	0.579
Carbon dioxide	304.2	7.38	0.468
Ethane	305.4	4.88	0.203
Propylene	365.0	4.62	0.233
Propane	369.8	4.24	0.217
Ammonia	405.6	11.30	0.235
Diethyl ether	467.7	3.64	0.265

n-Pentane	469.6	3.37	0.237
Acetone	508.1	4.70	0.278
Methanol	512.6	8.09	0.272
Benzene	562.1	4.89	0.302
Toluene	591.7	4.11	0.292
Pyridine	620.0	5.63	0.312
Water	647.3	22.00	0.322
Xenon	289.7	5.84	1.113
Ethanol	516.0	6.40	0.276
Tetralin	719.0	3.60	0.302

Properties of Super critical fluid are between gas and liquid as shown in Table 2.5. The supercritical fluid's density value closes to liquid. When use supercritical fluid as a solvent the solute's molecule surrounded by supercritical fluid's molecule by interaction to each other, enthalpy's energy decreases then it is easy to solubility. At the same line properties of supercritical fluid has the viscosity's value and the diffusion's value as same as gas this reason is why supercritical fluid can penetrate into the solute matrix according to this properties. Supercritical fluid can use as solvent better than supercritical liquid because there is a faster mass transfer and high quality in solvent power.

There are 2 different lines (Fig 2.7) in supercritical fluid as we desire. The first line starts at point A, the substance exist in liquid phase then increase the pressure to be higher than critical pressure at constant temperature. Next increasing the temperature to be higher than critical temperature at constant pressure until this substance stay at supercritical point or on point C. The second line start at point B, the substance exists in gas phase; add heat energy until the substance has higher temperature than critical temperature at pressure at constant. Then increasing the pressure to be higher than critical pressure at constant temperature.

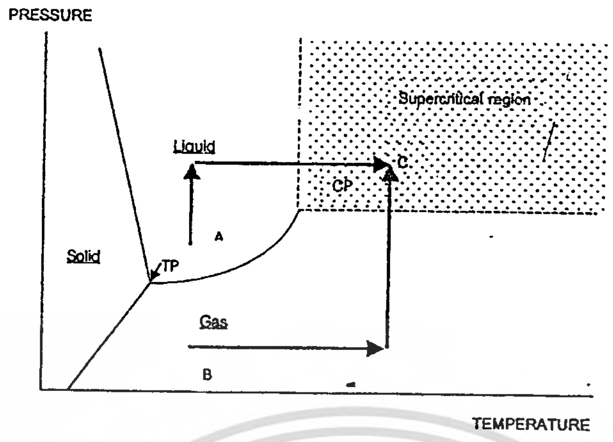


Figure 2.7. Lines of Supercritical (C point) from liquid (A point) and gas (B point). [18]

Table 2.5 Properties of supercritical fluid compare with gas and liquid. [18]

State of Fluid	Density (g/cm^3)	Diffusivity (cm^2/sec)	Viscosity (g/cm sec)
Gas			
P=1 atm, T=15-30°C	$(0.6\text{-}2)\times10^{-3}$	0.1-0.4	$(1\text{-}3)\times10^{-4}$
Liquid			
P=1 atm, T=15-30°C	0.6-1.6	$(0.2\text{-}2)\times10^{-5}$	$(0.2\text{-}3)\times10^{-2}$
Supercritical			
$P=P_c$, $T=T_c$	0.2-0.5	0.7×10^{-3}	$(1\text{-}3)\times10^{-4}$
$P=4P_c$, $T=T_c$	0.4-0.9	0.2×10^{-3}	$(3\text{-}9)\times10^{-4}$

2.5.1 Properties of supercritical fluid [19]

Transport properties: According to properties of supercritical fluid has low viscosity and high diffusion coefficiency, so it can diffuse in whole area. It can penetrate into the inner structure of solute; this can make the solute which is dissolved into the supercritical fluid diffusion out of the area which is easy to extraction. That means it has good transport properties, so this can make the supercritical fluid is good solvention.

However, the viscosity and diffusion coefficiency of supercritical fluid relate with many conditions, such as temperature, pressure and type of supercritical fluid. Then it has to be adjusting the conditions to be property for good extraction (get high quality and low contaminate). The velocity rate of mass transport depends on viscosity, diffusion ability of supercritical fluid, diffusion distance and diffusion barriers, which are the conditions from inner structure of solute.

Solvent power: This is a one of properties of supercritical fluid. This is due to supercritical fluid better than general liquid solvent because supercritical fluid is adjusted the value less more by supercritical fluid's conditions adjustment. First of all is temperature, in general when increasing temperature to liquid solvent, so dissolving increasing too. Anyway, there are two effects which oppose each other when increasing temperature in supercritical fluid.

1. Increasing the solute's dissolving.
2. Decreasing the density which make the supercritical fluid molecule and solute stay apart, so solute's dissolving decrease.

An ultimate conclusion of these two oppose effects is solvent power of supercritical fluid. The second point can corrected by raising the pressure to supercritical fluid, which is consistent the density to be close to previous condition (before increasing temperature).

To summarize, the variable which is affected directly to solvent power is temperature and density, beside that pressure is indirect affected to solvent power by pass through density.

The relationship between solvent power, temperature and density of supercritical fluid show as Chrastill's equation as follow[19].

$$C = d^{k} \exp\left(a / (T + b)\right) \qquad (2\text{-}4)$$

Where :

C is the intensity of solute in supercritical fluid (g/l)

d is the density of supercritical fluid (g/l)

k is association number, which show about compact formed between solute-solvent.

T is temperature (K)

a,b are constant values.

Selectivity properties: is the supercritical fluid's properties that can adjust the temperature and pressure of solvent power to be suitable for supercritical fluid extraction, by the need of high quality (high quantity) and the lowest contamination.

According to supercritical fluid has high selective so it is enable to fractionated extraction the conditions starting at critical point and then gently adding temperature and pressure. From this technique, it is enable to fractionated extraction by portions such as pepper's extraction. Which is can separate the sweet part and spicy part.

2.5.2 Supercritical fluid selective [19]

The selection of supercritical fluid to be used as solvent depends on many conditions. The most important condition is solvent power of supercritical fluid. The solvent power may be shown as Hildebrand solubility parameter (δs).

The modifiers adding (Entrainers or Entrained Solvent) is second order solvent, that's each types of conventional solvent which is completed dissolving with primary fluid to have impact on solvent power of supercritical fluid.

However, modifers adding can cause the phase diagram changing, so the predication of solvent behaviors is difficult because of limited knowledge of this field. So the result of modifiers from experimental uses as decision.

For examples from modifier using.

- Propane adding into supercritical carbon dioxide to helpful in triglyceride and fatty acid extraction.
- Acetone adding into supercritical carbon dioxide to extract triglyceride can reduce the pressure from 13.5 MPa (1,960 psi) to 8 MPa (1,160 psi) the expense decrease up to 30%.
- 0.1% H_2O adding in supercritical carbon dioxide is helpful in velocity rate in elimination of 1-Butanol and n-butyl acetate, which is contaminate from Penicillin G extraction.

2.5.3 Benefits of supercritical fluid.

Even though, supercritical fluid has been popular for a long time but the using of supercritical fluid in experimental just begin recently.

The benefit of supercritical fluid can summarize as follow.

1. Use as supercritical fluid extraction in order to get high quantity extraction and the development in low quantity of extraction because it can take this extract to further analysis.
2. Use as mobile phase in supercritical fluid chromatography.
3. Discover that some products which is get from supercritical fluid extraction is stay as microfile crystals (10-50 micrometer), when study with x-ray diffraction showing that crystal structure of product is same as the previous (at staring point). Then this property is offered to use supercritical fluid as milling to avoid the high temperature.
4. Discover that supercritical fluid extraction can kill or destroy microorganism, so this property is offer to use supercritical fluid in sterilization of the substance which is not endure at high temperature or can use supercritical fluid as preliminary of extract product from foster microorganism.

CHAPTER 3

The Experimental Details

Liquefaction of high density polyethylene and wasted rubber gloves has been studied. The equipment and materials were used as follow :

3.1 Liquefaction Instruments

3.1.1 Batch reactor

Batch reactor has a cylinder shape made from stainless steel tubular reactor and its internal diameter is 3 cm. There is an open / closed valve that uses to compress gas for flowing to batch reactor. It also has a safety valve for protection of excess pressure in reactor. Batch reactor can be operated at high temperature and pressure as shown in Figure3.1

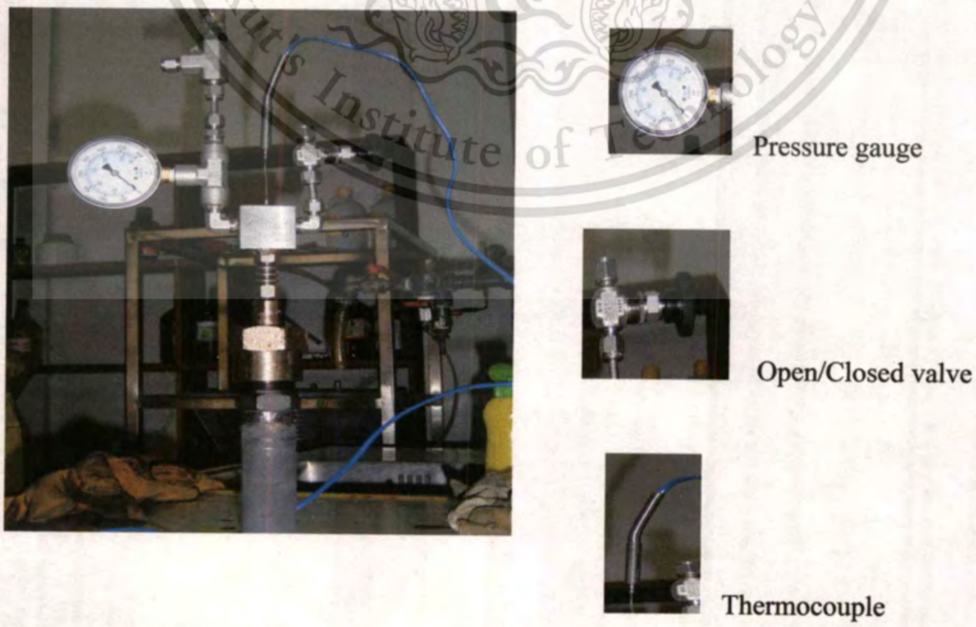


Figure 3.1. Batch reactor

3.1.2 Heating Equipment and Temperature Controller

This process requires rapidly increasing temperature from initial to final temperature. That is a reason why heating equipment and control temperature are one of important components. Heating equipment has a higher temperature panel, which matches to cylindrical wall reactor. It uses 250 watts of electric power with direct current adapter that can adjust to appropriate value. The external part shields with insulator fiber which can tolerate to high temperature. The digitally automatic temperature controller detects the signal comel-alumel thermocouple type K at temperature range 0-1200 ^{0}C as shown in Figure 3.2

Heater 950 w 220 v

Temperature Control

Model :FCR-13A-R/M
Range :MULTI-RANGE
Power : 100 to 240 V AC
Supply 50/60 Hz
Serial no.: 197093
SHINKO TECHNOS CO.LTD

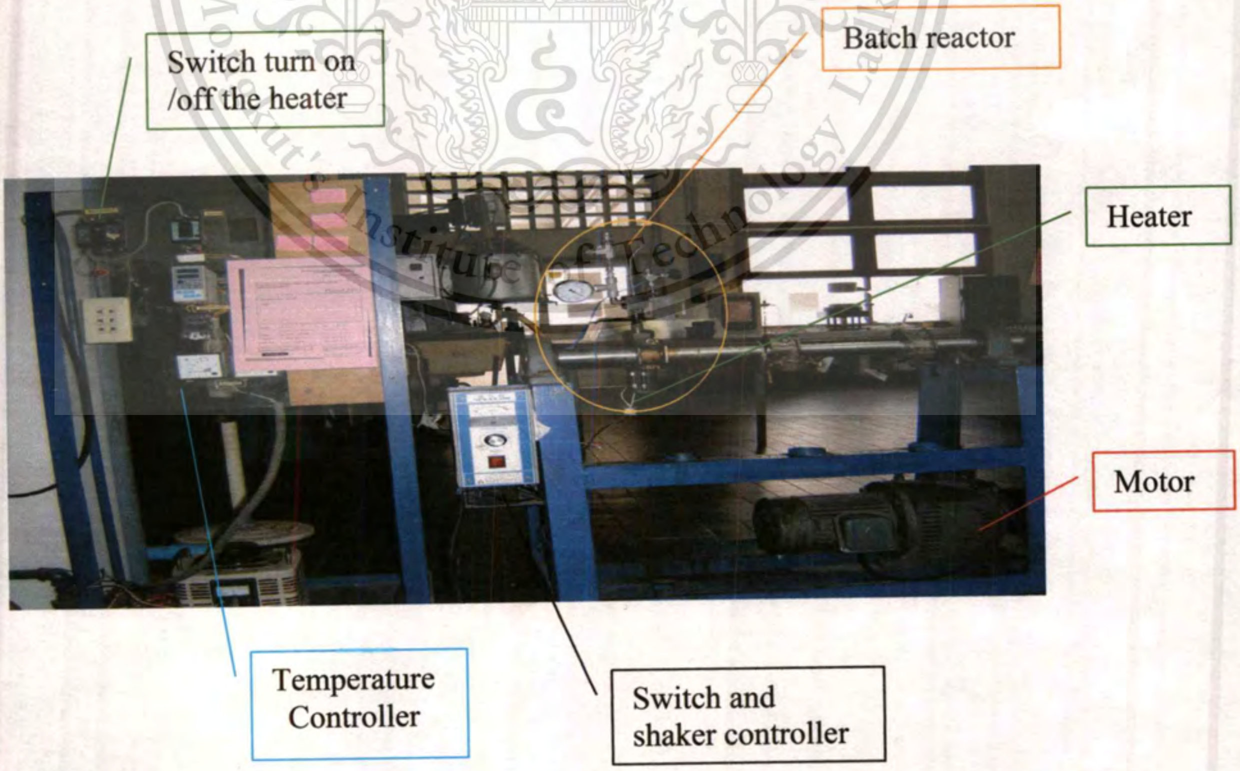
Figure 3.2 Heater and Temperature Controller

3.1.3 Shaker Machine

The shaker movement is controlled by motor. Its shapes looks like an axle with perpendicular to 90^0 core axis, as shown in Figure 3.3

Figure 3.3 . Shaker machine

The assembly for three parts of liquefaction process as mention before was shown in Figure 3.4



F igure 3.4. The assembly of liquefaction machine

3.2 Delicate Scale Weighing

This apparatus was used for weighing scraped sample. It was shown in Figure 3.5

SCIENTIFIC PROMOTION CO.,LTD
MODEL 1712
S/N 3411106

Figure 3.5 Delicate Scale Weighing

3.3 Gas Chromatography

Gas chromatography was used to determine quantity of hydrocarbon compound. It was shown in Figure 3.6

THAI UNIQUE CO.,LTD

Instrument GC3800
Model GC 3800 + SIM DIS

Figure 3.6 Gas chromatography

3.4 Material

3.4.1 Toluene : $C_6H_5CH_3$ CARLO ERBA REAGENTI ACS-ISO-For analysis Code no. 488555 CAS N. 108-88-3.

3.4.2 Natural Rubber Glove : Sempermed rubber examination gloves Co.,Ltd., size M, Code no. 0108.

3.4.3 High Density Polyethylene : TTC Siam Drinking Water Co.,Ltd. Unknown grade.

3.5 Experimental

This project can be divided into two parts, the effect of pressure, temperature and ratio between wasted high density polyethylene (WHDPE) and wasted rubber gloves (WRG) to liquefaction process.

For the reason why temperature at 400 and 450°C were selected, there has been examination of appropriate temperature for scraped WHDPE and WRG (10g) by using tube furnace set at different temperatures 350,400,450 and 500 °C for 1 hour and examined every ratio 0:10, 2:8, 4:6 ,6:4 ,8:2 and 10:0. It found that at temperature 350°C WRG and WHDPE were not melted completely. At temperature 400 and 450 °C WRG and WHDPE were melted completely. For temperature 500°C WRG and WHDPE were ignited and turned to be ash.

3.5.1 The effect of reaction time to liquefaction of WHDPE.

In this experiment, WHDPE was taken from waste bottles Of TTC Siam Drinking Water Co.,Ltd. It was cut into tiny pieces as raw material for 10 grams. The pressure and temperature were constant at 5 MPa and 400°C, respectively. The reaction time was changed from 30 min to 60 min . The procedure of this study was as follow :

1. Put 10 grams of WHDPE and toluene into batch reactor. Then the top of the batch was closed securely.
2. Controlled pressure of batch reactor at 5 MPa.

3. Assembly of batch reactor with shaker machine and set temperature controller at the same time.
4. Adjusted temperature to 400^0C until required temperature was reached.
5. Turned on the shaker machine until the reaction time was completed at 30 min.
6. After reached 30 min, took the heater out and let the reactor cooled down at room temperature.
7. Released gas molecules out of the reactor by opening the valve.
8. Pulled the thermocouple out and open the batch reactor carefully.
9. Recorded the volume and kept in glass bottles.
10. Took the samples for weighing and then recorded the value.
11. Repeated 1 to 10 by changing the reaction time to 60 min.

3.5.2 The Effect of reaction time to liquefaction of rubber glove.

In this experiment wasted rubber gloves (WRG) was taken from Siriraj Hospital and manufactured by Sempermed latex examination gloves Company Co.,Ltd. as raw material. It was cut into tiny pieces and then put 10 grams to liquefaction process. Toluene was added to the process with constant pressure and temperature of 5 MPa and 400^0C ,respectively. The reaction time was also varied from 30 min to 60 min. The procedure of this study was as follow :

1. Put 10 grams of WRG and toluene into batch reactor. Then the top of batch reactor was closed securely.
2. Controlled pressure of batch reactor at 5 MPa.
3. Assembly of batch reactor with shaker machine and set the temperature at the same time.
4. Adjusted temperature to 400^0C until required temperature was reached.
5. Turned on the shaker machine until the reaction time was completed at 30 min.

6. After reached 30 min, took the heater out and let the reactor cooled down at room temperature.
7. Released gas molecules out of the reactor by opening the valve.
8. Pulled the thermocouple out and open the batch reactor carefully.
9. Recorded the volume and kept in glass bottles.
10. Took the samples for weighing and then recorded the value.
11. Repeated 1 to 10 by changing the reaction time to 60 min.

3.5.3 The effect of pressure, temperature and ratio between WHDPE and WRG.

After the appropriate reaction time of WHDPE and WRG was known from 3.5.1 and 3.5.2. The effect of pressure, temperature and the ratio of WHDPE and WRG was further studied. The starting material was still 10 grams (mixed of WHDPE and rubber glove ; for each 5 grams). Set the liquefaction at constant pressure 5 MPa. At this moment, the temperature was changed from 400^0C to 450^0C, as well as the ratio of WHDPE and WRG was also changed to 0:10, 2:8, 4:6, 6:4, 8:2 and 10:0, respectively.

The procedure of this study was as follow :

1. Weighed 10 grams of mixed WHDPE and WRG with the ratio of WHDPE 0:10 g.
2. Put the sample and toluene into batch reactor. Then the top of the batch reactor was closed securely.
3. Controlled temperature of batch reactor at 5 MPa.
4. Assembly of batch reactor with shaker machine and set the temperature at the same time.
5. Adjusted temperature to 400^0C until required temperature and appropriate time (from section 3.5.1 and 3.5.2) were reached.

6. After reached 60 min, took the heater out and let the reactor cooled down at room temperature.
7. Released gas molecules out of the reactor by opening the valve.
8. Pulled out the thermocouple and open the batch reactor carefully.
9. Recorded the volume of each samples and kept in glass bottles.
10. Took the samples for weighing and recorded the value.
11. Repeated 1 to 10, but changed the ratio of WHDPE and rubber glove to 2:8, 4:6, 6:4, 8:2 and 10:0 ,respectively.
12. Repeated 1-10, but changed temperature to 450^{0}C.
13. Repeated 1-10, but changed pressure to 10 MPa and 15 MPa.
14. Kept all samples for each parameter to analysis hydrocarbon composition by gas chromatography.

CHAPTER 4

Results and Discussion

This project was studied the effect of reaction time and operating pressure, temperature and the ratio of WHDPE and WRG to the percentage amount of conversion to liquid oil and quality of hydrocarbon compound by using gas chromatography by calculation from the area under peak (Appendix A and Appendix B)

4.1 Percentage of liquid conversion.

The WHDPE and WRG were studied by liquefaction process with toluene as supercritical solvent. It was varied temperature from 400 to 450°C and varied pressure to 5, 10 and 15 MPa. The results were shown in Table 4.1-4.6 and Figure 4.1-4.3.

In addition, from the experimental had to varied the quantity of toluene with control constant pressure (5, 10 and 15 MPa) because toluene was directly effected to pressure. This was due to different structure of WRG and WHDPE. Structure of WRG was easier to decomposition then it used amount of toluene lower than WHDPE. Meaning that, the quantity of toluene was depended on the quantity of WHDPE (Appendix C).

4.1.1 Effect of Temperature.

Temperature is the most significant to decomposition of WHDPE and WRG to liquid. If the temperature was changed from 450°C (Table 4.1-4.3) to 400°C (Table 4.4-4.6) and Figure 4.1-4.2 as the pressure constant. The liquid conversion was higher. It was pointed out that at temperature of 400°C, same volatile molecules of WRG could be condensed to liquid before WHDPE. This was dued to melting point and volatile properties of WRG. As the temperature was higher to 450°C, WRG was partially decomposed to gas, therefore the percentage of liquid conversion was decreased, because volatile molecule could not repeating condense to be liquid. Some volatile molecules (gas) were released out through releasing valve.

4.1.2 Effect of Pessure

Consider at constant temperature, pressure was increased to 5,10 and 15 MPa (Table 4.1 -4.6) and Figure 4.3. The liquid conversion was decreased, particularly at 15 MPa. Normally, from the theoretical when the pressure was higher, then the liquid conversion had to be higher too. In this experimental was not followed as the theory, this could be explained by the slightly effect of time when applied higher pressure to the process can caused the molecule easier to volatile and turned to be gas in batch reactor(gas molecule can take place well). For some volatile molecule needs enough time (higher than 1 hour) to condense as a liquid product but in this process, time was fixed to 1 hour, leading to gas molecule not have enough time to condense as a liquid. It could be pointed out that at the lower pressure, the higher the liquid conversion. The other reason was gas molecule escaping from the batch rector because there was leaking when the pressure was higher.

4.1.3 Effect of WHDPE Ratio

The WHDPE ratio was also influenced to liquid conversion, but it was not so significant especially at higher WHDPE (Table 4.1-4.6). This could be explained by molecular structure of WRG. It was easier to volatile to liquid than WHDPE (Figure 4.1-4.3).

In mixing of WHDPE to WRG at different ratio had slightly effect to liquid conversion, From the graph showed that at different ratio of WHDPE most of liquid conversion rather stable , consideration of all effects, the percentage of liquid conversion was as follows: the highest liquid conversion was 77.91% obtained from WRG 8 g and WHDPE 2 g at temperature of 400°C

Table 4.1. The amount conversion of WHDPE and WRG to liquid oil at temperature 450 °C and pressure 5 MPa.

HDPE:Rubber	% liquid	% gas
10:0	63.35	36.65
8:2	62.74	37.26
6:4	64.64	35.36
4:6	63.83	36.17
2:8	69.08	30.92
0:10	53.86	46.14

Table 4.2. The amount conversion of WHDPE and WRG to liquid oil at temperature 450 °C and pressure 10 MPa.

HDPE:Rubber	% liquid	% gas
10:0	61.05	38.95
8:2	57.66	42.34
6:4	53.93	46.07
4:6	61.84	38.16
2:8	66.19	33.81
0:10	39.86	60.14

Table 4.3. The amount conversion of WHDPE and WRG to liquid oil at temperature 450 °C and pressure 15 MPa.

HDPE:Rubber	% liquid	% gas
10:0	36.41	63.59
8:2	44.34	55.66
6:4	51.03	48.97
4:6	56.83	43.17
2:8	61.63	38.37
0:10	34.94	65.06

Table 4.4. The amount conversion of WHDPE and WRG to liquid oil at temperature 400 °C and pressure 5 MPa.

HDPE:Rubber	% liquid	% gas
10:0	69.04	30.96
8:2	75.44	24.56
6:4	76.12	23.88
4:6	75.56	24.44
2:8	77.91	22.09
0:10	72.95	27.05

Table 4.5. The amount conversion of WHDPE and WRG to liquid oil at temperature 400 °C and pressure 10 MPa.

HDPE:Rubber	% liquid	% gas
10:0	68.50	31.50
8:2	59.59	40.41
6:4	61.38	38.62
4:6	57.31	42.69
2:8	69.80	30.20
0:10	64.16	35.84

Table 4.6. The amount conversion of WHDPE and WRG to liquid oil at temperature 400 °C and pressure 15 MPa

HDPE:Rubber	% liquid	% gas
10:0	41.55	58.45
8:2	57.24	42.76
6:4	58.57	41.43
4:6	47.46	52.54
2:8	64.66	35.34
0:10	62.03	37.97

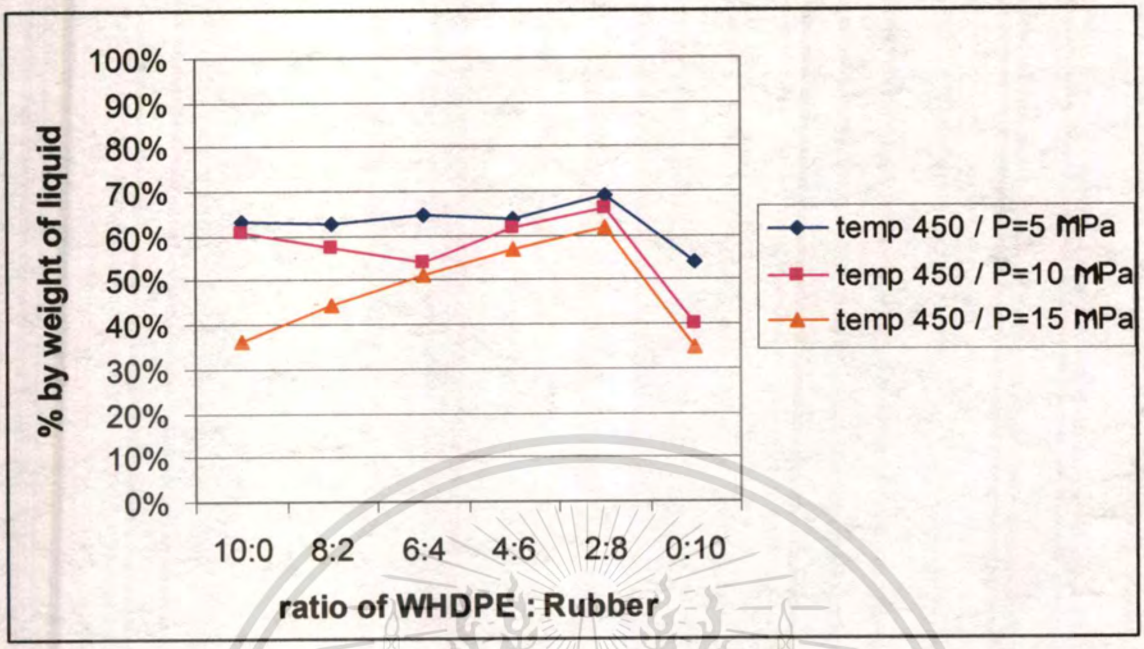


Figure 4.1. The relationship between ratio of WHDPE and WRG and percent by weight of liquid oil at constant temperature (450 °C) with varied pressure.

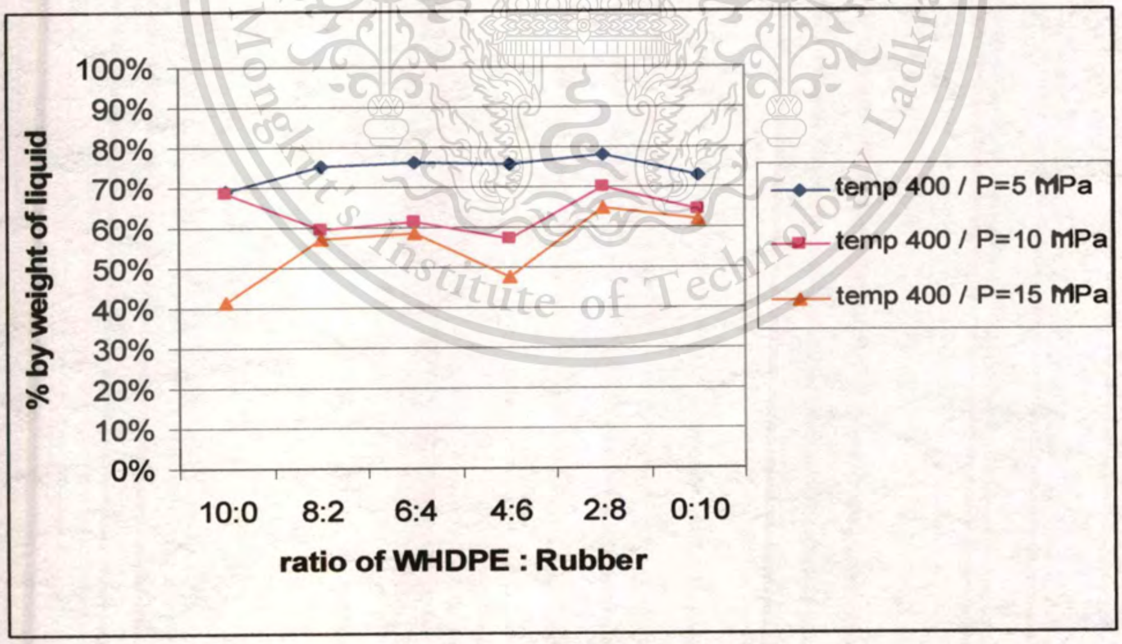


Figure 4.2. The relationship between ratio of WHDPE and WRG and percent by weight of liquid oil at constant temperature (400 °C) with varied pressure.

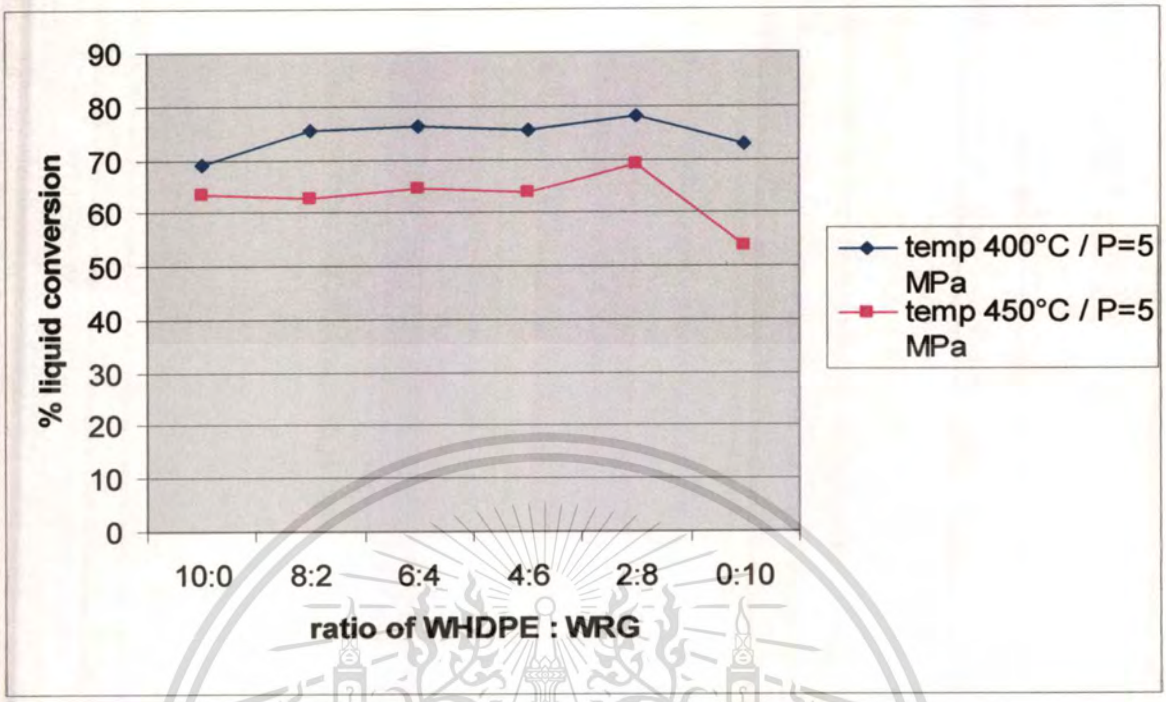


Figure 4.3. The relationship between ratio of WHDPE and WRG and percent by weight of liquid oil at constant pressure 5 MPa with varied temperature.

4.2 Quantity of hydrocarbon compound (Carbon)

Classification of hydrocarbon compound from petroleum oil guide book, were light hydrocarbon, naphtha, gasoline, kerosene, gas oil etc [20]. From gas chromatography determination

(Appendix D)liquid samples contained more unknown peaks but in this experimental would be considered only gasoline (Table 4.13).

4.2.1. The Effect of Temperature.

When the temperature was increased caused the percent of heavy oil and gas oil fell down. In addition, increasing of temperature was good to promote percent of gasoline yield. At lower temperature some portion of light molecule was cracked from heavy molecule but not complete indicating low quality. When the temperature rose up, the lighter hydrocarbon compounds were separated from heavy hydrocarbon compound indicating higher quality. This was the reason why percent of gasoline yield was increased shown in Table 4.7-4.12.

4.2.2 The Effect of Pressure

Consider at 10 g of WHDPE and WRG at 450°C, gasoline was decreased when pressure was increased. This was dued to higher temperature and higher pressure, the reactivity of reaction was faster and occured severely, then hydrocarbon was easier to crack to be lighter hydrocarbon than lower condition. Therefore at this temperature there was higher existing of naphtha more than gasoline yield see Table 4.7-4.12.

Consider at 10 g of WHDPE at 400°C, gasoline was increased when pressure was raised up because pressure had directly effected to gasoline yield, which could make the reactivity of reaction was faster and more efficiency. The higher the pressure, the heavy hydrocarbon in WHDPE was easier to crack to be light molecule such as gasoline. In the other hand, for 10 g of WRG at 400°C the quantity of gasoline was decreased because WRG was composed of lighter hydrocarbon than WHDPE. This was effected to carbon molecules in WRG cracking to be lighter molecules such as naphtha, see Table 4.7-4.12.

4.2.3 The Effect of WHDPE Ratio

Consider at temperature 450°C, the WHDPE ratio was directly effect to percent of gasoline yield. If there was high amount of mixed WHDPE with mixed in WRG, the carbon compound of WRG was not easily to crack to be light molecule such as naphtha. The mixed WHDPE in WRG was supported to increase gasoline conversion.

Consider at temperature 400°C, the WHDPE ratio was effect to gasoline conversion. If there was higher amount of mixed WHDPE in WRG, the percentage of gasoline conversion was decreased because the molecules of WHDPE was difficult to crack at temperature 400 °C. Therefore this could cause the higher percentage of heavy hydrocarbon compound, such as gas oil more than gasoline was shown in Table 4.7-4.12 and Figure 4.4-4.5.

Table 4.7. The amount conversion of hydrocarbon compound at temperature 450 °C and pressure 5 MPa.

HDPE:Rubber	% Naphtha (C_5 - C_9)	% Gasoline (C_{10} - C_{16})	% Gas oil (C_{17} - C_{25})	% Heavy HC (over C_{25})
10:0	34.06	53.80	11.11	1.04
8:2	40.10	50.74	9.17	0.00
6:4	30.55	45.79	16.63	7.03
4:6	39.85	44.80	13.60	1.75
2:8	35.01	45.88	17.07	2.04
0:10	34.75	60.17	5.08	0

Table 4.8. The amount conversion of hydrocarbon compound at temperature 450 °C and pressure 10 MPa.

HDPE:Rubber	% Naphtha (C_5 - C_9)	% Gasoline (C_{10} - C_{16})	% Gas oil (C_{17} - C_{25})	% Heavy HC (over C_{25})
10:0	42.37	39.62	13.74	4.28
8:2	38.65	46.02	11.94	3.39
6:4	48.09	43.34	8.56	0.00
4:6	47.74	39.07	5.86	0.00
2:8	38.56	45.37	16.07	0.00
0:10	52.79	33.65	13.57	0.00

Table 4.9. The amount conversion of hydrocarbon compound at temperature 450 °C and pressure 15 MPa.

HDPE:Rubber	% Naphtha (C_5 - C_9)	% Gasoline (C_{10} - C_{16})	% Gas oil (C_{17} - C_{25})	% Heavy HC (over C_{25})
10:0	30.91	38.23	18.69	12.17
8:2	35.77	41.29	12.13	10.81
6:4	38.94	30.82	16.71	13.52
4:6	41.47	32.99	16.50	9.04
2:8	22.59	45.12	21.89	10.40
0:10	57.79	30.15	12.06	0.00

Table 4.10. The amount conversion of hydrocarbon compound at temperature 400 °C and pressure 5 MPa.

HDPE:Rubber	% Naphtha (C_5 - C_9)	% Gasoline (C_{10} - C_{16})	% Gas oil (C_{17} - C_{25})	% Heavy HC (over C_{25})
10:0	24.08	36.13	19.46	20.33
8:2	28.25	37.45	18.67	15.63
6:4	25.27	38.11	17.96	18.66
4:6	27.78	42.62	19.59	10.00
2:8	26.42	50.66	20.53	2.39
0:10	21.85	61.68	16.47	0.00

Table 4.11. The amount conversion of hydrocarbon compound at temperature 400 °C and pressure 10 MPa.

HDPE:Rubber	% Naphtha (C_5 - C_9)	% Gasoline (C_{10} - C_{16})	% Gas oil (C_{17} - C_{25})	% Heavy HC (over C_{25})
10:0	25.09	38.22	16.12	20.57
8:2	28.64	36.90	17.75	16.71
6:4	26.61	37.79	17.14	18.47
4:6	25.75	45.95	17.25	11.05
2:8	26.89	31.39	20.14	21.58
0:10	24.69	61.62	13.69	0.00

Table 4.12. The amount conversion of hydrocarbon compound at temperature 400 °C and pressure 15 MPa.

HDPE:Rubber	% Naphtha (C_5 - C_9)	% Gasoline (C_{10} - C_{16})	% Gas oil (C_{17} - C_{25})	% Heavy HC (over C_{25})
10:0	27.97	41.47	14.60	15.95
8:2	29.02	36.16	15.92	18.90
6:4	33.12	35.10	14.55	17.23
4:6	25.85	32.87	21.20	20.08
2:8	31.75	28.69	19.97	9.59
0:10	25.40	49.20	18.68	6.71

Table 4.13. The amount conversion of hydrocarbon compound at temperature 450 °C (without toluene).

No toluene at temperature 450°C

HDPE:Rubber	% Naphtha (C_5 - C_9)	% Gasoline (C_{10} - C_{16})	% Gas oil (C_{17} - C_{25})	% Heavy HC (over C_{25})
10:0	18.11	49.22	19.80	12.87
0:10	25.03	50.83	15.19	8.96

In addition, toluene had slightly effected to hydrocarbon ratio. There were pure WRG and WHDPE of 10 g did the reaction at temperature 450 °C without toluene contamination. Percentage of gasoline yield was not significantly different when compared to the other samples that contained toluene as a solvent and at temperature of 400°C. There was no data because WRG and WHDPE were not melted completely.

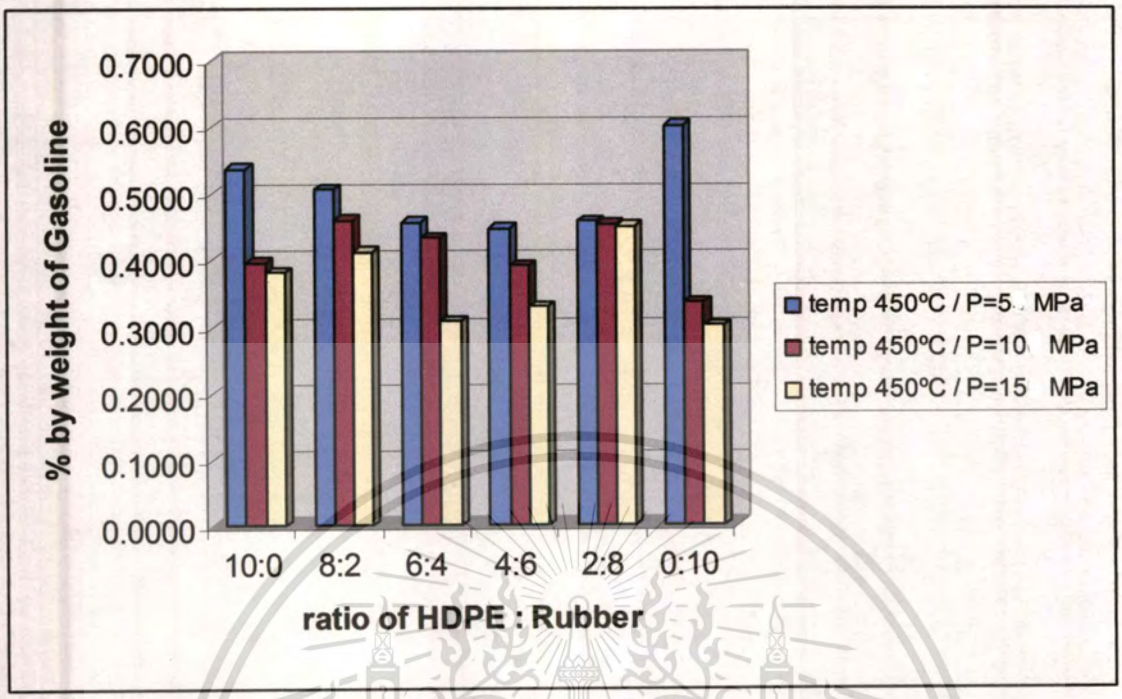


Figure 4.4. The relationship between ratio of WHDPE and WRG and percent by weight of gasoline at constant temperature (450 °C) with varied pressure.

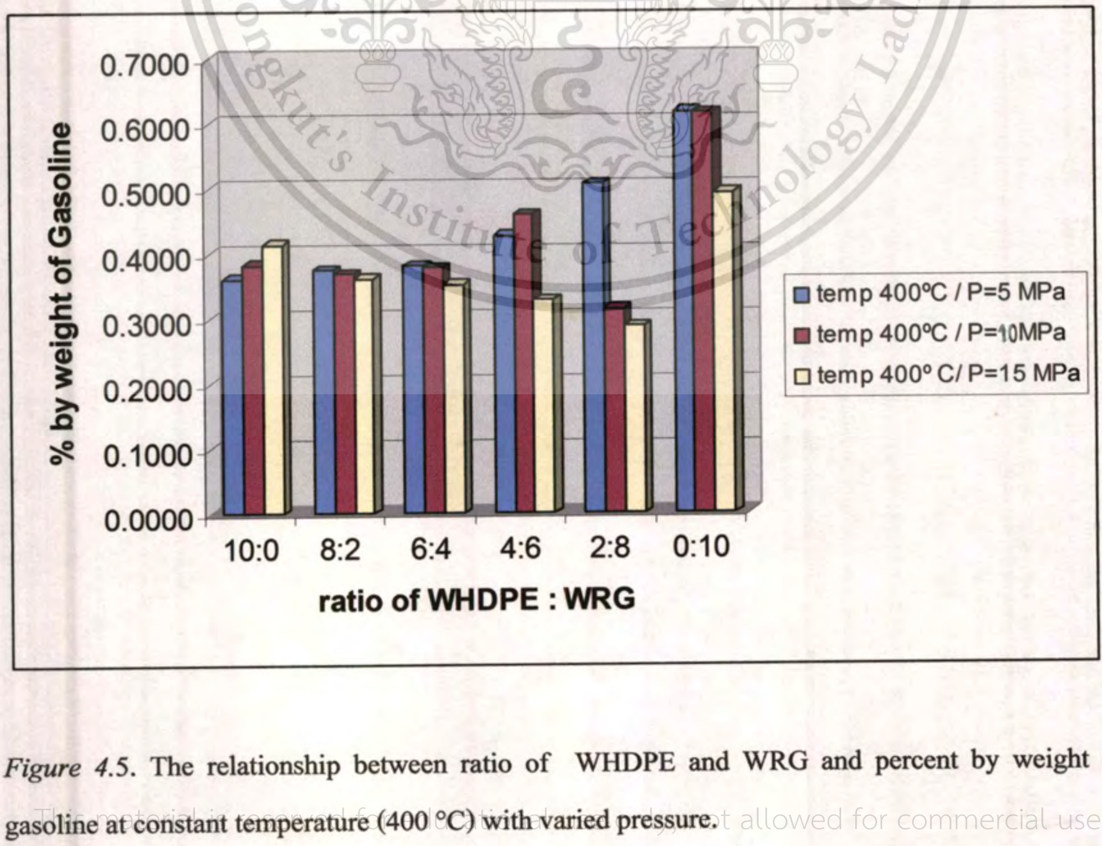


Figure 4.5. The relationship between ratio of WHDPE and WRG and percent by weight of gasoline at constant temperature (400 °C) with varied pressure.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

The study of liquefaction of WHDPE and WRG by using supercritical toluene as solvent, temperature of 400 and 450 °C, pressure of 5,10 and 15 MPa and the ratio of WHDPE and WRG as 10:0, 8:2, 6:4, 4:6, 2:8 and 0:10, it was found that:

1. The most effect to the percentage of liquid conversion was temperature and pressure.
2. Considering for percentage of liquid conversion, the quantity of toluene was slightly effect to the products.
3. The conditions effected to quality of hydrocarbon compound were temperature and pressure.
4. The conditions effected to chemical structure of hydrocarbon compound was temperature, pressure and ratio of WHDPE.
5. The appropriate conditions of co-liquefaction of WHDPE and WRG was at WHDPE 2 g and WRG 8 g.

The resulte were concluded as follow :

- Quantity of percentage by weight of liquid

Temperature	400 °C
Pressure	5 MPa
Ratio between WHDPE and WRG	2:8 g
Percentage by weight of liquid	77.91 %

- Quality of percentage by weight of liquid (gasoline)

Temperature	400 °C
Pressure	5 MPa
Ratio between WHDPE and WRG	2:8 g
Percentage by weight of liquid	50.66%

Recommendations:

1. For batch reactor, it should to install with insulator because it is important to control the accuracy temperature, no heat loss transfer to environment.
2. The percentage of gas conversion in this experimental was not accurate 100 % because percent of gas conversion got from calculation. Therefore installation of gas container measurement is so important to evaluate the percent of gas.
3. Analysis of gas molecules which release from valve (volatile molecule) are recommended for data analysis.
4. Use the varieties of waste polymers or waste plastics in the co-liquefaction process, because they give out the varieties of carbon compound.
5. The gas chromatography of hydrocarbon compound indicating that there are amount of heavy hydrocarbon compound (low quality). Therefore thermal cracking to be light hydrocarbon compound (high quality) was possibly by using of distillation unit.

Reference :

1. Weibing, D., Jing L. and Anderson, L.L. Catalysis and Frocesses for Heavy Oil Conversion. *International Symposium on Advances in Catalysis and Processes for Heavy Oil Conversion*, (1997) : 428- 432.
2. Feng, Z., Zhao, J., Bailey, D. and Huffman, G. Direct Liquefaction of Waste Plastic and Co-liquefaction of Coal-plastic Mixtures. *Fuel Processing Technology* 49 (1996) : 17.
3. Taghlei, M.M., Feng, Z., Huggins, F.E. and Huffman, G.P. *Energy and fuel* 8 (1994) : 1228-1232.
4. Huffman, G.P., Feng, Z., Huggins, F.E. and Mahajan, V. Direct Liquefaction of Waste Plastics and Co-liquefaction of Wasted plastics with coal.*Int Conf Coal Science.* (1995) : 1519-1522.
5. Tuntawiroon, W., Anderson, L.L. and Ding, W.B. Coal Liquefaction of Coal and Waste Plastics. *Int Conf Coal Sci* .(1995) : 1515-1518.
6. Shishido, M., Mashiko, T., Adschiri, T. and Arai, K. The Gasification *Reactivity of Residual Coal Chars from Supercritical Fluid Extraction of Coal.* Fuel 70 (1991) : 539.
7. Ding, W.B., Tuntawiroon, W., Liang, J. and Anderson, L.L. Reaction *Egineering in Direct Coal Liquefaction* (Hydrogenation- Hydrocracking Science and Technology no.3). Candana : Addision- Wesley Publishing Co.,Inc., 1981.
8. ฤทัย ลีสุขสันต์. เชื้อเพลิงเหลวที่ได้จากพอลิเอทิลีนที่ใช้แล้ว. วิทยานิพนธ์ปริญญามหาบัณฑิต สาขาวิชาปิโตรเคมีและ วิทยาศาสตร์พอลิเมอร์ คณะ วิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย,2543.
9. วันนิภา อมาตยกุล. เชื้อเพลิงเหลวที่ได้จากยางธรรมชาติผสมกับถ่านหินโดยใช้คาร์บอนไดออกไซด์ภาวะเหนือวิกฤต. วิทยานิพนธ์ปริญญามหาบัณฑิต สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย, 2540.

10. สาริช แสงกรณ์. กระบวนการร่วมของถ่านหินในการผลิตเชื้อเพลิงเหลว. วิทยานิพนธ์ปริญญามหาบัณฑิต. ภาควิชา เคมีเทคนิค คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย,2543.

11. Ying-anong Arthasart, *Influence of reprocessing on the properties of High Density Polyethylene*, Thesis of Chulalongkron University (2000).

12. Aziz A. bin Kadir S. A., *Rubb. Chem. Technol.* 67, 537 (1994).

13. Subramaniam A. in Aziz A. bin Kodir S. A. Kodir, ed.,*Proceedings of International Rubber Technology Conference,Kuala Lumpur,* Rubber Research Institute of Malaysia (RRIM), p. 19.1993

14. Baker C. S. L., *Vulcanization with Urethane Reagents*, NR Technical Bulletin,Malaysian Rubber Producers' Research Association, Brickendonberry, U.K., 1978.

15. Apichart Siripochanawan, Somkiat Ngamprasertsith, and Pattarapan Prasassarakich, *Co-liquefaction of Coal and Polypropylene in Supercritical Solvent,* Department of Chemical Technology, Faculty of Science, Chulalongkron University (2003)

16. Nowacki, P. *Liquefaction Process*. New York : 1979.

17. Smith J.M., Van Ness H.C. , Abbott M.M., *Introduction to Chemical Engineering Thermodynamics,* The McGraw-Hill Companies, Inc., New York, p. 308-311.

18. Lugue de Castro, M.D., Valcarcel M. and Tena M.T. *Analytical Supercritical Fluid Extraction.* Germany : Springer-Vertag Berlin Heidelberg, 1994.

19. Akgerman, A., Roop R.K., Hess R.K., and Yeo S.D., Supercritical extraction in environmental control, in: *T.J. Bruno,J.F. Ely (Eds) Supercritica lFluid Technology: Review in ModernTheory and Applications*, CRC Press, Bocca Raton, FL, chap.14 (1991).

20. ดร. ปราโมทย์ ไชยเวช และ ดร. นุรักษ์ กฤษดานุรักษ์ *ปิโตรเลียมเทคโนโลยี*, ภาควิชา เคมีเทคนิค คณะ วิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย พิมพ์ครั้งที่1, 2543.

APPENDIX A

The RF values of carbon composition for calculation of quantity and quality of hydrocarbon compound normalization.

Standard compound

Peak no.	Peak name	Area	% by weight	RF
1		163389		
2	C_6	481745	6	1.24547E-05
3	C_7	561184	6	1.06917E-05
4	C_8	821212	8	9.7417E-06
5	C_9	870308	8	9.19215E-06
6	C_{10}	1349750	12	8.89054E-06
7	C_{11}	1381050	12	8.68904E-06
8	C_{12}	1389205	12	8.63803E-06
9	C_{14}	1304400	12	9.19963E-06
10	C_{16}	1050145	10	9.52249E-06
11	C_{18}	518221	5	9.64839E-06
12	C_{20}	201397	2	9.93063E-06
13	C_{24}	194098	2	1.03041E-05
14	C_{28}	91636	1	1.09127E-05
15	C_{32}	84451	1	1.18412E-05
16	C_{36}	76752	1	1.3029E-05
17	C_{44}	70100	1	1.42653E-05

APPENDIX B

Table from calculation, the percentage of composition of carbon atom.

At temperature 450 °C

WRG and WHDPE (0:10)

Name	Area in sample	Area x RF	$\frac{\text{area x RF x 100}}{\text{total area x RF}}$
C_6	233435	2.907	5.560
C_7	290710	3.108	5.944
C_8	948007	9.235	17.664
C_9	750706	6.900	13.198
C_{10}	699110	6.215	11.888
C_{11}	785344	6.823	13.051
C_{12}	117526	1.015	1.941
C_{14}	619028	5.694	10.892
C_{16}	101087	0.962	1.841
C_{18}	320456	3.091	5.913
C_{20}	284410	2.824	5.402
C_{24}	122870	1.266	2.421
C_{28}	128140	1.398	2.674
C_{32}	70809	0.838	1.603
	TOTAL	52.282	100

WRG and WHDPE (2:8)

Name	Area in sample	Area x RF	area x RF x 100 total area x RF
C_6	179896	2.240	16.134
C_7	75300	0.805	5.797
C_8	71416	0.695	5.009
C_9	117938	1.084	7.806
C_{10}	459600	4.086	29.424
C_{11}	72036	0.625	4.507
C_{12}	80912	0.698	5.032
C_{14}	241263	2.219	15.982
C_{16}	76191	0.725	5.224
C_{18}	73109	0.705	5.079
	TOTAL	13.886	100

WRG and WHDPE (4:6)

Name	Area in sample	Area x RF	area x RF x 100 total area x RF
C_6	192885	2.402	3.996
C_7	259761	2.777	4.620
C_8	1056823	10.295	17.127
C_9	843943	7.757	12.905
C_{10}	756100	6.722	11.183
C_{11}	172882	1.502	2.499
C_{12}	842070	7.273	12.101
C_{14}	919441	8.458	14.071
C_{16}	389412	3.7081	6.169
C_{18}	322098	3.107	5.170

C_{20}	282260	2.803	4.663
C_{24}	122735	1.264	2.103
C_{28}	110421	1.204	2.004
C_{32}	70215	0.831	1.383
	TOTAL	60.109	100

WRG and WHDPE (6:4)

Name	Area in sample	Area x RF	$\frac{\text{area x RF x 100}}{\text{total area x RF}}$
C_6	579309	7.215	24.995
C_7	190192	2.0334	7.044
C_8	467479	4.554	15.776
C_9	228503	2.100	7.276
C_{10}	228837	2.034	7.048
C_{11}	247211	2.148	7.441
C_{12}	161269	1.393	4.825
C_{14}	346026	3.183	11.027
C_{16}	181855	1.731	5.999
C_{18}	133887	1.291	4.475
C_{20}	118864	1.180	4.089
	TOTAL	28.865	100

WRG and WHDPE (8:2)

Name	Area in sample	Area x RF	$\frac{\text{area x RF x 100}}{\text{total area x RF}}$
C_6	516374	6.431	19.245
C_7	158552	1.695	5.072
C_8	481155	4.687	14.026

C_9	341580	3.139	9.396
C_{10}	295613	2.628	7.864
C_{11}	231408	2.010	6.017
C_{12}	239836	2.071	6.199
C_{14}	440129	4.049	12.116
C_{16}	241177	2.296	6.872
C_{18}	202817	1.956	5.855
C_{20}	173421	1.722	5.153
C_{24}	70635	0.727	2.178
	TOTAL	33.416	100

At temperature 400 °C

WRG and WHDPE (0:10)

Name	Area in sample	Area x RF	area x RF x 100 total area x RF
C_6	129993	1.619	3.894
C_7	145692	1.557	3.746
C_8	516291	5.029	12.098
C_9	434699	3.995	9.611
C_{10}	444274	3.949	9.500
C_{11}	85357	0.741	1.784
C_{12}	445346	3.846	9.253
C_{14}	468325	4.308	10.363
C_{16}	349541	3.328	8.006
C_{18}	331941	3.202	7.703
C_{20}	300398	2.983	7.175
C_{24}	182223	1.877	4.516
C_{28}	213404	2.328	5.601

C_{32}	148658	1.760	4.234
C_{36}	119997	1.563	3.760
C_{40}	76679	1.098	2.642
	TOTAL	43.192	100

WRG and WHDPE (2:8)

Name	Area in sample	Area x RF	area x RF x 100 total area x RF
C_6	88313	1.099	2.961
C_7	110958	1.186	3.194
C_8	471250	4.590	12.362
C_9	374134	3.439	9.261
C_{10}	373595	3.321	8.944
C_{11}	212330	1.844	4.968
C_{12}	317912	2.746	7.395
C_{14}	514351	4.731	12.742
C_{16}	334250	3.182	8.571
C_{18}	324557	3.131	8.432
C_{20}	268717	2.668	7.186
C_{24}	143272	1.476	3.975
C_{28}	135912	1.483	3.994
C_{32}	100281	1.187	3.197
C_{36}	80166	1.044	2.812
	TOTAL	37.134	100

WRG and WHDPE (4:6)

Name	Area in sample	Area x RF	$\frac{\text{area x RF x 100}}{\text{total area x RF}}$
C_6	130925	1.530	4.148
C_7	134336	1.436	3.654
C_8	405602	3.951	10.053
C_9	366332	3.367	8.567
C_{10}	404352	3.594	9.146
C_{11}	317233	2.756	7.013
C_{12}	303551	2.622	6.671
C_{14}	756748	6.961	17.713
C_{16}	417441	3.975	10.113
C_{18}	442674	4.271	10.867
C_{20}	278040	2.761	7.025
C_{24}	100461	1.035	2.633
C_{28}	86113	0.939	2.390
	TOTAL	39.302	100

WRG and WHDPE (6:4)

Name	Area in sample	Area x RF	$\frac{\text{area x RF x 100}}{\text{total area x RF}}$
C_6	89816	1.118	4.322
C_7	101200	1.081	4.183
C_8	186699	1.818	7.032
C_9	257409	2.366	9.148
C_{10}	329237	2.927	11.317
C_{11}	211540	1.838	7.107

C_{12}	126849	1.095	4.236
C_{14}	906022	8.335	32.228
C_{16}	182871	1.741	6.733
C_{18}	80213	0.773	2.992
C_{20}	205864	2.044	7.904
C_{24}	70021	0.721	2.789
	TOTAL	25.862	100

WRG and WHDPE (8:2)

Name	Area in sample	Area x RF	area x RF x 100 total area x RF
C_6	129470	1.612	4.234
C_7	138401	1.479	3.885
C_8	457335	4.455	11.698
C_9	365547	3.360	8.823
C_{10}	367594	3.268	8.581
C_{11}	90865	0.789	2.073
C_{12}	366083	3.162	8.303
C_{14}	423340	3.894	10.226
C_{16}	308556	2.938	7.715
C_{18}	279642	2.698	7.084
C_{20}	253455	2.516	6.609
C_{24}	150005	1.545	4.058
C_{28}	137853	1.504	3.950
C_{32}	133292	1.578	4.144
C_{36}	126689	1.650	4.334
C_{40}	113658	1.628	4.276
	TOTAL	38.082	100

WRG and WHDPE (10:0)

Name	Area in sample	Area x RF	area x RF x 100 total area x RF
C_6	109614	1.365	3.243
C_7	132274	1.414	3.360
C_8	492338	4.796	11.395
C_9	394145	3.623	8.607
C_{10}	424336	3.772	8.963
C_{11}	142033	1.234	2.932
C_{12}	364192	3.145	7.474
C_{14}	508716	4.68	11.119
C_{16}	322585	3.071	7.298
C_{18}	300415	2.898	6.886
C_{20}	270573	2.686	6.383
C_{24}	157947	1.627	3.866
C_{28}	144004	1.571	3.733
C_{32}	145639	1.724	4.097
C_{36}	135502	1.765	4.194
C_{40}	117828	1.688	4.011
C_{44}	71745	1.023	2.431
	TOTAL	42.089	100

APPENDIX C

The whole data of volume toluene.

temp 450°C / P=5 MPa

HDPE:Rubber	vol.toluene(ml)	weight toluene(g)	total weight(g)	weight product(g)	% liquid	% gas
10:0	8	6.896	16.896	12.704	75.19	24.81
8:2	8	6.896	16.896	10.601	62.74	37.26
6:4	8	6.896	16.896	10.921	64.64	35.36
4:6	8	6.896	16.896	10.785	63.83	36.17
2:8	8	6.896	16.896	11.671	69.08	30.92
0:10	8	6.896	16.896	5.101	30.19	69.81

temp 450°C / P=10 MPa

HDPE:Rubber	vol.toluene(ml)	weight toluene(g)	total weight(g)	weight product(g)	% liquid	% gas
10:0	19.0	16.378	26.378	16.105	61.05	38.95
8:2	18.0	15.516	25.516	14.713	57.66	42.34
6:4	23.0	19.826	29.826	10.761	36.08	63.92
4:6	18.5	15.947	25.947	12.778	49.25	50.75
2:8	18.5	15.947	25.947	16.889	65.09	34.91
0:10	18.0	15.516	25.516	10.171	39.86	60.14

temp 450°C / P=15 MPa

HDPE:Rubber	vol.toluene(ml)	weight toluene(g)	total weight(g)	weight product(g)	% liquid	% gas
10:0	28	24.136	34.136	10.430	30.55	69.45
8:2	26	22.412	32.412	14.370	44.34	55.66
6:4	24	20.688	30.688	5.660	18.44	81.56
4:6	21	18.102	28.102	16.460	58.57	41.43
2:8	22	18.964	28.964	19.850	68.53	31.47
0:10	22	18.964	28.964	12.120	41.85	58.15

temp 400°C / P=5 MPa

HDPE:Rubber	vol.toluene(ml)	weight toluene(g)	total weight(g)	weight product(g)	% liquid	% gas
10:0	21.0	18.102	28.102	15.403	54.81	45.19
8:2	19.0	16.378	26.378	19.900	75.44	24.56
6:4	18.0	15.516	25.516	20.423	80.04	19.96
4:6	18.0	15.516	25.516	19.280	75.56	24.44
2:8	11.0	9.482	19.482	15.750	80.84	19.16
0:10	10.0	8.620	18.620	13.840	74.33	25.67

temp 400°C / P=10

MPa

HDPE:Rubber	vol.toluene(ml)	weight toluene(g)	total weight(g)	weight product(g)	% liquid	% gas
10:0	23	19.826	29.826	23.430	78.56	21.44
8:2	22	18.964	28.964	17.260	59.59	40.41
6:4	21	18.102	28.102	17.250	61.38	38.62
4:6	20	17.240	27.240	15.610	57.31	42.69
2:8	19	16.378	26.378	13.810	52.35	47.65
0:10	18	15.516	25.516	15.370	60.24	39.76

temp 400°C / P=15

MPa

HDPE:Rubber	vol.toluene(ml)	weight toluene(g)	total weight(g)	weight product(g)	% liquid	% gas
10:0	30	25.860	35.860	14.900	41.55	58.45
8:2	30	25.860	35.860	20.528	57.24	42.76
6:4	29	24.998	34.998	20.499	58.57	41.43
4:6	29	24.998	34.998	16.610	47.46	52.54
2:8	29	24.998	34.998	21.630	61.80	38.20
0:10	27	23.274	33.274	24.710	74.26	25.74

APPENDIX D

The sample graph of gas chromatography analysis.

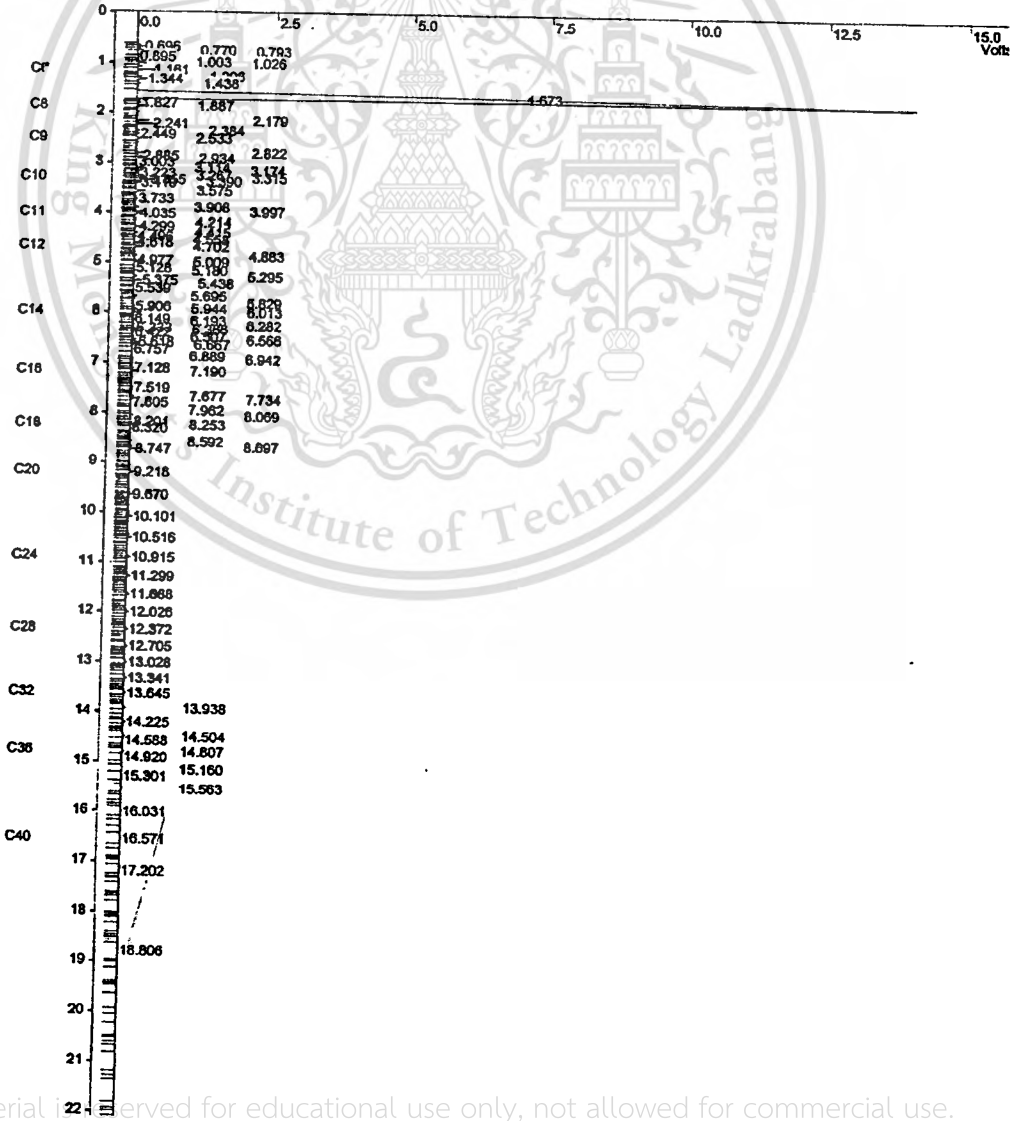
```
Title       :
Run File    : c:\star\simultated distallation\ratchnee\papaphan\hdpe24.run
Method File : c:\docume~1\admini~1\locals~1\temp\~2887(rubber).tmp
Sample ID   : hdpe24

Injection Date: 6/5/2547 16:25     Calculation Date: 6/5/2547 17:01

Operator    : ratchnee              Detector Type: 3800 (1 Volt)
Workstation: Chem Tech              Bus Address  : 44
Instrument  : Varian Star #1        Sample Rate  : 10.00 Hz
Channel     : Front = FID           Run Time     : 22.987 min

** Star Chromatography Workstation Version 6.00 ** 02802-64d0-c65-00b0 **

Chart Speed =    0.95 cm/min    Attenuation = 1019          Zero Offset = 166%
Start Time  =   0.000   min      End Time     = 22.987  min    Min / Tick  = 1.00
```



```
'rint Date: Thu May 06 17:04:13 2004                       Page 1 of 2
itle          :
.un File      : c:\star\simultated distallation\ratchnee\papaphan\hdp
:ethod File   : c:\docume~1\admini~1\locals~1\temp\~2887(rubber).tmp
ample ID      : hdpe24

njection Date: 6/5/2547 16:25       Calculation Date: 6/5/2547 17:01

perator    : ratchnee                 Detector Type: 3800 (1 Volt)
orkstation: Chem Tech                 Bus Address   : 44
nstrument : Varian Star #1            Sample Rate   : 10.00 Hz
hannel     : Front = FID              Run Time      : 22.987 min

* Star Chromatography Workstation Version 6.00 ** 02802-64d0-c65-0

un Mode             : Analysis
eak Measurement: Peak Area
alculation Type: Percent

                                  Ret.     Time                          Widt
Peak      Peak        Result      Time    Offset      Area       Sep.     1/
 No.      Name          ()        (min)    (min)     (counts)    Code   (sec
---- ------------ ----------  ------- -------  ----------    ----   ----
  1                 0.5915    0.696    0.000      140564      VV     1.
  2                 0.7169    0.770    0.000      170378      VV     1.
  3                 1.5216    0.793    0.000      361624      VV     0.
  4                 0.3860    0.895    0.000       91732      VV     4.
  5                 0.4238    1.003    0.000      100707      VV     0.
  6                 0.7597    1.026    0.000      180549      VV     0.
  7 C6              1.3802    1.161    0.060      328005      VV     0.
  8                 0.3988    1.296    0.000       94772      VV     1.
  9                 0.9852    1.344    0.000      234144      VV     1.
 10 C7              0.3330    1.438   -0.000       79143      VV     1.
 11                39.6879    1.673    0.000     9432045      VV     9.
 12                 0.3256    1.827    0.000       77371      TF     0.
 13 C8              0.9937    1.887    0.010      236151      TF     0.
 14                 0.7163    2.179    0.000      170229      TF     0.
 15                 2.0021    2.241    0.000      475799      VV     0.
 16                 0.3451    2.384    0.000       82017      VV     1.
 17                 0.2989    2.449    0.000       71031      VV     0.
 18 C9              0.9855    2.533   -0.016      234212      VV     0.
 19                 0.9339    2.822    0.000      221954      VV     0.
 20                 1.0165    2.885    0.000      241587      VV     2.
 21                 0.6938    2.934    0.000      164875      VV     1.
 22                 0.3670    3.003    0.000       87221      VV     1.
 23                 0.9369    3.114    0.000      222654      VV     1.
 24                 0.6633    3.174    0.000      157632      VV     1.
 25                 0.4529    3.223    0.000      107643      VV     1.
 26                 1.0073    3.267    0.000      239395      VV     1.
 27 C10             1.0610    3.315    0.022      252154      VV     1.
 28                 1.5964    3.355    0.000      379403      VV     1.
 29                 0.4786    3.390    0.000      113745      VV     0.
 30                 0.5425    3.418    0.000      128924      VV     0.
 31                 1.1316    3.575    0.000      268939      VV     1.
 32                 0.3556    3.733    0.000       84510      VV     1.
 33                 0.4129    3.908    0.000       98137      VV     1.
 34                 0.8341    3.997    0.000      198224      VV     1.
 35 C11             0.7379    4.035    0.004      175358      VV     1.
 36                 0.2965    4.214    0.000       70469      VV     2.
 37                 0.5038    4.299    0.000      119726      VV     1.
 38                 0.3438    4.415    0.000       81708      VV     1.
 39                 0.2946    4.496    0.000       70012      VV     1.
 40                 0.3061    4.558    0.000       72748      VV     0.
 41                 0.4586    4.618    0.000      108977      VV     1.
 42 C12             0.8223    4.702   -0.040      195433      VV     1.
 43                 0.3292    4.883    0.000       78236      VV     1.
 44                 0.3162    4.977    0.000       75138      VV     1.
 45                 0.5997    5.009    0.000      142526      VV     1.
 46                 0.3669    5.128    0.000       87203      VV     0.
 47                 0.3439    5.180    0.000       81733      VV     1.
 48                 0.7265    5.295   -0.000      172647      VV     2.
 49                 0.8081    5.375    0.000      192040      VV     1.
 50                 0.3955    5.438    0.000       93995      VV     0.
 51                 0.3565    5.539    0.000       84731      VV     1.
 52                 0.6459    5.695    0.000      153494      VV     0.
 53                 0.3017    5.829    0.000       71709      VV     0.
 54                 0.4601    5.906    0.000      109355      VV     0.
 55                 0.5095    5.944    0.000      121091      VV     1.
 56 C14             1.2952    6.013   -0.042      307809      VV     1.
 57                 0.2994    6.149    0.000       71151      VV     0.
 58                 0.3458    6.193    0.000       82181      VV     0.
```

```
Print Date: Thu May 06 17:04:13 2004                    Page 2 of 2
   72                      0.3231    7.519   0.000     76792   VV   2.0
   73                      0.4799    7.677   0.000    114052   VV   2.0
   74                      0.8280    7.734   0.000    196780   VV   1.1
   75                      0.3180    7.805   0.000     75585   VV   0.0
   76                      0.3582    7.962   0.000     85131   VV   0.0
   77                      0.3018    8.069   0.000     71731   VV   1.4
   78                      0.4267    8.201   0.000    101405   VV   1.7
   79  C18                 0.7274    8.253  -0.025    172878   VV   1.1
   80                      0.4360    8.320   0.000    103615   VV   0.0
   81                      0.3029    8.592   0.000     71995   VV   1.7
   82                      0.3304    8.697   0.000     78511   VV   1.9
   83                      0.7236    8.747   0.000    171966   VV   1.1
   84  C20                 0.6554    9.218  -0.013    155766   VV   1.1
   85                      0.4720    9.670   0.000    112175   VV   1.1
   86                      0.4416   10.101   0.000    104939   VV   1.1
   87                      0.4139   10.516   0.000     98358   VV   1.1
   88  C24                 0.3714   10.915  -0.017     88260   VV   1.1
   89                      0.3334   11.299   0.000     79225   VV   1.1
   90                      0.4023   11.668   0.000     95597   VV   1.3
   91                      0.3690   12.026   0.000     87701   VV   1.2
   92  C28                 0.3945   12.372  -0.008     93751   VV   1.4
   93                      0.4472   12.705   0.000    106268   VV   1.3
   94                      0.4262   13.028   0.000    101280   VV   1.3
   95                      0.4268   13.341   0.000    101432   VV   2.3
   96  C32                 0.4100   13.645  -0.010     97445   VV   2.2
   97                      0.4215   13.938   0.000    100183   VV   2.2
   98                      0.3848   14.225   0.000     91443   VV   2.1
   99                      0.5794   14.504   0.000    137692   VV   2.4
  100                      0.3771   14.588   0.000     89617   VV   0.0
  101  C36                 0.4185   14.807  -0.012     99468   VV   2.9
  102                      0.3638   14.920   0.000     86454   VV   0.0
  103                      0.4139   15.160   0.000     98377   VV   3.6
  104                      0.3689   15.301   0.000     87679   VV   0.0
  105                      0.4212   15.563   0.000    100107   VV   5.0
  106                      0.4099   16.031   0.000     97422   VV   8.1
  107  C40                 0.4139   16.571  -0.015     98366   VV  25.5
  108                      0.3042   17.202   0.000     72285   VV   0.0
  109                      0.3684   18.806   0.000     87541   VV   0.0
 ---- ------------- ========== -------- ======== ========== ---- -----  ------
      Totals:            100.0004          -0.141  23765564

Total Unidentified Counts :    20977094 counts

Detected Peaks: 371         Rejected Peaks: 262     Identified Peaks: 16

Multiplier: 1           Divisor: 1          Unidentified Peak Factor: 0

Baseline Offset: -54 microVolts          LSB:    1 microVolts

Noise (used): 38 microVolts - monitored before this run

Vial: 15      Injection Number: 1     Volume: 1.0  uL      Position: 1

Data Handling: All Coefficients for All Peaks are Zero
Data Handling: Default to A%
****************************************************************************
```