

# Hydrogen Transfer Cracking of Arabian Vacuum Residuum in Tetralin

by

Aziz Muhammad Abu-Khalaf

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES  
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS  
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the  
Requirements for the Degree of

**MASTER OF SCIENCE**

In

**CHEMICAL ENGINEERING**

June, 1988

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**Hydrogen transfer cracking of Arabian vacuum residuum in  
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**King Fahd University of Petroleum and Minerals (Saudi Arabia), 1988**

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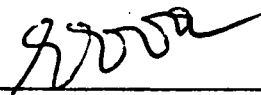
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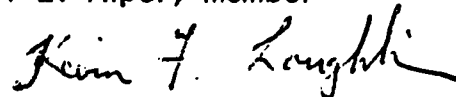
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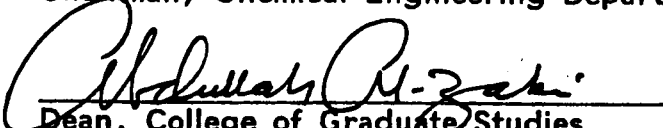
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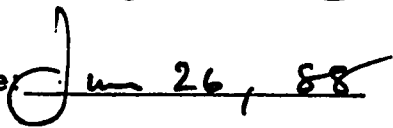
  
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وَقُلْ رَزَوْنِي عِلْمًا

## ACKNOWLEDGEMENT

Acknowledgement is due to King Fahd University of Petroleum and Minerals and King Abdul-Aziz City for Science and Technology for support of this research.

I wish to express my sincere appreciation to Dr. Abdallah Abdunnabi for reading the manuscript and the many valuable suggestions he offered.

The help of Professor E. Alper is gratefully acknowledged. He was responsible for and heavily involved in this part of research. He served as the actual advisor. Thanks also to Dr. D.K. Al-Harbi who served as an official advisor. I also wish to thank Dr. K.F. Loughlin for reading the manuscript, and Mr. A.N. Kosal from the Research Institute for helping in the analysis of some of the samples.

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## THESIS ABSTRACT

**Full Name : Aziz Muhammad Abu-khalaf**

**Title of Study : HYDROGEN TRANSFER CRACKING OF ARABIAN VACUUM RESIDUUM IN TETRALIN**

**Major Field : CHEMICAL ENGINEERING**

**Date of Degree : JUNE 1988**

Heavy Arabian residua were hydrocracked noncatalytically using tetralin as a hydrogen donor solvent. A bolted closure packless high temperature/high pressure autoclave with a magnedrive assembly was used batchwise for this purpose.

The effects of temperature, pressure and reactants ratio on the performance of the system were studied. The products were analysed both qualitatively and quantitatively. Methods of analysis included: hydrocarbon group analysis using an HPLC, simulated distillation using a GC, sulfur determination and API gravity, asphaltene and carbon residue determination according to ASTM standards.

Most of the experiments were performed on a prepared residuum boiling above 350°C. Two fractions were also employed for comparison; these are a commercial residuum boiling above 250°C, and a prepared heavy residuum boiling above 550°C.

Tetralin proved to be an effective donor for Arabian residua. HPLC and simulated distillation analysis showed that heavy compounds of the residuum were converted into lighter ones. When a ratio of tetralin to residuum less than 1/1 by weight was used coke formed in amounts proportional to tetralin. For ratios greater than 1/1 no coke formation was observed. A ratio of 2/1 was found to be a suitable ratio and was used in all runs.

It was found that a minimum initial pressure of nitrogen gas was sufficient to keep the reactants in the liquid state. Otherwise pressure had no effect on the conversion.

As the temperature was increased the conversion to lighter products increased. The relative percentage change of both asphaltenes and carbon residue increased with temperature. Degree of desulfurization also increased with temperature. It was found that higher conversions were achieved with heavier residua.

MASTER OF SCIENCE DEGREE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS

Dhahran, Saudi Arabia

JUNE 1988



## خلاصة الرسالة

أسم الطالب الكامل : عزيز محمد أبوخلف

عنوان الدراسة : هدرجة البقايا الفراغية للنفط العربي الثقيل بالتترالين .

التخصص : الهندسة الكيماوية .

تاريخ الشهادة : ذوالقعدة ١٤٠٨ هـ .

حزيران ١٩٨٨ م .

تم في هذا البحث هدرجة بقايا النفط العربي الثقيل باستخدام مادة التترالين كوسط مانح للهيدروجينات دونما استخدام للحواجز ، وذلك في مفاعل يعمل في درجة حرارة وضغط عاليين بتشغيل متقطع . كما درست تأثيرات كل من درجة الحرارة والضغط ونسب المواد المتفاعلة . وقد حلت النتائج كما وكيفا باستخدام طرق تحليلية عدة هي : طريقة تحليل المجموعات الهيدروكربونية ، وطريقة التقطير الممثل ، وطريقة تعيين المحتوى الكبريتي ، وطريقة ايجاد الوزن النوعي النفطي ( أي . بي . أي ) ، وطرق تعيين المحتوى الاسفلتيني والبقية المتفحمة حسب معايير أي . أس . تي . ام .

أجريت معظم التجارب على بقية نفطية محضرة مخبريا درجة غليانها فوق ٣٥٠ م . كما أستخدمت بقيتان أخريان من أجل المقارنة : الأولى تجارية تغلي فوق ٢٥٠ م ، والأخرى ثقيلة محضرة مخبريا تغلي فوق ٥٥٠ م .

أثبت هذا البحث أن مادة التترالين مانح فعال وملائم لبقايا النفط العربي ، حيث تبين بالتحليل الكيفي تحول المكونات الثقيلة في البقايا الى مكونات خفيفة بفعول الهدرجة . لقد لوحظ تكون الفحم الكربوني عندما كانت النسبة المستخدمة بين التترالين والبقية النفطية ١:١ ، ولم يتكون الفحم لما كانت النسبة أعلى من ١:١ ، ووجد أن النسبة ١:٢ ملائمة للعمل بها ، لذا فقد أستخدمت في كل التجارب .

تبين من هذا البحث أن حدا أدنى من الضغط الغازي لابد من توفره من أجل الحفاظ على المواد المتفاعلة في حالة السيولة ، وليس للضغط أي تأثير آخر على التحول الكيماوي . كما تبين أن التحول يزداد بارتفاع درجة الحرارة ، حيث لوحظ ارتفاع نسبة تحول كل من الاسفلتين والبقية المتفحمة مع زيادة درجة الحرارة . كما لوحظ أن درجة تحويل الكبريت نزا اذدادت بارتفاع درجة الحرارة ، وأن التحول في البقايا الثقيلة أعلى منه بالنسبة للبقايا الأخف منها .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

حزيران ١٩٨٨ م

## ***CHAPTER ONE***

### ***INTRODUCTION***

The merits and the advantages of using liquid petroleum products far exceeds that of other alternative resources. Although research in the petroleum alternatives development has been plentiful in the last decade, practically there is no satisfactory alternative to petroleum. Thus synthesizing transportation fuels or petrochemical feedstocks from coal, shale oil, and similar carbon-rich fossil sources is not economically feasible compared to petroleum refining.

Unfortunately petroleum resources are not inexhaustible, and light crudes, in specific, are claimed to be of limited future supply. Crudes themselves are becoming heavier due to biodegradation over usage of the lighter crudes and evaporation losses [53] . Thus refiners are faced with a large surplus of heavy crudes and also with heavy residua, also known as the bottom of the barrel, as a result of crude distilling and processing. This has challenged the petroleum industry to develop new technologies to be capable to handle these heavy oils, and to solve the technical problems arising from their processing, in particular the high yields of coke and the deposition of the metallic constituents, problems which can't be handled by conventional refining.

Vacuum residuum is the most intractable of all streams produced from crude oil. It is the major low value product in petroleum refining. Until recently, however, this created no serious embarrassment to refiners. Minor volumes were disposed of as road asphalt, and as feedstock for petroleum coke and partial oxidation. Disposal of the remainder as the major constituent of residual fuel oil generally posed no problem [1] .

Despite these facts residua make up a significant portion of crude oils. Residua of Arabian crudes represent more than 60% of the original crude. Over 55% of Arab Heavy oil is in the range  $370^{\circ}\text{C}^{+}$ , and over 43% of the Arab Light is in that range. Although residua are aromatic in nature, they still have a relatively high H/C ratio. Arabian residua, for example, have a ratio ranging from 1.3 to 1.7 [50,51,52] .

Buying petroleum and processing it is cheaper, easier, and economically more feasible than processing other resources. Liquid hydrocarbons are readily shipped, stored and kept for prolonged periods, characteristics which are not available in other resources. Residua might not last for a long time compared to shale oils, tar sands or coal but they can be used at least for the short term. However, they are cheaper and easier to process.

Upgrading of heavy crudes and residua is thus becoming an increasingly important subject. The reasons can be summarised as follows:

- (1) Light crudes are claimed to be of limited supply, and the discovery

of new resources will be expensive.

- (2) Heavy crudes and residua are readily available in large quantities with low prices compared to light crudes.
- (3) Other alternatives to produce transportation fuels are not economically feasible compared to petroleum resources.

Upgrading means converting nonvaluable materials into valuable products. Specifically it means here any process in which there is an increase in the hydrogen to carbon ratio with a simultaneous decrease in the specific gravity, the viscosity and the average molecular weight of the fraction to be upgraded. [12] . Two concepts are employed in the current upgrading conversion processes of heavy feedstocks: either by carbon rejection (e.g., coking) or hydrogen addition (e.g., hydroprocessing). Both of these steps aim at increasing the H/C ratio. Carbon rejection produces large quantities of refractory materials such as coke which then must be treated or disposed of because of the high percentage of sulfur and other impurities concentrated in it. This will, however, detract from the total amount of liquid product available. Hydrogenation on the other hand produces a larger quantity of relatively valuable liquid products and is more desirable than carbon rejection, if hydrogenation can be carried out at a reasonable cost. The final objective of any upgrading technique is to obtain premium products such as syncrude, petrochemical feedstocks, automotive fuel, and carbonaceous products with various industrial applications [37] .

This thesis is concerned with a hydrogenation upgrading route

involving reacting Arabian residua with a hydrogen donor solvent-tetralin. The function of the hydrogen donor solvent is to donate atomic hydrogen to the free radicals of the residuum thus converting it into lighter products. In that sense this process is a hydrogen addition route. It is, however, a mild, noncatalytic and highly selective process.

The objectives of this research can be summarised as follows:

- (1) Installation and operational control of the equipment.
- (2) Preparation and characterization of the residua.
- (3) Preliminary testing of the hydrocracking reaction between tetralin and the residuum.
- (4) Studying the effect of the following variables on the performance of the system:
  - (a) Temperature
  - (b) Pressure
  - (c) Ratio of reactants

The study of the kinetics of the system is not an objective of this project. There is no attempt to separate the finished products. The residua and their products are characterized and analysed in terms of the changes in sulfur and asphaltene contents and other hydrocarbon groups and properties.

The pertinent literature, including relevant terms, definitions and previous work are presented in chapter 2. The experimental setup and the procedure followed are described in chapter 3; while the analytical techniques are discussed in chapter 4. Finally the results and the

advantages of this process are discussed in chapter 5.

## **CHAPTER TWO**

### **LITERATURE SURVEY**

#### ***2.1 Characteristics and Properties of Heavy Oils and Residua***

Distillation is the primary means by which a crude oil is processed. Crude oil is fractionated first in the atmospheric unit resulting in a wide range of products such as light end, gasoline, kerosine, heavy oil and a bottom product known as atmospheric residuum. This residuum is further fractionated in a vacuum unit operated under a high vacuum (20 to 50 mm Hg). The bottom product of this vacuum operation is known as the vacuum residuum. Thus the crude oil residuum is the fraction remaining after the nondestructive distillation (atmospheric or vacuum) has removed the volatile materials [2]. The residual oils fall in the category usually called heavy oils. This term is often used in a general way to specify crudes low in API gravity and high in impurities. The definition of a heavy crude oil or a heavy fraction of an oil is arbitrary, although the second UNITAR Conference recommended specific definitions based on gravity and viscosity [53]. According to Speight [2], the term heavy oil is generally applied to a petroleum that has an API gravity less than 20° and usually, but not always, has a sulfur content higher than 2% by weight. For our convenience, a residuum is defined in terms of some of its physical and chemical

properties (e.g., API and sulfur content), the cut point or the boiling range and the conditions of preparation (atmospheric or vacuum).

Heavy crudes and residual oils can be compared to average crudes as oils with [32] :

- . Higher viscosity.
- . Higher sulfur, metal and asphaltene contents.
- . Higher average boiling point.
- . Lower H/C ratio.

Speight [2] discusses the chemical and physical tests used to characterize heavy oils and residua. Among the tests used are: sulfur content, density and specific gravity, viscosity, carbon residue, metal content, and distillation characteristics.

Sulfur content (ASTM D-1551) along with the API gravity (ASTM D-287, D-1298, D-941, D-1555) represent the two properties which have the greatest influence on the value of a heavy oil and residuum. Viscosity (ASTM D-445, D-88, D-2161, D-341, D-2270) is a most important fluid characteristic and indicates the relative mobility of various crude oils and their products. Carbon residue (ASTM D-189 for Conradson, D-524 for Ramsbottom) presents indications of the heaviness or more correctly the coke forming propensity of an oil or residuum. Metal content (ASTM D-482) of a feedstock is usually determined as the inorganic ash remaining after ignition and burning of the organic material. Individual metals may then be determined by subjecting the ash to a spectrographic analysis. Distillation characteristics (ASTM



D-86, D-216, D-285, D-477, D-2892) of a crude oil give an indication of the relative proportions of the various products present. For a residuum there will be little gain from an examination of the distillation characteristics, while an asphaltic crude oil might be able (according to the distillation characteristics) to produce some of the lower boiling petroleum products.

The chemical composition of a petroleum or its fractions cannot be determined exactly due to its extremely complex nature. Hydrocarbons are the major constituents and they are primarily paraffinic, naphthenic and aromatic groups (olefinic and acetylenic groups are very rare and can be neglected). Crude oils and its fractions contain appreciable amounts of organic nonhydrocarbon constituents, mainly sulfur-, nitrogen- and oxygen-containing compounds and in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension. These constituents appear throughout the entire boiling range of the crude oil but tend to concentrate mainly in the heavier fractions and in the non-volatile residua. Although their concentrations may be small, their influence is often extremely important.

Heavy oils and residua are difficult to characterize by ultimate analysis (elemental composition) insofar as the elemental composition varies only slightly (to a first approximation) over narrow limits no matter what the origin of the material: carbon:  $85 \pm 2$  %; hydrogen:  $12 \pm 2$  %; nitrogen:  $0.4 \pm .2$  %; oxygen:  $1.0 \pm .5$  %; sulfur:  $3.0 \pm 2.0$  %; nickel plus vanadium  $150 \pm 50$  ppm. The characteristics of heavy oils and

residua can be more conveniently defined in terms of four major fractions: (a) the saturates; (b) the aromatics; (c) the resins; and (d) the asphaltenes. The definition of any particular fraction is actually an operational aid [27] (Fig. 2.1).

The asphaltene fraction is particularly important because as proportions of this fraction in a crude oil increases, there is concomitant increase in thermal coke and a decrease in the relative rate of hydrodesulfurization. Asphaltene is defined as that fraction of an oil or a residuum which precipitates when an excess of a light hydrocarbon (e.g., n-pentane) is added to the sample. The asphaltene fraction is actually a solubility class [27]. It is now recognized that to ensure stable asphaltene yields from heavy oils it is necessary to employ: (a) >30 ml. hydrocarbon per gram feedstock; (b) pentane or heptane are the hydrocarbons of choice although volatility constraints and stability of asphaltene-type are tending to favor the use of n-heptane; (c) 8-16 hours contact time is preferable. To guarantee consistency of the asphaltene fraction, a reprecipitation sequence to remove any adsorbed resin-material is necessary. This involves dissolution of the asphaltenes in benzene or toluene (10 ml. per gram asphaltene) followed by the addition of the precipitant (50 ml. precipitant per ml. benzene or toluene) to the solution.

### *2.1.1 Properties of Arabian Heavy Crude and Residua*

Arabian Heavy is a relatively low gravity (28.3 degree API), high sulfur (2.8 wt%), paraffinic wax-containing crude oil. It comprises

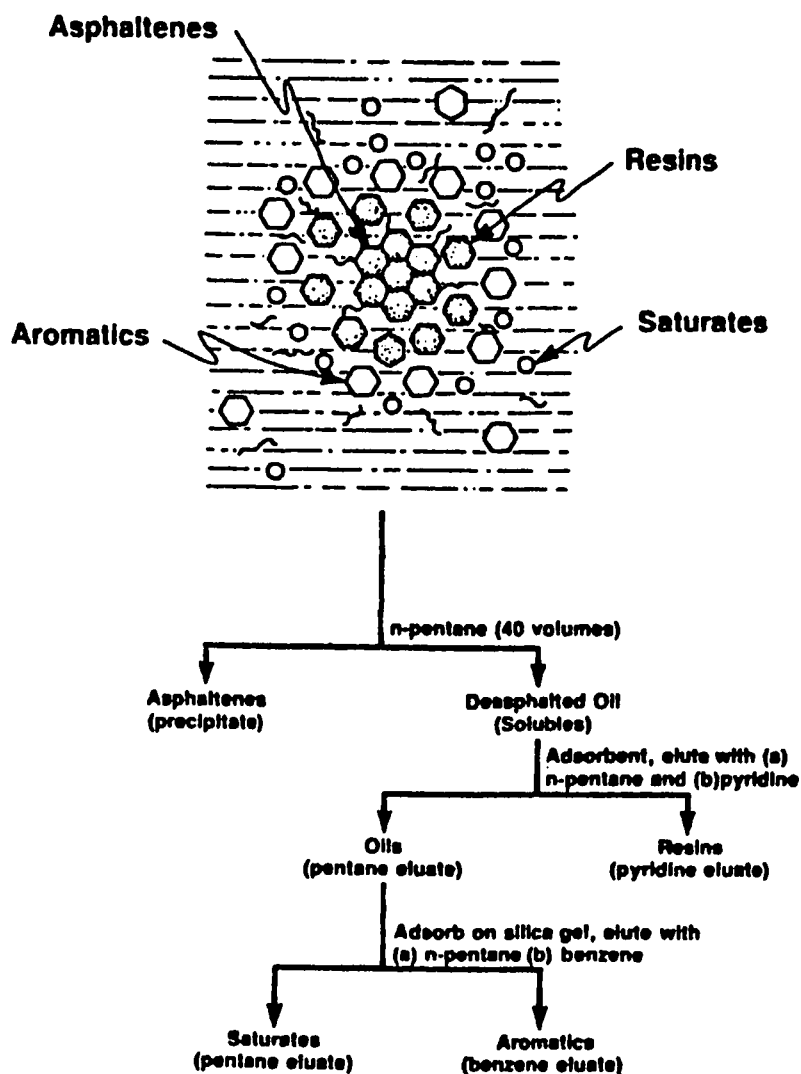


Figure 2.1 : Schematic Representation of the Different Fractions of Petroleum and a Simple Fractionation Sequence [27]

oil from an offshore field, Safaniya, located about 125 miles northwest of the exporting terminal Ras Tanura and known to be the world's largest offshore oil field.

Ali et.al [50,51,52] analysed vacuum distillates from four Arabian crude oils and identified their compositional differences. Arabian residua represent up to about 66% of the original crude, depending upon the nature of crude oil. Arab Heavy has a much higher percentage of materials in the heavy end fractions than others. Over 55% of the Arab Heavy oil is found in the 370°C+ residuum. Arab Light has 43% as a residuum fraction. It has been shown that the Arab Heavy residua have greater concentrations of carbon residue, sulfur and metals than others.

Arab Heavy crude oil residua have a lower H/C ratio than others. This ratio ranges from 1.55 for the fraction 370°C+ to 1.31 for the fraction 675°C+ of the Arab Heavy. The aromaticity of the Arab Heavy residua is relatively high and amounts to 33% of the total carbon. However, they contain short paraffinic chains. As much as 39% of the aromatic carbons appear as bridgehead carbons. Heavy Arabian residua consist mostly of polynuclear aromatic hydrocarbons polysubstituted by groups.

Schucher [41] provides a breakdown of the Arabian Heavy residuum in a recent paper. The typical residuum is composed of 23.9% asphaltenes, (Molecular Weight, MW- 7500), 60.3% polar aromatics (MW-1900), 10.4% aromatics (MW -900) and 5.4% saturates (MW-900). Of

particular interest is the H/C ratio being lowest for the asphaltenes at 1.15, and higher for the aromatics and saturates at 1.44, 1.68 and 1.94 respectively.

Delayed coking yields for Arabian Light, Arabian Heavy and Alaskan residua were reported recently [40], with striking differences in coke and oil yields for the Arabian Heavy when the residua were hydrodesulfurised before coking. These results show that after hydrodesulfurization the coke yield for Arabian Light bottom is reduced only 41% while that of the Arabian Heavy bottom is reduced by 73% and that the yield for the Arabian Heavy is only half that of the Arabian Light. Arabian Heavy is greatly different from other crudes and therefore has different processing characteristics. For example, a South American residuum contains >1000 ppm of nickel and vanadium; Iranian contains 525 ppm and a residuum from Boscan contains 1325 ppm. Arab Heavy residuum contains around 200 ppm of these metals. However, it is the highest in sulfur content.

## ***2.2 Upgrading Processes of Heavy Feedstocks***

The conversion of heavy oils and residua is, essentially, a new art, and is, of course, encountering problems arising as a result of a lack of processing knowledge of these feedstocks [27] .

Residua may be upgraded using either of two principles : hydrogen addition or carbon rejection, or a combination of both. Removal of carbon (coke) results in a lowering of the carbon/hydrogen ratio of the

product. Examples of this route include delayed coking , solvent deasphalting, partial oxidation and some of the newer catalyst processing technologies [2,28,29] .

The coke is essentially a reject stream that contains most of the impurities originally in the feedstock. Adding hydrogen to the feedstock molecules results in removing the impurities and reducing the tendency to produce coke. Examples of this route include residuum hydroprocessing with fixed or ebullating beds, hydrotreating, and reactive extraction using a hydrogen donor solvent. Commercial applications often necessitates combinations [30] . Examples are coking followed by hydrotreating, coking followed by hydrocracking, or desulfurization followed by either coking or solvent deasphalting. The ABC process developed by the Japanese consists of hydrocracking and deasphalting, with continuous recycle to the hydrocracker unit to eliminate the asphaltenes [31] .

The three most common processes for carbon rejection (i.e., coke formation, or coking ) are (a) visbreaking, (b) delayed coking and (c) fluid coking. Visbreaking has been used for many years to convert residua to more fluid materials, to meet the specifications for fuel oils. Delayed coking and fluid coking have recently become popular means of converting the heavier feedstocks to liquid fuels [3] .

Hydrocabon processes for petroleum oils may be classified as destructive and nondestructive [38] . In destructive hydrogenation (hydrocracking or hydrogenolysis) carbon-carbon bonds are cracked

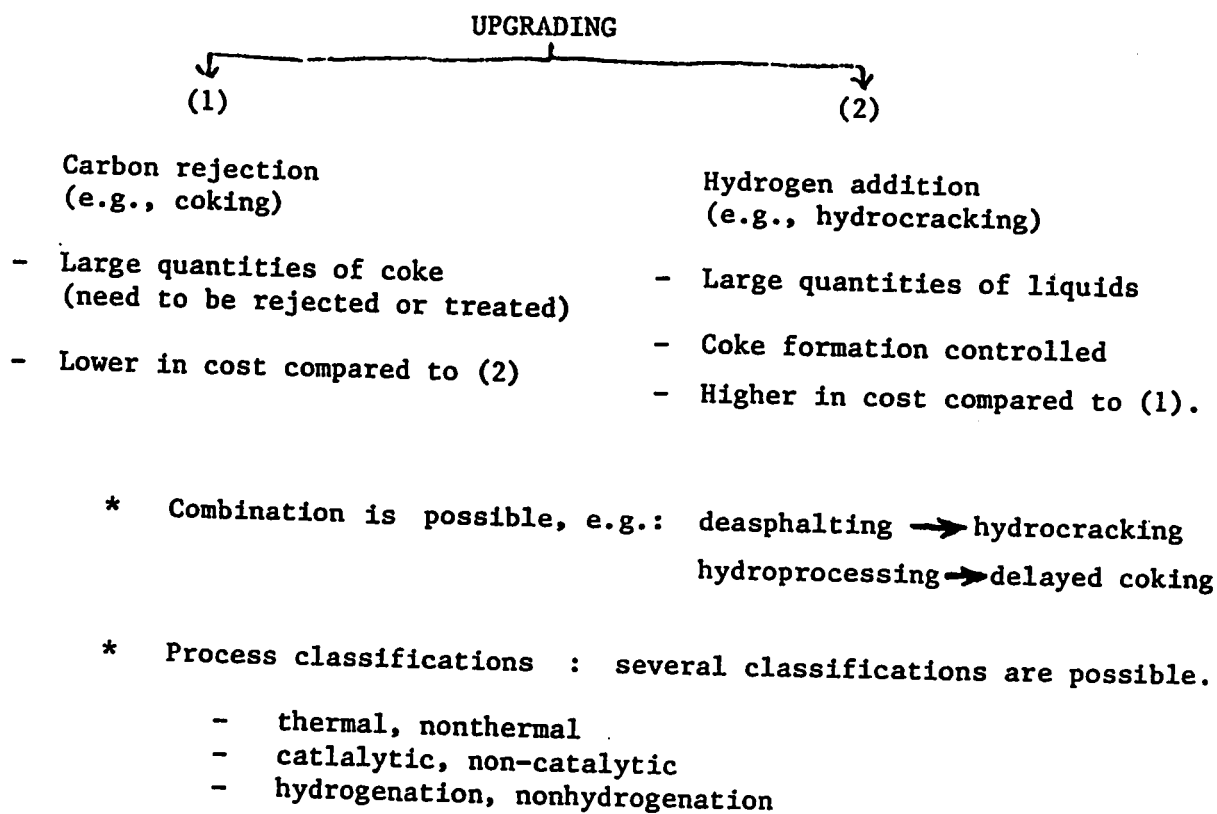
and the fragments saturated by hydrogen to produce lower boiling products. Severe processing conditions are employed; high hydrogen pressures are required to minimize polymerization and condensations leading to coke formation.

Essentially nondestructive hydrogenation or hydrotreating, is used to improve oil quality without appreciably altering boiling range. Milder processing conditions are employed so that only the more unstable materials are attracted, and production of lower boiling materials is minimized. Thus, bonds between carbon and such elements as sulfur and nitrogen are broken with the formation of hydrogen sulfide or ammonia; olefin bonds are saturated and unstable coke-formers are converted to more stable materials. A summary of the upgrading routes and process classification is presented in Table 2.1.

One process, first developed about 30 years ago, uses a donor solvent [6,7,12,23,24]. The process does not require the use of a catalyst or any hydrogen. A hydrogen donor solvent is used to prevent formation of reactive intermediates during the heat treatment (400-480°C) of heavy feedstocks. The donor solvent can be recovered as a hydrogenated solvent stream; rehydrogenation and recycle of the solvent are part of the process (see section 2.4.3).

Many summaries of the various upgrading processes have appeared in the literature [3,32,33,34,35,36,37]. Speight [3] discusses upgrading processes of both conventional and heavy feedstocks. The occurrence and properties of heavy oils and residua are reviewed along with the

**Table 2.1 : Upgrading routes and Process Classifications**



Hydrogenation

- Hydrocracking (destructive) - 430-470°C  
- 100-200 bar
- Hydrotreating (nondestructive) - 400-440°C  
- 50-250 bar  
- catalytic
- Donor Solvent (noncommercial, noncatalytic)
- Hydrovisbreaking (Under research) → H<sub>2</sub> gas  
→ Donor solvent
- Catalyst hydrogenation with hydrogen generated in situ.  
(e.g., by methanol decomposition).  
(Under research)

Nonhydrogenation

- Visbreaking (low cost, viscosity reduced) - 450-510°C  
- 5-20 bar
- delayed coking - 480-510°C  
- 7 bar
- fluid coking - 480-565°C  
- 1 bar
- Catalytic cracking (Catalyst deactivation) - 465-510°C  
- 10-16 psi
- Deasphalting - 40-80°C  
- 25-35 bar  
(ratio of solvent/feed = 5:1-13:1,  
solubility limitations)



current and future options for refining these materials. Hadley-Coates and Long [37] outline the problems associated with upgrading residual oil and present an overview of commercial processes currently available for this purpose. Four methods are discussed- two non-catalytic: thermal cracking and solvent extraction; and two catalytic methods: hydroprocessing and catalytic cracking. These form the basis of almost all present-day technologies.

Thermal cracking and solvent extraction are the oldest but still the most popular processes, although the latter is in a period of slight decline. Thermal cracking offers a very wide range of treatments, from simple viscosity reduction (visbreaking) to total gasification. Solvent extraction is principally a de-asphalting/demetallation process, although advances are being made by incorporating the latest supercritical technology. Catalytic cracking and hydroprocessing involve catalytic steps- metals management is identified as the most important operating criterion. Hydroprocessing is subdivided into low-metal (<200 ppm) and high metal (>200 ppm) technologies. Catalytic cracking is not yet capable of handling the most contaminated feedstocks directly.

### *2.3 Hydrogen Donor Materials*

Hydrogen donor materials are well known for their ability to release hydrogen to a hydrogen-deficient oil in a thermal cracking zone, and thereby to convert heavy hydrocarbon oils to more valuable lower-boiling products. The donor is aromatic-naphthenic in nature and, having released hydrogen in the thermal cracking zone, can be

catalytically rehydrogenated in a separate hydrogenation zone and recycled as a hydrogen donor. Hydrogen donor cracking processes make possible the conversion of heavy oils in the absence of a catalyst and with the formation of little, if any, coke, at substantially lower pressures than are necessary with the use of molecular hydrogen in hydrocracking [12] .

Paraffin and single-ring naphthenic compounds are ineffective hydrogen transfer agents; a condensed ring naphthenic compound such as decalin is somewhat effective; a mixed naphthenic-aromatic condensed-ring compound such as tetralin is much more effective [6] .

#### ***2.4 Tetralin***

Tetralin is the trade name for 1,2,3,4-Tetrahydronaphthalene [ $C_{10}H_{12}$ ] with a molecular weight of 132.2, a boiling point of 207°C, and a flash point of 75°C . It's specific gravity is 0.967 at 20°C [13] .

Tetralin is a condensed ring aromatic-naphthenic compound. It is a relatively expensive material derived from naphthalene by partial hydrogenation. It's ability to donate hydrogen is very well known. It has been used as a hydrogen donor solvent in heavy oils and residuum upgrading, in coal liquifaction and in wood liquifaction.

##### ***2.4.1 Tetralin in Coal and Wood Liquifaction***

Liquifaction, in general, refers to the thermal reactions experienced by coals at temperature usually above 400°C in suitable solvents. These

reactions produce a complex mixture of solubilized (liquified) and gasified products in high yield over short times intervals.

The noncatalytic pressure extraction (solvation, dissolution) of coal has been extensively studied since the early work of Pott and Broche [5] with a tetralin-phenol-naphthalene solvent. Pott and Broche were the first to use tetralin in the absence of hydrogen for thermal dissolution of coal up to about 825°F. The usefulness of a high boiling point, a hydroaromatic structure (e.g., tetralin), and polarity (e.g., a phenolic hydroxyl or an amine) in the solvent has been shown by the work of Orchin and Storch [14] and others [15]. Particularly elegant work on the comparative kinetics of coal pyrolysis, dissolution, and hydrogenation has been published by Hill, Wiser and co-workers [16,17]. It has been generally accepted that a hydroaromatic solvent donates hydrogen to coal during the extraction process, with resultant mild hydrogenolysis.

Yen et al. [15] studied the liquifaction and hydrosulfurization of a high Kentucky coal in batch autoclave experiments, with tetralin or methylnaphthalene as solvents and several Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalysts. They have shown that even though tetralin is an excellent hydrogen-donating solvent, the presence of gas phase hydrogen and of Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst plays a very important roles in the conversion of asphaltene to oil and in the extent of desulfurization.

Cassiday et al. [18] studied the role of hydrogen and hydrogen-

donor solvent in the liquifaction of brown coal without added catalyst and in the presence of iron- and tin-based catalysts. They have also examined model ethers and proposed a tentative mechanism.

In a recent article Kamiya and Nagao [19] studied the relative reactivity of hydrogen donor solvents in coal liquifaction. They have examined five hydrogen donor solvents, which are more reactive than tetralin, and established that 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydroquinoline exhibited outstanding hydrogen donating abilities. Kawai et al. [20] examined the hydrogen donating abilities of tetrahydroquinoline and tetrahydroisoquinoline, and found that they were more reactive than tetralin. A 1:3 ratio by weight mixture of tetrahydroquinoline and petroleum pitch was found to be a very effective donor.

In a recent study, Naaln [21] found that the presence of hydrogen and tetralin increased the liquifaction yields and the effects were additive. In an interesting study, Kershaw and Overbeek [22] investigated the supercritical fluid extraction of coal with hydrogen donor solvents.

Wood was directly liquified in the presence of a hydrogen donor solvent (tetralin) at 400°C and 10 MPa, with a high conversion into liquid and gaseous products [6]. Liquifaction is produced under hydrogen or nitrogen, with or without catalyst. This study shows that tetralin plays an important role in hydrogen transport for wood liquifaction process. This has been shown in terms of the ratio of

tetralin/naphthalene found in the liquid recovered after reaction from runs performed under hydrogen and nitrogen blankets. They suggested a free radical mechanism taking place in the liquid phase, in light of the fact that the hydrogen donor solvent is active in hydrogen transfer.

#### *2.4.2 Tetralin in Heavy Oil and Residua Upgrading*

According to Carlson et al. [6] D'Yakova and Malenteva used tetralin for thermal dissolution of coal, peat, and asphaltines. Greensfelder [7] treated crude residuum noncatalytically with tetralin and hydrogen in the first stage, followed by catalytic hydrogenation. These processes do not prevent contamination of the catalyst by the metals and resins in the residuum. Early investigation did not appreciate the ability of condensed ring naphthene-aromatics to donate large amounts of hydrogen readily in a manner which prevents coke formation. Use of tetralin diluent in thermal cracking of a high asphalt Hungarian crude oil greatly reduced coke formation compared with cracking in the absence of diluent [6] .

The use of tetralin as a hydrogen donor during thermal cracking of various residua, asphalts, and lubricating oil extract was investigated by Carlson et al. [6] to determine its general utility. Conversion ranged from 50 to 94% with very little coke and low dry gas yields. Feed stock examined included: Kuwait asphalt, Hawkins asphalt, McMurry tar, Elk Basin residuum, Coleville residuum, Bachaquero residuum and Lubricating oil extract.

A sample representing 40% by volume of a 26% Kuwait residuum was treated with an equal weight of tetralin at 400 to 450°C and 400 to 500 psig (28 to 35 bar) for 0.5 hour. Approximately 50% was converted to material boiling below 850°F (455°C) with only a trace of coke.

Experiments were also made with 12.9% west Texas vacuum residuum in which the unconverted 1000°F bottoms from each experiment was diluted with an equal weight of tetralin and used as feed to the following experiment. A 90% conversion was obtained in only three cycles with a cumulative coke yield of only 0.65%. Extrapolation indicates that essentially complete conversion would be achieved in 9 or 10 cycles, with a cumulative coke yield of 0.7%.

Yoshida et al. [23] subjected the atmospheric residuum from Khafji crude to thermal cracking at 420-460°C in the presence of a diluent, namely, nitrogen, hydrogen, or tetralin as a hydrogen donor. The feed and the product residua were separated into six fractions. They stated that Khafji feed has a larger share of asphaltenes and a smaller share of saturates and monoaromatics, compared with three other feeds, namely, Arabian Heavy, Iranian Heavy and Taching. The Khafji topped crude was markedly susceptible to thermal cracking. The yield of distillate, in which the share of kerosene was relatively large, was 22 wt%, at best. Significant changes in physicochemical properties of the visbroken residua were observed, namely, a decrease in viscosity and an increase in Conradson carbon. The yield and structural change of the six fractions by thermal cracking were accounted for by a

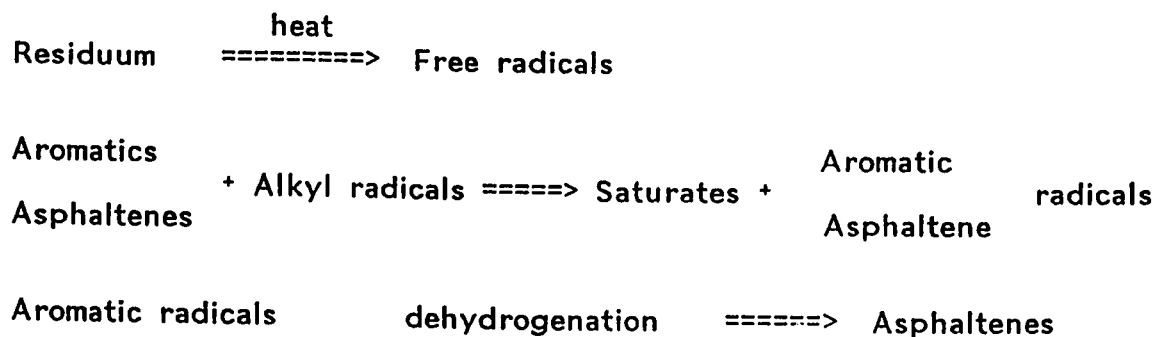
mechanism consisting of unimolecular decomposition and radical chain reaction.

In a recent article, Bakshi and Lutz [24] discussed the advantages of adding a hydrogen donor to an existing visbreaking process. Hydrogen donor visbreaking is a combination of two proven processes : visbreaking and mild gas-oil hydrogenation. The process gives a substantially higher conversion of residual fuel oil to gas oil and higher products than does conventional visbreaking. The hydrogen donor may be an internally generated recycle stream or alternatively, a catalytic cracking unit fractionator bottoms, a light cycle oil, coal tar fractions, or aromatic tar from ethylene plants can be used.

## 2.5 Hydrogen Donor Chemistry

In the thermal cracking process, free radicals produced by dehydrogenation reactions condense to form asphaltene-like compounds. Thus, the asphaltic constituents build up and tend to separate from the bulk of the oil. This leads to deposits followed by coke formation in the cracking coil.

Carlson et.al [6] proposed the following mechanism of coke formation:



Asphaltene radicals      condensation  
                                 polymerization      =====> Coke

Pyrolysis of residuum produces free radicals which abstract hydrogen from the aromatics and asphaltenes to produce aromatic and asphaltic radicals. These radicals then undergo dehydrogenation, condensation, and polymerization reactions, aromatic radicals leading to asphaltenes and asphaltenes to coke. Condensation of aromatics to products of higher molecular weight during thermal cracking has been shown in a study of pyrolysis reactions of pure aromatic and heterocyclic compounds [25] . This mechanism suggests that condensation of free radicals to high molecular weight compounds and to coke could be minimized by providing a source of readily available hydrogen to satisfy the radicals as they form, and that relatively mild cracking conditions to minimize the formation of low molecular weight radicals (methyl, ethyl, etc.) would reduce coke formation. To meet these requirements, hydrogen transfer must take place readily at 750 to 850°F (400-450°C). Transfer of hydrogen to alkyl radicals will occur with any hydrocarbon diluent present under these conditions. Therefore, condensation can be prevented only by transfer of hydrogen to aromatic type radicals. The donor must possess highly activated hydrogen positions, reactive enough to give up hydrogen to the relatively stable aromatic and asphaltic radicals, and must be more reactive than the hydrogens in the aromatic and asphaltene structures by the mechanism



Alkyl radicals

Aromatic radicals + H-donor =====> hydrocabons +

Asphaltene radicals dehydrogenated donor

This is the basis for the thermal cracking, hydrogen transfer process. Failure to consider this requirement was responsible for the lack of success in the previous extensive hydrogen transfer work using paraffins, olefins, naphthenes, or selected refinery streams rich in saturated naphthenes as a source of hydrogen.

Hydrogenation of the donor may be done at surprisingly mild conditions because it is desirable not to hydrogenate the aromatic ring, but only the reactive rings [24]. A spent diluent cut can be isolated, rehydrogenated under conditions which would reform the condensed naphthene-aromatic structure, and recycled back with fresh feed. Figures 2.2 and 2.3 show a schematic representation of hydrogenation of the depleted donor. Carlson et al. [6] supported their theoretical considerations by conducting several experimental runs on 16% west Texas residuum. Six types of pure hydrocarbons were evaluated for their ability to donate hydrogen to prevent coke formation during thermal cracking. Cracking was carried out in a standard Aminco rocking bomb, using about equal amounts of residuum and diluent. The mixture was heated rapidly to temperature and maintained at 840°F (450°C) for 2.5 hours. At the conclusion of the run, the bomb

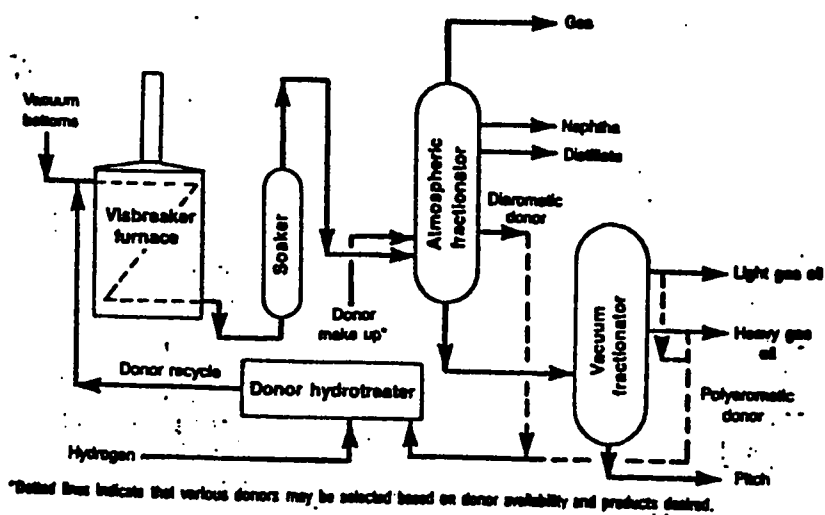


Figure 2.2 : Hydrogenation of the depleted hydrogen donor [24]

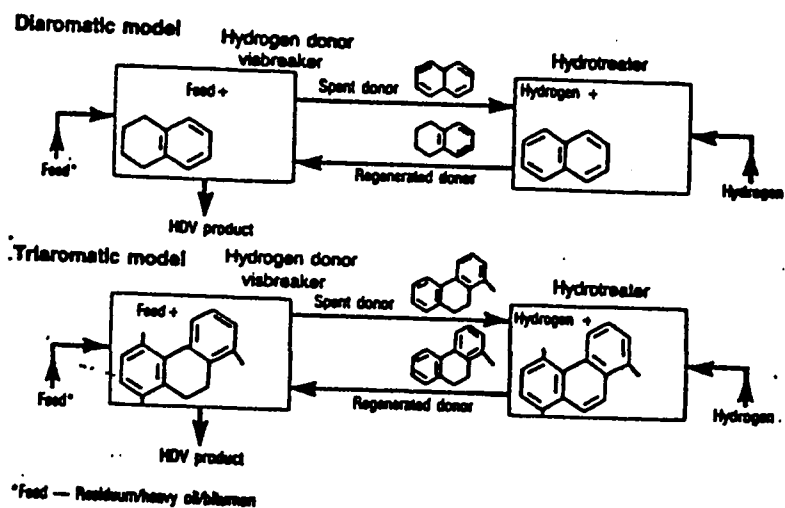


Figure 2.3 : Chemistry of Hydrogen Donor Solvent [24]

was allowed to cool in the shaker. The pressure attained was that exerted by the cracked products, no extraneous gas being added to the reaction mixture.

Carlson et al. showed that reduction of coke is marked with the fused ring aromatic-naphthene, tetralin, and less so with the fused ring naphthene, decalin. A single-ring naphthene, methylcyclohexane, has relatively little effect at the indicated conversion level. Results are explained as follows: Because alkyl radicals abstract hydrogen from these diluents, the low coke yield with tetralin was taken as evidence that it was donating hydrogen to the aromatic and asphaltene radicals, whereas the other diluents did not. The intermediate result of decalin was believed to be due to the formation of tetralin under these severe cracking conditions. The ineffectiveness of decalin as reported in the literature [5] , was stated to be due the fact that diluents had no effect in the thermal cracking of residuum in the presence of hydrogen. However, only saturated diluents were studied and they do not contain sufficiently reactive hydrogens. This emphasizes the outstanding effect obtained with tetralin, which possesses hydrogens in the saturated ring highly activated by the adjacent aromatic ring . Further support for this view was reported in a study of the rate of abstraction of hydrogen from paraffins, isoparaffins, aromatics, alkylated aromatics, cyclohexane, decalin, and tetralin by tert-butoxyl radicals [26] .

More concrete evidence that aromatic radicals undergo condensation and polymerization during thermal cracking and that tetralin prevents

such reactions was obtained with clarified oil- the refractory, highly aromatic bottoms from catalytic cracking, which consist predominately of condensed ring structures. When clarified oil is thermally cracked, many aromatic radicals are formed. These radicals polymerize and dehydrogenate further, leading to high coke yields. 20% coke was formed in the nondiluent experiment, but essentially none in the presence of tetralin under the same cracking conditions. The high 455 to 850°F liquid yield and the elimination of coke in the tetralin run are taken as evidence that tetralin effectively prevented condensation of aromatics to products of higher molecular weight. 34.7% of the tetralin was dehydrogenated to naphthalene. With hydrogen donor diluent cracking, the distillate products may be desulfurized by conventional methods, avoiding contamination of the desulfurization catalyst with residuum ash components.

## *2.6 Pyrolysis of Tetralin*

The pyrolysis of tetralin has been the subject of several publications. Jones [8] pyrolyzed 1,2,3,4-tetrahydronaphthalene (tetralin) at 530°C, although the action started at 490° to 500°C. Naphthalene was the solid product obtained, while the gases were made up of 3.5% benzene and higher olefins , 3.5% ethylene, 80.2% hydrogen, 9.0% methane and 4.0% ethane.

According to Egloff [9] , a more complete study of the pyrolysis of tetralin was made by Sundgren who summarized the reactions of tetralin at temperatures of 580° to 650°C under atmospheric pressure and under

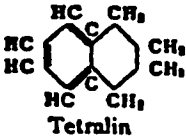
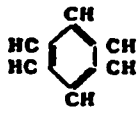
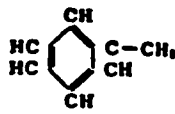
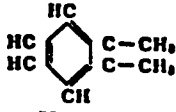
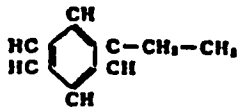
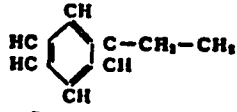
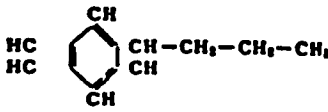
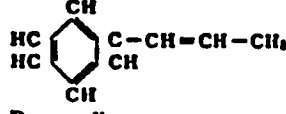
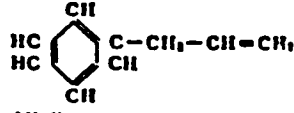
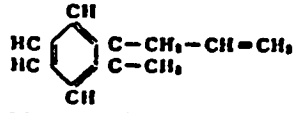
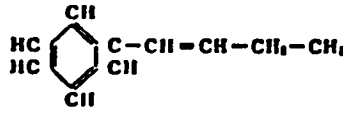
pressures of 10,15,25, and 30 kg/ cm<sup>2</sup> as follows:

- (1) Decomposition to aromatic hydrocarbons with unsaturated side chains.
- (2) Cracking, characterized by the rupture of the hydrogenated ring to form aromatic hydrocarbons.
- (3) Dehydrogenation to naphthalene.
- (4) Decomposition to methane and carbon.
- (5) Under pressure with hydrogen, decomposition was the same except that methane was the total product from the hydrogenation of the products of complete dislocation. Table 2.1 summarizes the possible products of these reactions.

Increased temperature increased the speed of reaction, but not to the same extent for all of the above reactions, decreased the number and length of side chains in the products and changed the manner of rupture of molecules. Increased pressure favored carbon-carbon scission and allowed better heat transfer. More symmetrical rupture of the molecule was also noted. The use of catalysts slightly increased cracking while decidedly aiding dehydrogenation.

The gases formed in Sundgren's experiments contained quantities of methane, ethylene and hydrogen varying with the different temperatures used. Hydrogen, however, was always the chief constituent of the gases comprising 56-85%, while methane made up 13-39%. Ethylene constituted only a small part of the total, about 1-4%. Analysis of the low boiling liquid products from the pyrolysis of tetralin

Table 2.2 : Products of Tetralin Pyrolysis [9]

 <p>Tetralin</p>	$\text{CH}_4$ Methane	 <p>Benzene</p>	 <p>Toluene</p>
	$\text{H}_2\text{C}=\text{CH}_2$ Ethylene		
	 <p>Xylene</p>	 <p>Ethylbenzene</p>	
	 <p>Styrene</p>	 <p>Propylbenzene</p>	
		 <p>Propenylbenzene</p>	
		 <p>Allylbenzene</p>	
		 <p>Methylallylbenzene</p>	
		 <p>Butenylbenzene</p>	

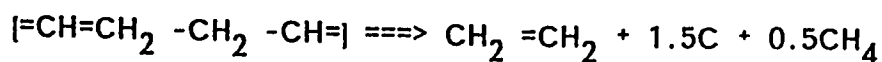
showed the following compounds: benzene, toluene, o-xylene, ethylbenzene, propylbenzene, styrene, allylbenzene, propylbenzene, methylbenzene and butenylbenzene.

According to Egloff [9] Ruzicka and Rudolph obtained a 70% yield of naphthalene by heating tetralin with sulfur. Schroeter treated tetralin with 1.0 to 1.5% of anhydrous aluminium chloride at 30° to 40°C and obtained a 30% yield of a mixture of hydrocarbons. Continuing the study, Schroeter treated 1500 g of tetralin with 30 g of anhydrous aluminum chloride for 6 to 10 hours at a temperature of 50° to 70°C. Distillation of the product after hydrolysis with dilute acid gave 120 g of pure benzene.

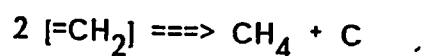
The effect of time and pressure upon catalytic thermal decomposition of tetralin was emphasized by Hugel as stated by Egloff [9]. As a result of his study of the catalytic decomposition of tetralin, Hugel postulated that the cracking reaction proceeded first by loosening the bonds between carbon and hydrogen atoms, or between carbon atoms, under the influence of heat. These loosened bonds could then split into unsaturated radicals which would react to form primary products. Further action may also take place, forming secondary products. The structure of tetralin indicates that the hydrogenated ring may disintegrate in several different ways by splitting the carbon-carbon linkages at various points or series of points. The following free radicals may be formed, according to Hugel, on splitting of the ring  $[=CH-CH_2-CH_2-CH=]$ ,  $[=CH-CH_2-CH=]$ ,  $[=CH-CH=]$ , and  $[=CH_2]$

These radicals, once formed, may behave so as to :

- (1) Dehydrogenate to a more unsaturated radical.
- (2) Hydrogenate to a paraffin.
- (3) Internally satisfy the bonds, such as the formation of butadiene from  $(=CH-CH_2-CH_2-CH=)$ .
- (4) Further decompose, for example :



- (5) Disproportionate to form a saturated compound and an unsaturated residuum or even carbon as :



Hooper et al. [10] studied the thermal dissociation of tetralin between 300° and 450°C. Some of the related literature was reviewed. In their work tetralin was heated for various periods at temperatures between 300° and 450°C without hydrogen or coal, and the products were analysed by capillary chromatography. The main products formed were naphthalene and the tetralin isomer 1-methyl indan. Tetralin did not disproportionate to naphthalene and decalin, although this has been suggested in the literature as a mechanism for the formation of the naphthalene usually observed. Naphthalene was produced, at temperatures as low as 350° to 400°C, by dehydrogenation of the saturated ring. This ring also rearranged to give 1-methyl indan, and at higher temperatures broke open to yield alkyl benzenes. This cracking of the saturated ring was found to enhance the naphthalene formation.



According to Cronaur et al. [45] Penninger and Slatboom heated tetralin to a temperature of 540°C under a hydrogen pressure of 8 MPa. They reported that hydrocracking occurred, and a complex mixture of alkylated benzenes was produced. They further reported their results in terms of an equilibrium between naphthalene, hydrogen and tetralin, a reaction which may have been catalysed by the vessel walls. The catalytic hydrogenation of naphthalene has long been known.

The pyrolysis of tetralin at 500°C has been studied by Benjamin et al. [11]. The pyrolysis products resulting from the decomposition of tetralin were analysed by n.m.r. spectroscopy. They found that no equilibrium between tetralin and naphthalene plus hydrogen takes place in the absence of a catalyst. When tetralin was heated at 400°C for 1 hour a trace of it was converted to naphthalene and 1-methylindane. If the heating was continued for 18 hours at 400°C, about 1% decomposition occurred. However, when tetralin was heated at 500°C for 1 hour extensive decomposition was observed, only about 25% of the tetralin remaining. Naphthalene was the major product and small amounts of 1-methylindane, indane, ethylbenzene, and toluene were formed. Yields were not determined because they change depending on the time and temperature of heating. Between 1% and 3% each of several other compounds were identified as benzene, o-xylene, methylethylbenzene, butylbenzene, 2-methylindane, and  $\alpha$ - and  $\beta$ -methylnaphthalene. Trace amounts of numerous other compounds were detected. Among them the following could be identified : propylbenzene, two other C<sub>3</sub>

benzenes,  $\alpha$ - and  $\beta$ - ethylnaphthalene, 1-and 2-ethylindane, the three binaphthyls, and chrysene. The last four compounds represent condensation products with higher molecular weights than the starting tetralin.

The gas fraction produced when tetralin was heated to 500°C contained 35% hydrogen, 45% methane, 31% ethane, and 13% propane. Propene and butane were also detected in small amounts. The products of pyrolysis of tetralin over porcelain chips at 700°C and ambient pressures have been reported. A large proportion of condensation products was formed under those conditions.

## **CHAPTER THREE**

### **EXPERIMENTAL SET-UP AND PROCEDURE**

#### **3.1 Description Of The Reactor**

The main equipment is a bolted closure packless autoclave with a magne-drive assembly. The bolted closure consists of the body, cover, closure gasket and cap screws. The gasket is made of stainless steel to withstand the high temperature range of 400-470°C.

*The agitation drive assembly* consists of a magne-drive which has been designed to fulfill additional requirements not obtained in conventional packed drives. Here high speed rotary agitation is affected by the rotation of external magnets which actuate internal magnets fastened to the shaft.

The external drive magnet assembly consists of an outer aluminium holder containing the stator magnets. This outer holder is placed over a pressure sealed housing containing the encapsulated rotor magnets which are mounted on a center rod. A strong magnetic field makes the inner center rod rotate at the same speed as the outer holder. The variable speed motor drive is an AC motor and it is connected to a control cabinet with a variable speed controller and "on-off" switch. The drive assembly has a maximum allowable working pressure which is equal to the vessel maximum. Maximum speed is 2800 rotation per minute. The maximum horsepower capacity is 0.75 HP at 2800 rpm and

the minimum available torque is 1.8 mN.

Accessories of the bolted closure consisted of the following:

- Safety head assembly.
- Pressure gauge.
- Sample tube and valve assembly.
- Cooling coil.
- Thermowell.
- Charging opening.
- Agitator.
- Digital tachometer indicator.
- Furnace and temperature control system.

*The Safety Head Assembly* consists of five parts: the safety head body which threads into the body of the autoclave, the safety head body gasket which provides the seal at this connection, the rupture disk, the hold down ring which conforms to the shape of the rupture disk and presses against its seat and the hold down nut which exerts the force to seat the rupture disk.

*The Pressure Gauge* is a standard pressure gauge. It is a 100 mm dial gauge with a 316 Ti SS Bourdon tube. Gauge indicates always the pressure in vessel whether the vent is opened or closed.

*The Sample Tube and Valve Assembly* is mounted in and on the cover of the autoclave. System pressure can be held across the seat of the valve and it does not disturb the connections between the valve and the cover in order to open the vessel. Pressure seal on the cover is

made with a positive bite joint. Samples may be drawn directly into the beaker or through tubing by opening the valve carefully.

*The Cooling Coil* is made from 316 SS tubing. Connection of the coil to the cover is accomplished at the inside cover face with positive bite connections. The high pressure system seal is made at this point and the outside cover connections need hold only water pressure. These outside connections are standard female pipe thread to facilitate use of standard tubing adapters and/or snap-on connections; snap-on connectors are also conveniently provided.

*The Thermowell* is made from 316 SS tubing. Since it is directly exposed to the reactants in the unit, good response is obtained.

*The Agitation System* is the type dispersimax which was developed and patented by Autoclave Engineers. It is a turbine-type agitator which is provided with a hollow shaft used in connection with removable baffles in the vessel. When in operation, a low pressure area is created at the turbine impeller. The gases are drawn down through the hollow shaft and dispersed through the liquid. The bubbles are broken by the baffle provided.

A *Digital tachometer indicator* shows the actual speed of the inner shaft of the magnetic agitator with a hall effect pick-up. This indicator has been preset at the factory to indicate accurate inner shaft speed. However, indicated speed vs. actual speed was also checked in the laboratory while the unit was running without internal pressure by

removing the cover from the housing and putting a hand tachometer on the inner magnet assembly. The comparison was good.

### ***Furnace and Temperature Control***

The furnace consists of a Jacket-type heater which has resistance windings (1800 W) and insulation enclosed in a sleeve-type jacket which slides onto the body of the autoclave. It is specially designed for heating high pressure vessels with high thermal inertia. Specially designed element supports permit the use of coiled wire elements in a tubular furnace thus keeping the watt loading of the wire low, which maximises the element life. The design consists of "1-zone control".

The temperature controller is a 1-zone CTK 24-1 microprocessor controller. It provides a 3 mode (proportional, integral and derivative) temperature controller with control thermocouple temperature displayed digitally. Apart from a PID control around a set point, it is also possible to ramp the temperature whenever it is desired. It has an accuracy of less than 1% of the full scale and a reproducibility of better than 0.3%. The thermocouple which is dipped into a thermowell is a K-type chromel alumel.

A secondary temperature controller and an overtemperature thermocouple for furnace and vessel protection is also provided. This feature is located inside the unit and is factory preset at 750°C.

### ***3.2 Preparation of the residua***

Arab Heavy crude oil was obtained from the Arabian American Oil Company (ARAMCO). A residuum from their refinery in Ras Tanura was also obtained. This commercial residuum is referred to as residuum # 1 throughout this study. The heavy Arabian crude oil was first distilled at atmospheric conditions followed by vacuum distillation at 10-12 mm Hg using a tilting-funnel distillation column assembly. This yielded a residuum of 343°C+ (650°F+) which is then further distilled under high vacuum in a wiped wall molecular still. This operation yielded a vacuum residuum of 565°C+ (1050°F+). This prepared residuum is referred to as residuum # 3. Another residuum referred to as residuum # 2 was obtained by atmospheric distillation of the crude followed by vacuum distillation using a simple distillation column. This operation yielded a residuum of 350°C+.

### ***3.3 Experimental Set-up and Control***

Figure 3.1 shows the arrangement of the experimental set-up including control boxes and the cooling water circulation. The high pressure/high temperature reactor was connected to a nitrogen cylinder through a high pressure regulator. This arrangement enables the reactor to be pressure tested and allows also the reaction to be run under a nitrogen atmosphere.

Cold water from a cooling bath (model Lauda) can be circulated in parallel through the cooling coil of the reactor as well as through the

shaft of the magnetic drive. The latter is always practiced when the stirrer is on.

In thermal systems a proportional-integral-derivative (PID) mode is usually employed. Heat transfer is a slow process, and tuning a three mode controller is somewhat difficult because three control setting variables have to be altered; also there might be an interaction between them.

Two procedures are usually followed to tune a controller:

- (i) Trial-and-error
- (ii) Zigler-Nicholas formula.

In the first option the controller settings are set at their maximum or any other suitable values and then altered to obtain the optimum choice. In the second option certain formulas are used to calculate starting values of the settings.

Trial-and-error was followed in tuning the Minicor Digital controller. The proportional band was set at 6% and the integral time at its maximum (199 min), while the derivative time was at zero value. This situation created an offset. Integral time was decreased until this offset was eliminated. However, this situation created oscillations and the derivative time was altered until cycling was eliminated.

A sample of residuum was heated to 400°C. The best setting for this case is as follows:

Proportional band      6 %



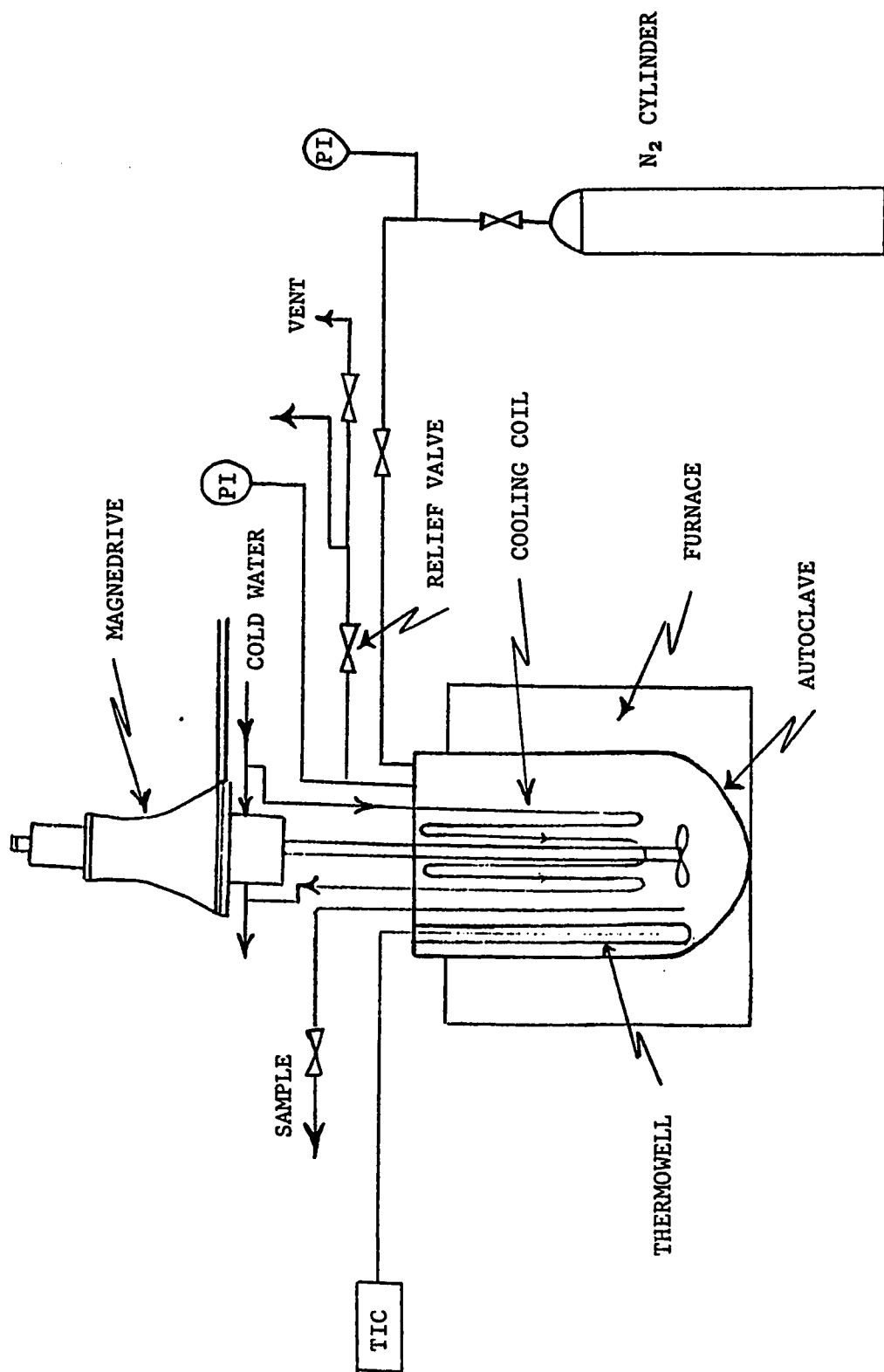


FIGURE 3.1 : SCHEMATIC OF THE EXPERIMENTAL UNIT

Integral time            10 min.

Derivative time         5 sec.

It has been found that settings are function of the material used. Thus for a mixture of tetralin and residuum settings differ. This is also the case with different temperatures. Occasionally, cooling was used to reset the temperature in certain cases during operation.

### ***3.4 Experimental Procedure***

Following were the experimental steps:

- (1) Tetralin and the residuum were mixed well until a homogeneous mixture was obtained. The reactants were mixed in a precise ratio , with the total being always 150 g. They were then loaded in to the autoclave.
- (2) The autoclave was purged by nitrogen to remove air as much as possible. Then it was pressurised by nitrogen to 60 bar for leakage tests.
- (3) The nitrogen pressure was brought down to the initial operating pressure (mostly 5 bar).
- (4) Heating was turned on with proper controller settings to take the system to the required temperature set point.
- (5) Cooling system was put on in order to circulate cooling water to the agitation shaft. The shaft was usually started at the early stage of heating at a speed of 608 rpm to obtain uniform temperature distribution.
- (6) The reaction was permitted to proceed isothermally for certain

times (mostly 90 minutes) started from the time it reached the set point.

- (7) Experiments were repeated for different temperatures and different initial pressures.
- (8) At the end of the experiment the reactor was left to cool at ambient conditions, occasionally using cooling water.
- (9) The cooling temperature and pressure were recorded and the products were collected. Liquid products were collected through the sample line in a preweighed beaker, weighed and then kept for analysis. Gases were collected in a rubber balloon after being evacuated under a vacuum line for about 15 minutes, and then sent for analysis.
- (10) The autoclave was cleaned thoroughly using toluene or benzene or a mixture of them. The washing liquid was taken out by vacuum suction.

### *3.5 Pyrolysis of Tetralin*

Tetralin was subjected to the same pyrolytic conditions in order to see what changes will occur. The autoclave was cleaned thoroughly by toluene or benzene or a mixture of them in order to remove any dirt or oil from previous experiments. This was done several times. The reactor was flushed with these solvents after being closed and pressurised by Nitrogen at 0.5 MPa in order to clean sample lines and gas outlets. Then, after being disassembled, the reactor was cleaned by tetralin alone. In all runs liquid was sucked out through a vacuum line.

A sample of 100 gram of Tetralin was loaded in the autoclave which was then pressurised at 0.5 MPa of nitrogen for leakage test. The reactor was flushed several times by nitrogen to remove air. The pressure of nitrogen was set at 0.5 MPa. The reactor was heated to the set point at 425°C, then left for 90 minutes after reaching the set point.

At the end of the experiment, the reactor was allowed to cool. The final pressure and the pressure after cooling both were recorded. Gases were collected in a rubber balloon after it had been evacuated for 15 minutes by a vacuum line to eliminate air as much as possible. These gases were sent for analysis. The liquid was collected and kept for HPLC analysis.

Tetralin as purchased from Fluka has a purity of 97%, a boiling range 204-207°C, a density of 0.967 and a refractive index of 1.540 at 20°C. It was used as obtained in all runs.

## **CHAPTER FOUR**

### **ANALYSIS**

#### **4.1 Introduction**

The separation of heavier oil fraction and residua into individual components and the identification of these compounds is neither practically feasible nor desirable. Instead, the chemical composition of a crude oil or fraction can be obtained in terms of the average structural parameters by existing analytical techniques. Hydrocarbon components of petroleum are considered to be composed of (1) paraffinic, (2) naphthenic, and (3) aromatic groups which leads to structural group analysis. Structural group analysis occupies a position midway between ultimate (elemental) analysis, in which atoms are the components, and molecular analysis, in which molecules are the components. The ultimate analysis can often be obtained by analysing the combustion products by gas chromatography which results in carbon, hydrogen, nitrogen and sulfur contents and oxygen by difference. Structural group analyses have been made by physical property methods or by spectroscopic methods. These methods and others have been reviewed by Speight [28].

#### **4.2 Analytical Techniques**

Thermal hydrogenation results in different gaseous and liquid products. In presence of excess tetralin, no coke is formed. Liquid

products have been analysed by different techniques:

- (1) Total sulfur by ASTM D1551 method.
- (2) API gravity by ASTM D941
- (3) Qualitative analysis of the hydrocarbon groups using a high performance liquid chromatography (HPLC).
- (4) Asphaltenes by ASTM D2007.
- (5) Simulated distillation by 5800 A gas chromatograph corresponding to ASTM D 2887-73 method.
- (6) Carbon residue by Ramsbottom method corresponding to ASTM D524.

Gaseous products were analysed by Refinery Gas Analyser 5880 A.

#### ***4.2.1 Sulfur Determination***

Sulfur was determined by the quartz tube method. This method is applicable to the determination of sulfur in organic materials, gas oils, fuel oils, residuum, etc. It is acidimetric, but nitrogen compounds less than 1% which form nitric acid don't affect its results. Nitrogen in any of the residua tested in this study is less than 0.4% by weight. Metals that form stable sulphates under the conditions of the test will interfere, causing results to be low. The standard deviation of the method is 0.007 percent sulfur.

The material to be examined is volatilized in an excess of air and burned by passing it through a section of red-hot quartz tubing. The sulfur dioxide (and trioxide) in the exit gas is collected in an absorption apparatus containing a solution of hydrogen peroxide and the

sulfuric acid formed is subsequently titrated with standard alkali (NaOH). The method requires that no acid-forming element besides sulfur be present in the sample.

#### ***4.2.2 Simulated Distillation D2887***

The simulated distillation option completes a chromatographic system which is configured and pretested to determine the boiling range distribution of petroleum products by ASTM method D2887-73.

The system consists of a Level 4 5880A Gas Chromatograph, equipped with a flame ionization detector (FID), a cartridge tape unit (CUT), and BASIC programming. The FID has a 0.030 inch ID jet installed and an identifying label. If more than one FID is installed on the instrument, the label will show which one has this special jet.

The column supplied for simulated distillation is: 1/8 x 20 inch stainless steel, 10% UC-W982 on 80/100 mesh Chromosorb P-AW [43]. This column is attached to the FID with the 0.030 inch jet. A liquid sampler is part of the system.

The ASTM D2887 chromatographic technique yields analysis times which are comparable to the ASTM D86 (atmospheric distillation) or ASTM D1160 (vacuum distillation) method. The precision is better and results agree closely with TBP (true boiling point) distillation.

The method is limited to petroleum fractions with final boiling points of 1000°F (538°C) or less. It is further limited to samples with a range

of boiling points of at least 100°F (55°C). Good precision can be obtained at half this range, provided that highly reproducible injection, temperature programming and data acquisition equipment is used.

The sample is injected into a gas chromatographic column of limited efficiency which separates hydrocarbons in boiling point order. While the column temperature is programmed up, the area under the chromatogram is measured as a function of time. The resulting data may be represented as a graph of cumulative area (total area up to a given time) versus time. The area axis is normalized to 100% to obtain percent recovered at a given time. The time axis is converted to boiling point using a calibration curve obtained by analyzing a mixture of hydrocarbons of known boiling points under identical conditions.

#### ***4.2.3 Ramsbottom Carbon Residue ASTM D524***

This method covers the determination of the amount of carbon residue left after evaporation and pyrolysis of an oil, and is intended to provide some indication of relative coke-forming propensity. The method is generally applicable to relatively nonvolatile petroleum products which partially decompose on distillation at atmospheric pressure.

The sample, after being weighed into a special glass bulb having a capillary opening, is placed in a metal furnace maintained at approximately 1020°F (550°C). The sample is thus quickly heated to the point at which all volatile matter is evaporated out of the bulb with or



without decomposition while the heavier residuum remaining in the bulb undergoes cracking and coking reactions. In the latter portion of the heating period, the coke or carbon residue is subject to further slow decomposition or slight oxidation due to the possibility of breathing air into the bulb. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and again weighed. The residue remaining is calculated as a percentage of the original sample, and reported as Ramsbottom carbon residue.

#### *4.2.4 Hydrocarbon Group Analyser*

A Waters Hydrocarbon Group Analyser which is a high performance liquid chromatograph (HPLC) was used to analyse for liquid products. This system works isocratically, and has a programmable piston pump for solvent delivery (Model 590). The mobile phase is normally n-hexane pumped at a rate of 2.0 ml/min. The column is the Waters energy analysis (NH<sub>2</sub>) column which incorporates a specialised packing with an amino propylsilane chemically bonded to 10 $\mu$  fully porous silica particles. Separation of crude oils and residua into saturates, aromatics and polar is easily achieved.

In this system, saturates (including olefins) passes unretained and is detected by a refractive index detector; neutral aromatics passes also through the column and is detected by an UV absorbance detector. The detectors work in series. After 9 minutes the flow is reversed in the column so that using backflush the polar aromatics are pushed out

as a single unresolved peak. Although the equipment is very reproducible and yields accurate qualitative data immediately, quantification of Hydrocarbon Group Analyser requires calibration of the equipment with standards of known polar aromatics, aromatics and saturates. For this purpose, a standard sample is injected to the equipment under calibration mode and response factors (conversion factor for detector response to wt%) are calculated from the known composition and integrated areas for polar aromatics and aromatics. An unfortunate feature of this equipment is that there is no single response factor which can be used for all hydrocarbon fractions.

The sample to be analysed is weighed accurately (usually 0.5 g) and then deasphalted with 20 ml of n-hexane. Thus a ratio of sample/solvent of 1/40 is used as recommended by ASTM. The sample is sonicated and filtered in a Milipore filter. 10 microliter of the deasphalted sample is then injected to the HPLC. Hexane of HPLC grade is used with a boiling point of 69°C, at a wavelength cut of 250 and a refractive index of 1.375.

#### ***4.2.5 Asphaltenes according to ASTM D-2007***

Asphaltene is the insoluble matter that can be separated from a solution of oil in an excess of n-pentane. A sample of  $5 \pm 0.5$  is weighed in a preweighed 250-ml conical flask. 100 ml of n-pentane is then added and mixed well with the sample. The mixture is warmed occasionally in a warm water bath for a few seconds with intermittent swirling to hasten solution. The mixture is allowed to stand for 30 min at room

temperature. A stirring rod together with intermittent warming and swirling is occasionally used. A 150-ml capacity glass Buchner funnel with fine porosity filter disk is used to filter the sample-pentane mixture. The conical flask is rinsed twice with 10 and 20 ml of pentane; the washings are poured through the funnel. Walls of the funnel are washed with 20 ml pentane.

The filter funnel and contents are subjected to a gentle stream of air for 45 min. The filter is removed from the flask, dried and the weight of n-pentane insolubles is determined.

## **CHAPTER 5**

### **RESULTS AND DISCUSSION**

#### **5.1 Introduction**

Tetralin has proved to be an effective hydrogen donor. It has been chosen as a donor solvent in this study because it has been known as an effective donor in hydrogenating other heavy feedstocks. It is the aromatic-naphthenic nature of tetralin which makes it a powerful donor.

Most of the experiments of this study were done on a fraction boiling above 350°C. Some runs were performed on a commercial residuum from ARAMCO. This fraction boils above 250°C. Another fraction boiling above 550°C was also studied for comparison. These fractions have been labeled as residuum # 1 for the commercial, residuum # 2 for the first and # 3 for the third. Table 5.1 summarizes some characteristic properties of these fractions.

In the following sections, the results are presented and discussed. First the mechanism of thermal hydrogenation by the donor solvent is discussed. The properties of the residuum are presented and compared to the literature in section 5.3. The preliminary steps which were taken during the progress the reaction are discussed in section 5.4, followed by a discussion on the methods of analysis and problems encountered. In sections 5.6, 5.7, and 5.8 the effect of reactant ratio, pressure and

**TABLE 5.1*****Residua and their Properties***

Number	Type	API	Sulfur wt%	Asphaltene wt%	Carbon Residue wt%
1	commercial	19.3	2.8	7.5	6.5
2	prepared	9.7	4.5	19.2	13.7
3	prepared	3.0	5.8	33.3	26.0
ASTM METHOD		D941	D1551	D2007	D524

temperature are discussed respectively. The pyrolysis of tetralin is discussed in section 5.9. The sulfur analysis and the proposed lumped kinetics are discussed in the following section. Finally the advantages of this process compared to other are discussed in the last section.

### *5.2 Mechanism of hydrogen donor reactions*

In thermal cracking a whole range of products can be produced. Besides liquids, substantial amounts of gases and coke are formed. Gases can be as much as 14% by weight as in a typical coking process [24]. In hydrogenation using a donor solvent, no coke is formed when a proper ratio is used and the amount of gases produced is small and does not exceed 3% by weight in best cases [46]. Gases produced in this research were only 2% by weight. Gases produced in both cases include hydrogen, methane, ethane, propane, butane, ethylene, acetylene, propylene, hydrogen sulfide and butylene. Hydrogen donor produces a lesser amount.

The free radical chain mechanism has been widely accepted as a thermal decomposition mechanism [47]. According to this theory, free radicals are formed when C-C or C-H bonds are thermally split. The free radicals react to form new radicals or new products. They can rearrange or recombine, but they are incapable of producing branching and cyclization chains. The same mechanism has been adopted to explain coke formation. Alkyl radicals are formed as a result of cracking and by reacting with aromatic and asphaltenes; free radicals of the lateres are formed. These radicals can condense and polymerize to form large

molecules which eventually dehydrogenate to form coke.

In the presence of an effective hydrogen donor and under mild conditions the radicals formed can be stabilized by abstracting atomic hydrogens from the donor, thus preventing condensation and polymerization, and thus coke is eliminated.

This has been exactly the case in this research. When a ratio of tetralin to residuum of 2/1 was used no coke formed at all. However when this ratio is decreased to 1/1, traces of coke are formed. More coke is formed when lower ratios are used. The nonformation of coke is strong evidence of the activity of the donor. Also a small percentage of gases is formed. Internal compounds of the aromatic-naphthenic nature may also act as donors. Aromatic rings need to be partially hydrogenated. This is a catalytic process. When the residuum was heated alone to 400°C, a lot of coke and gases formed.

When tetralin gives hydrogens it is converted to naphthalene. Decomposition to molecular hydrogen is not significant under these conditions. Molecular hydrogen cannot hydrogenate the radicals without a catalyst. Noncatalytic dissociation of molecular hydrogen to atomic hydrogen needs very severe conditions (up to 2500°C) [48].

Formation of molecular hydrogen in the gaseous product may be due to the insignificant decomposition of tetralin and to the dehydrogenation of alkanes. Around 500°C, most of the alkanes decompose to form olefins, gaseous hydrogen, and methane.

### 5.3 Characterization of Residua

Residuum # 1 of ARAMCO has a relatively high API gravity (19.3) and a low sulfur content (2.8 wt %) compared to residua # 2 and # 3. Simulated distillation (Figure 5.1) shows that the true boiling range of this cut is 250°C+. Simulated distillation is a gas chromatographic technique by which the percentage distilled of the fraction is plotted against the true boiling range. Comparison with literature is, in general difficult unless the boiling range is specified. This difficulty arises because definitions of residua and other heavy fractions are arbitrary, and the best way may be to specify the cut range and the conditions used to obtain the residuum (i.e., atmospheric or vacuum). It is not sufficient to say that a residuum is atmospheric or vacuum unless the cut point and conditions are specified.

Simulated distillation (Figure 5.2) shows that the boiling range of residuum # 2 is 350°C+. This cut has an API of 9.7°, a sulfur content of 4.5 wt % and an asphaltene content of 19.2 wt %. Inspection of Table 5.2 shows that residuum # 2 has properties similar to the cut 370°C+, which has an API of 10.7, a sulfur content of 4.36 wt % and carbon residue of 14.2 wt % compared to 13.7 wt % for residuum # 2.

Residuum # 3 is a very heavy Arabian vacuum residuum. It is solid at room temperature. It has an API gravity of 3°, a sulfur content of 5.7 wt %, an asphaltene content of 33.3 wt % and a carbon residue of 26.0 wt % on Ramsbottom basis and 28.4 wt % on a Conradson basis. Table 5.2 shows that this residuum is in a place somewhere between the

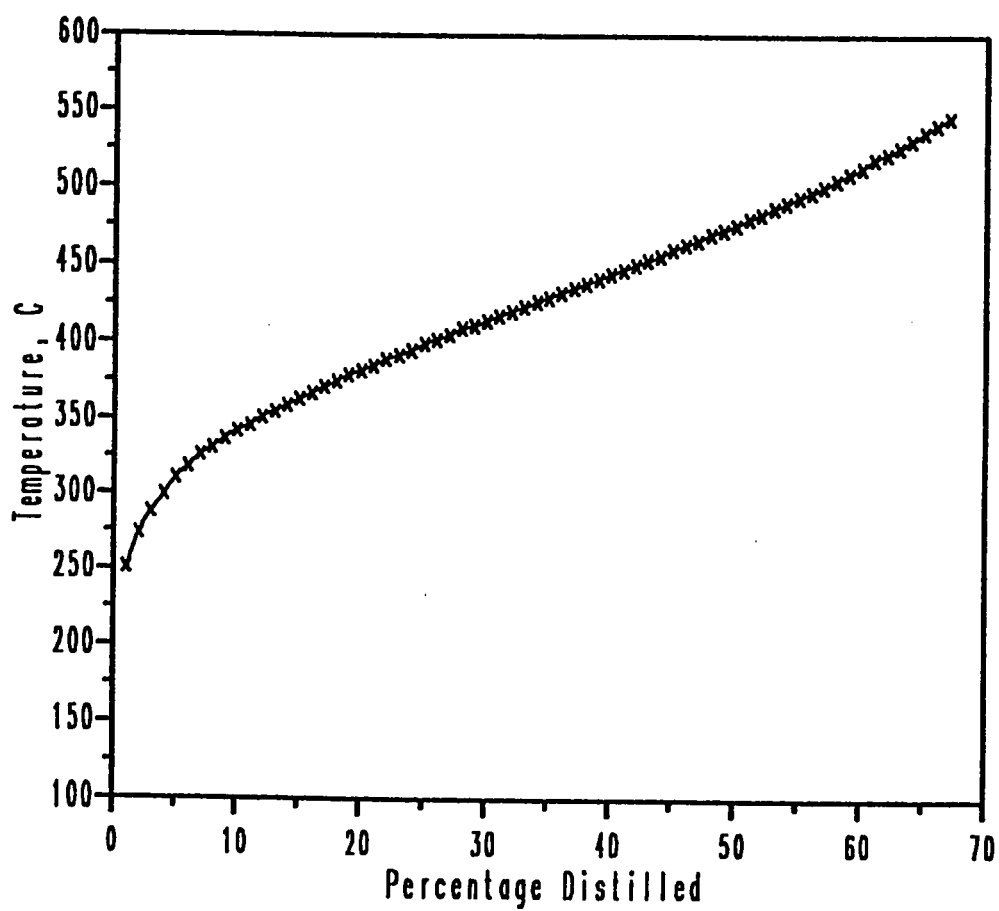


cut 535°C+ and the cut 675°C+. It is closer to the second cut. When compared to Table 5.3, different values for carbon residue (24 wt %) and asphaltene content (25 wt %) are given. This could be attributed to using different techniques of analysis. Also the definition of asphaltenes is operational and asphaltene itself is not a single compound. So characterization on the basis of asphaltenes is not common. Aalund [44] reported a sulfur content value of 6.0 wt %, a carbon residue on a Conradson basis as 27.7 wt % and a API gravity of 3.0°.

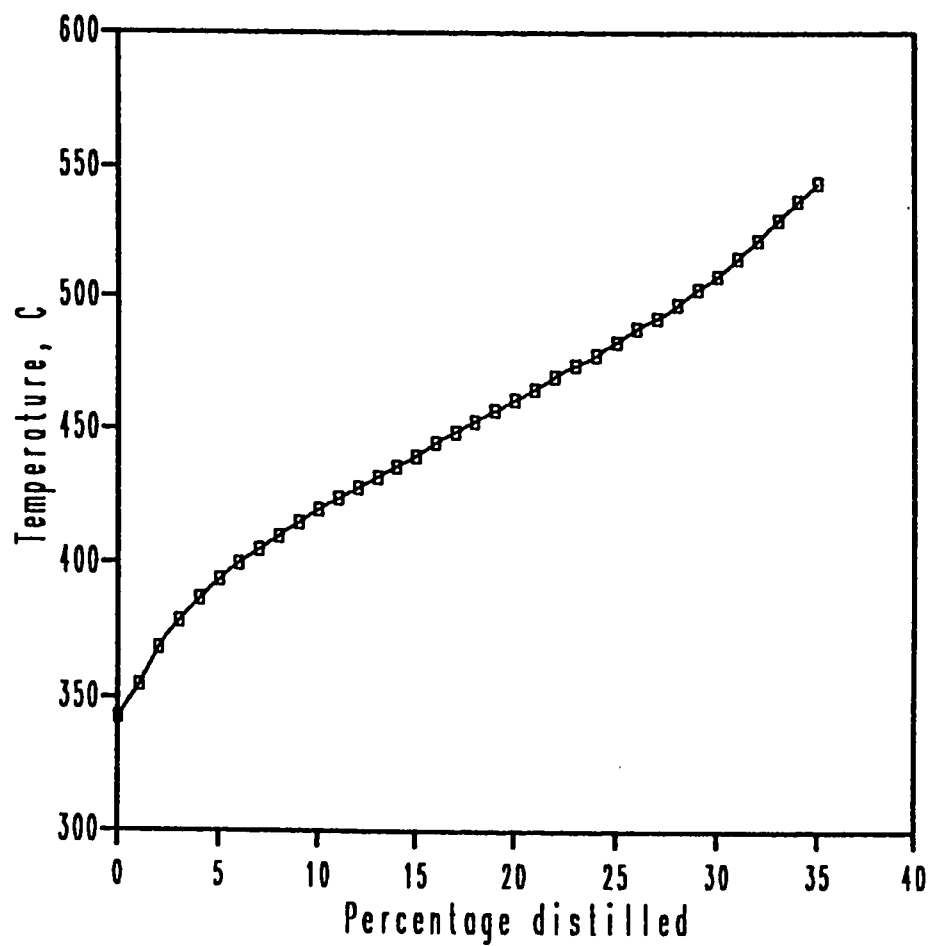
Figures 5.3, 5.4, 5.5 show the hydrocarbon group analysis of residua # 2, 3, and 1. These figures give a qualitative picture of the composition of these residua in terms of the saturates, aromatics and polararomatics (resins). Saturates also include olefins, besides the aliphatics (paraffins and naphthenes). Polararomatics are the aromatics containing heteroatoms like oxygen, sulfur, nitrogen and metals. It can be seen from these Figures that residuum # 1 has more saturates and aromatics than the other two. Residuum # 3 is the least in saturates. Polararomatics come out as one unresolved peak.

#### ***5.4 Preliminary Studies***

Cracking is endothermic i.e., it needs energy, and in order to hydrogenate the residuum, free radicals have to be formed. Free radicals are not expected to be formed at temperatures less than 400°C which is close to the initial boiling point of the residuum. Pressure is needed to keep reactants in liquid form. Changes in the preliminary



*Figure 5.1 Simulated TBP Curve for Residuum # 1*



*Figure 5.2 Simulated TBP curve of residuum # 2.*

Table 5.2 : Properties of Arabian Heavy Residua [51]

Residue °C	295°C	343°C	370°C	454°C	535°C	675°C
Residue °F	563°F	650°F	700°F	850°F	1000°F	1250°F
Yield cut range, wt %	32.8-100.0	40.5-100.0	44.7-100.0	57.4-100.0	67.4-100.0	84.7-100.0
Yield on crude, wt %	67.2	59.5	55.3	42.6	32.6	15.3
Mid. point, wt %	66.40	70.25	72.35	78.70	83.70	92.35
Specific gravity, 60/60°F	0.9719	0.9855	0.9950	1.015	1.032	1.055
Gravity, API	14.0	12	10.7	7.80	5.6	2.6
Viscosity @ 210°F (98.9°C) cSt	52	108	233	600	-	-
Viscosity @ 275°F (135°C) SFS	-	-	-	-	250	-
Pour point °C/°F	7/45	13/55	21/70	29/85	42/107	49+/120+
Carbon residue, wt %	11.7	13.2	14.2	17.5	22.4	30.0
Sulfur, wt %	3.90	4.12	4.36	4.70	5.2	5.90
Nitrogen, wt %	0.03	0.04	0.05	0.2	0.37	0.41
Nickel, ppm	27	30	32	38	46	60
Vanadium, ppm	83	93	105	120	148	197
Iron, ppm	12	14	17	19	33	33

**TABLE 5.3**

***Properties of Atmospheric and Vacuum  
residua of Arabian Light and Arabian Heavy*** [2]

Properties	Arabian Light	Arabian Heavy
Atmospheric residuum (650 °F+):		
Yield on crude, vol %	43.0	52.8
Gravity, °API	16.2	11.1
Sulfur, wt %	3.1	4.5
Metal (Ni + V), ppm	33	124
Vacuum residuum (1050 °F+)		
Yield on crude, vol %	13.2	26.0
Gravity, °API	6.5	4.0
Sulfur, wt %	4.1	5.7
Metal (Ni + V), ppm	100	239
Carbon residue (Ramsbottom)	22	24
Asphaltene (pentane insolubles), wt %	12	25

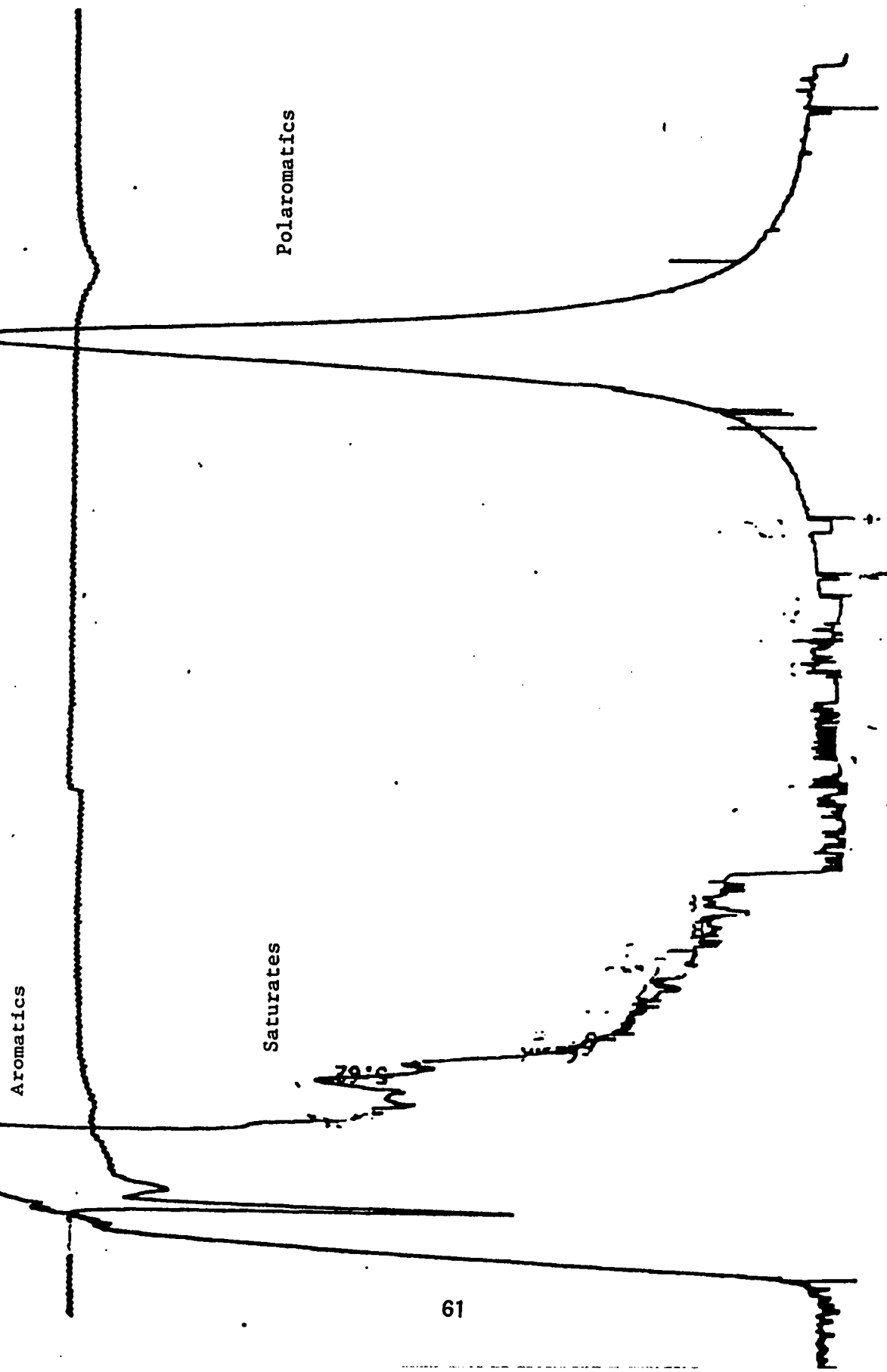


Figure 5.3 : Hydrocarbon group Analysis of Residuum #2.

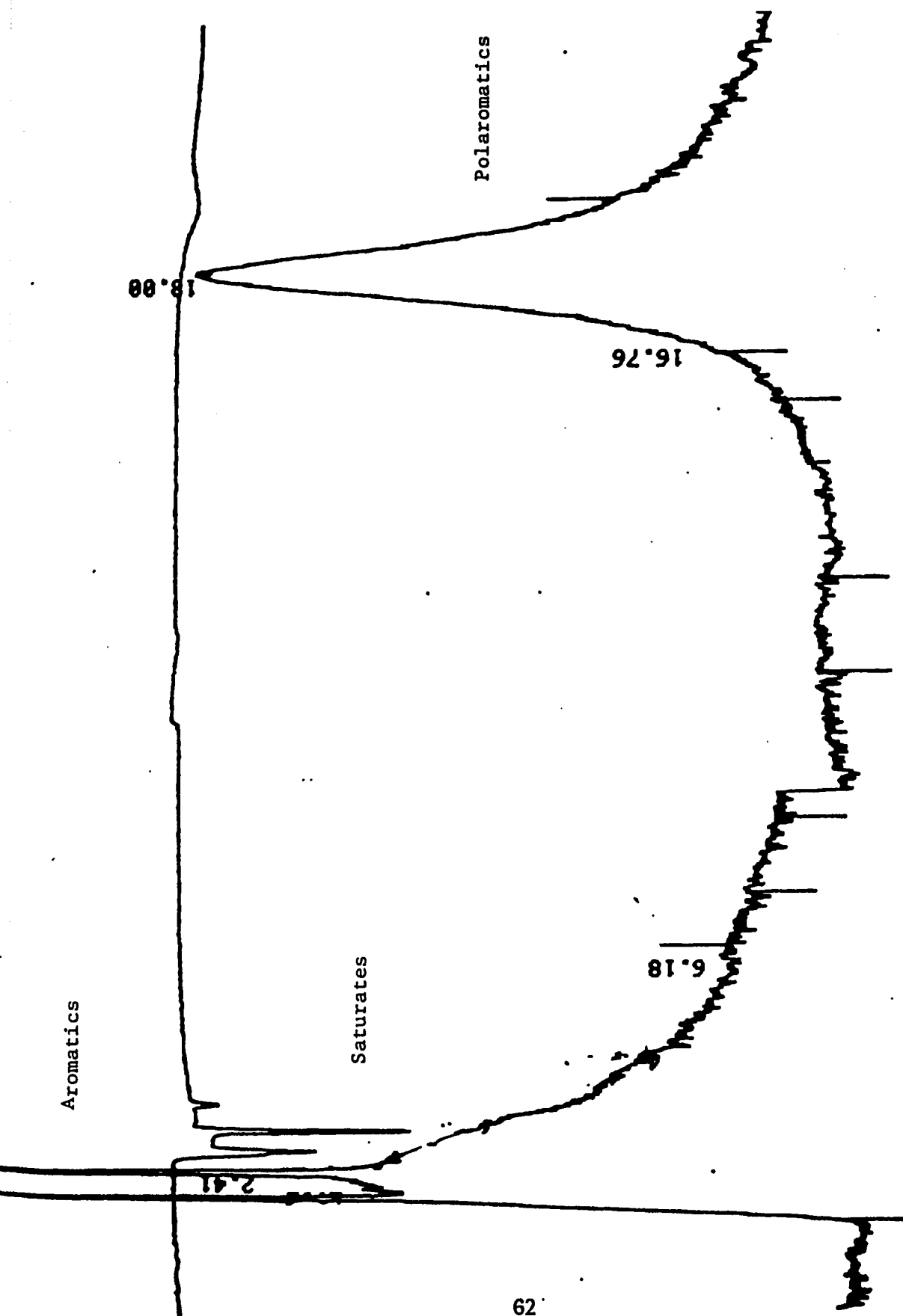


Figure 5.4 : Hydrocarbon group Analysis of Residuum # 3.

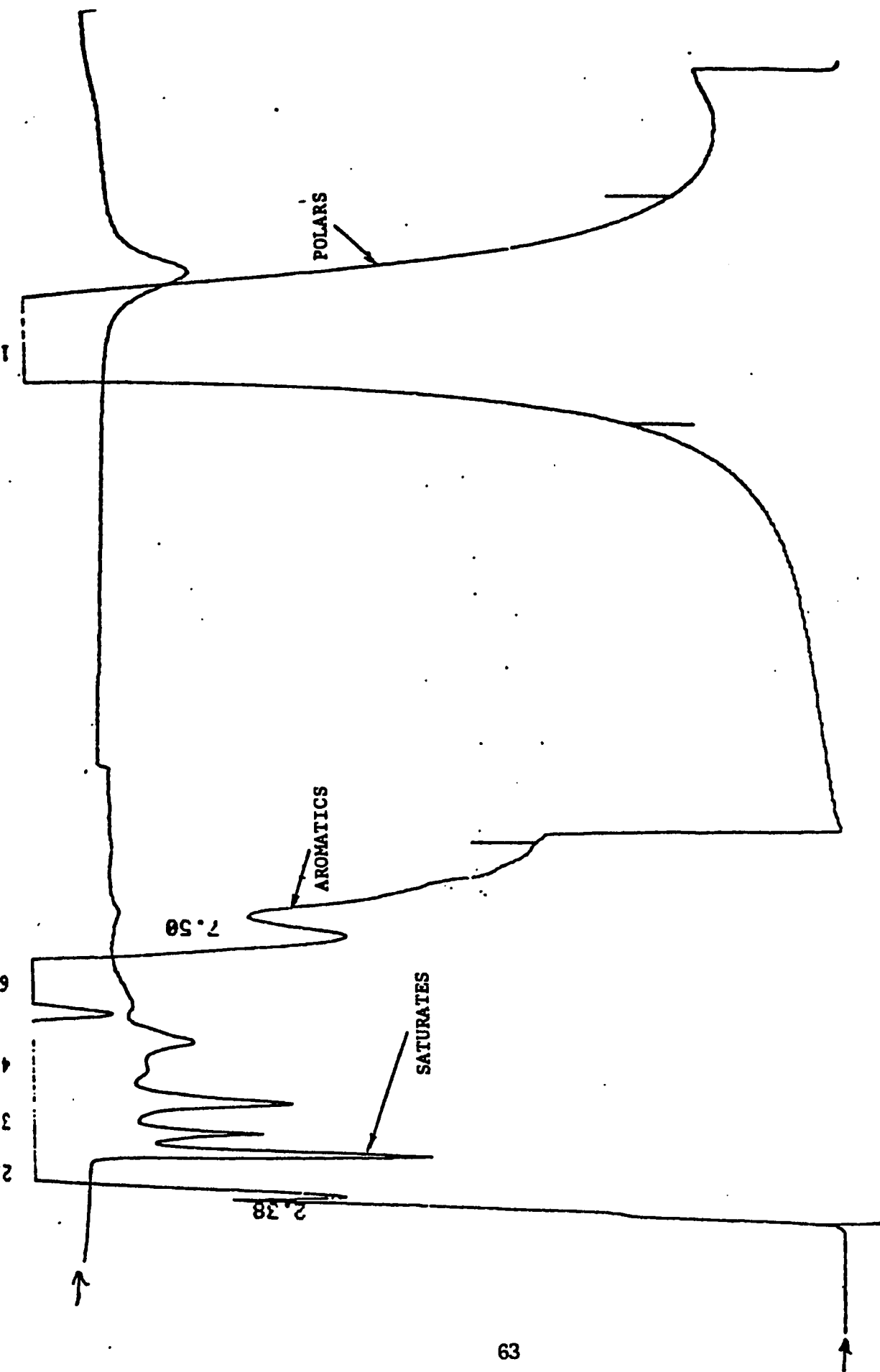


Figure 5..5 : Hydrocarbon Group Analysis of Residuum # 1.



stages were measured in terms of sulfur content only, and actions were taken accordingly. The relative percentage change of sulfur content wasn't significant at 400°C, therefore it was decided to increase the temperature. It was found that running the operations at 400°C and at an initial pressure of nitrogen of 4.0 MPa caused no problems. However at temperatures higher than 420°C using the same pressure, it was observed that there was an increase in pressure. This is attributed to the thermal expansion of nitrogen and to the the pressure of the formed gases. The reactor is supplied with a safety rupture disc set at 11.5 MPa. In one of the experiments this disc ruptured due to the runaway cracking. Accordingly a relief valve was installed and was set at 10 MPa. Any pressure beyond this point vents part of the gaseous products. Operating at temperatures higher than 435°C with pressures higher than 0.5 MPa of nitrogen created pressures greater than the set point. It was intended to operate at 400, 425, 450 and 475°C. The above restriction limited the work to 435°C only. A summary of the experimental runs is shown in Table 5.4.

### *5.5 Qualitative and Quantitative Analysis*

At the preliminary stages products were analysed qualitatively using an HPLC and a simulated distillation technique. This kind of analysis is useful. Any change due to the reaction between tetralin and the residuum is observed in terms of the qualitative change in the chromatographic peaks.

Table 5.4 : Summary of Experimental Runs

Sample weight: 150 g; Reaction time: 90 min. (after reaching the desired temperature); Stirring speed: 600 rpm  
Ratio = Tetralin/Residuum (wt/wt)

Run No.	Resi- duum #	Ratio	Temp. °C	Pressure (MPa)		Remarks
				Initial	Final	
1	2	2/1	400	1.5	5.6	Heating time = 45 min
2	2	1/1	400	1.5	5.7	Heating time = 45 min
3	2	1/2	400	1.5	6.0	Pressure after cooling = 2.0 MPa
4	2	1/5	400	1.5	6.5	Pressure after cooking = 2.0 MPa; Coke formed.
5	2	1/2	425	1.5	-	Experiment ran away; rupture disk was burst.
6	2	1/2	410	2.5	6.5	Temp. dropped rapidly to 300°C during operation.
7	2	1/2	415	2.5	-	Heating time = 50 min; overshoot of 5°C; back to set point in 5 min
8	2	1/2	420	2.5	8.0	--
9	2	1/2	420	4.0	-	--
10	2	2/1	425	4.0	10.0	Gas venting; heating time = 60 min
11	2	1/2	425	0.5	9.0	Pressure after cooling = 2.0 MPa
12	2	2/1	425	0.5	9.0	Pressure after cooling = 2.1 MPa
13	2	2/1	400	0.5	4.0	Pressure after cooling = 1.1 MPa
14	2	1/2	425	0.5	9.5	Pressure after cooling = 2.0 MPa; temp. overshoot
15	1	2/1	400	0.5	3.25	Pressure after cooling = 0.75 MPa; no coke.
16	1	1/2	425	0.5	7.0	Pressure after cooling = 1.75 MPa; traces of coke.

(Contd.)

Table 5.4 (Continued)

17	1	2/1	455	0.5	6.8	Pressure after cooling = 1.5 MPa
18	3	5/1	425	0.5	7.5	Pressure after cooling = 1.6 MPa
19	2	2/1	400	0.5	3.6	Pressure after cooling = 0.9 MPa
20	2	2/1	425	0.5	6.75	Pressure after cooling = 1.6 MPa
21	2	2/1	435	0.5	9.5	Pressure after cooling = 2.0 MPa; gas was vented.
22	2	2/1	400	1.5	5.7	Pressure after cooling = 2.0 MPa
23	3	2/1	425	0.5	7.4	Pressure after cooling = 1.75 MPa
24	2	2/1	400	2.5	7.25	Pressure after cooling = 2.75 MPa
25	Tetra- lin alone	100 gram	425	0.5	3.5	Heating period = 60 min; Pressure after cooling = 0.75 MPa.
26	Tetra- lin alone	100 gram	425	0.5	3.4	Heating period = 60 min; Pressure after cooling = 0.75 MPa
27	Tetra- lin alone	100 gram	425	0.5	3.5	Heating period = 60 min; Pressure after cooling = 0.75 MPa.

Figure 5.6 shows the chromatographic peaks, as determined by the simulated distillation technique, of the feed of residuum # 2 i.e., tetralin mixed with the residuum at a ratio of 2/1. In this Figure the main peak is that of tetralin; small peaks are also shown due to the contents of the residuum. This Figure can be compared with Figures 5.7, 5.8 and 5.9 which are the results of products at 400, 425 and 435°C respectively. Several peaks are observed around tetralin peak. On the left side of tetralin peak there is a long peak which could indicate the presence of a new compound lighter than tetralin. Naphthalene is hidden under the tetralin peak. It's boiling point is 217°C while that of tetralin is 207°C, the equipment detects compounds in the range of 50°. Same arguments can be applied to the other residua. Figure 5.10 shows the peaks of the feed of residuum # 3 and Figure 5.11 shows the peaks of its products. Figures 5.12 and 5.13 show the peaks of products of residuum # 2 at 400°C and 1.5 MPa and 2.5 MPa respectively. This confirms qualitatively the fact that pressure has no effect on the product distribution when it is beyond 0.5 MPa. From the above Figures it can be seen that many new peaks appeared; this indicates that heavy compounds have been converted into lighter ones. In other words they have been hydrocracked by tetralin.

HPLC results give some qualitative indications, and this is useful in particular in the qualitative characterization of residua. Figure 5.14 represents the hydrocarbon groups peaks of residuum # 2 feed, i.e., a mixture of tetralin and residuum mixed at a certain ratio. Figures 5.15 shows the peaks of products of this at 425°C. It can be seen by

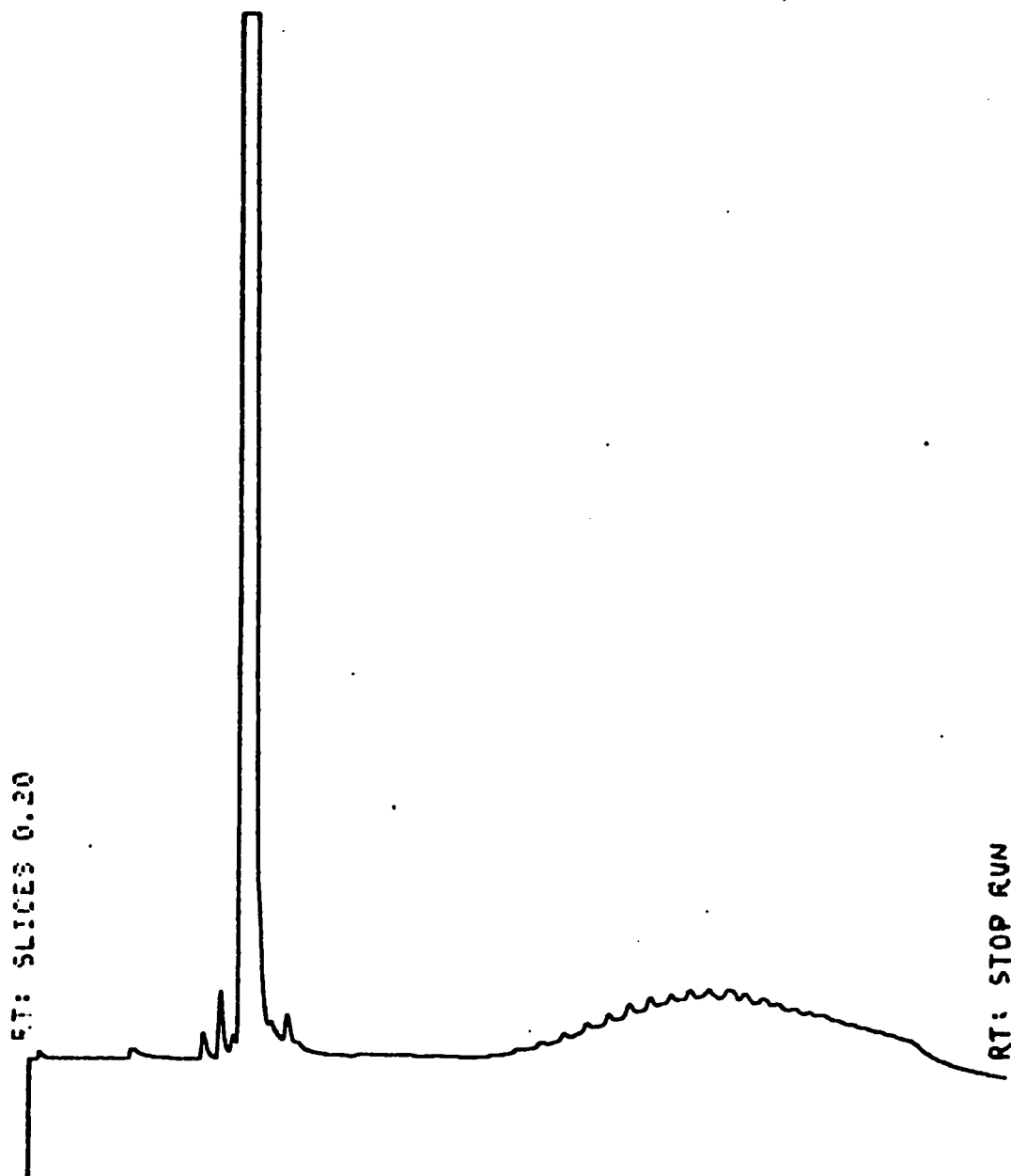


Figure 5.6 : GC Chromatogram of Residuum # 2 in Tetralin.

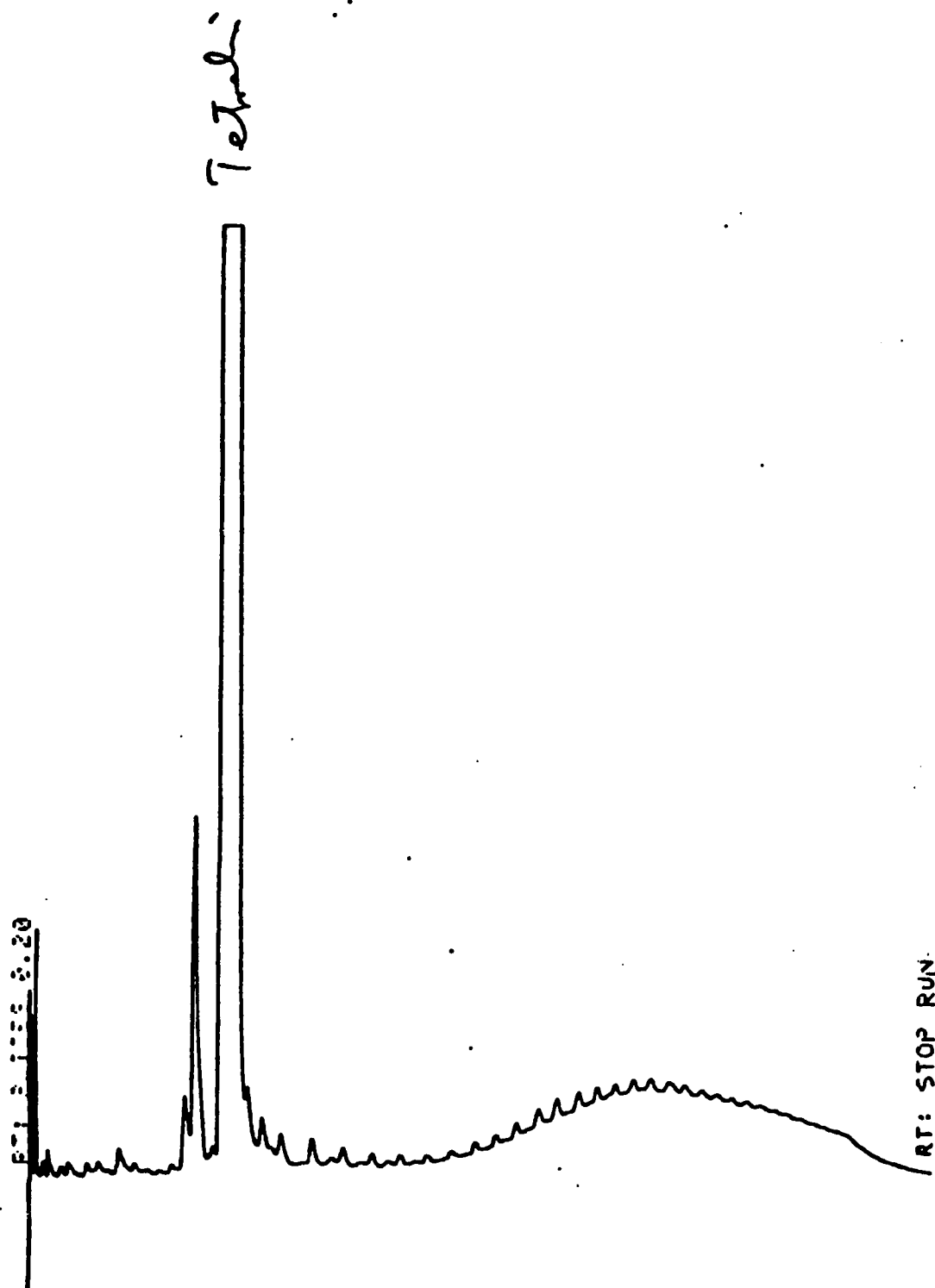


Figure 5.7 : GC Chromatogram of products of Residuum # 2  
in Tetralin at 400°C.

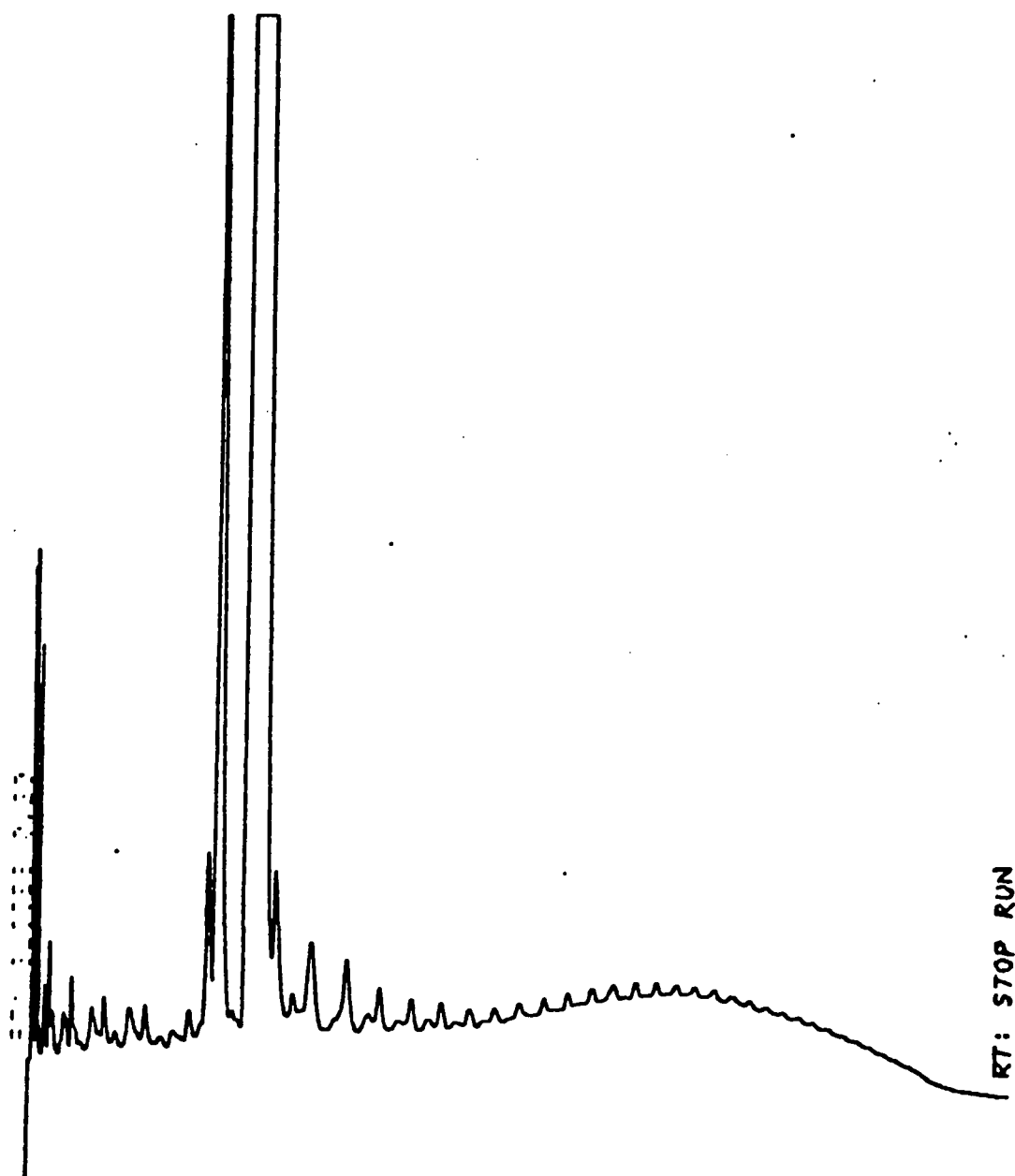


Figure 5.8 : GC Chromatogram of products of Residuum # 2  
in Tetralin at 425°C.

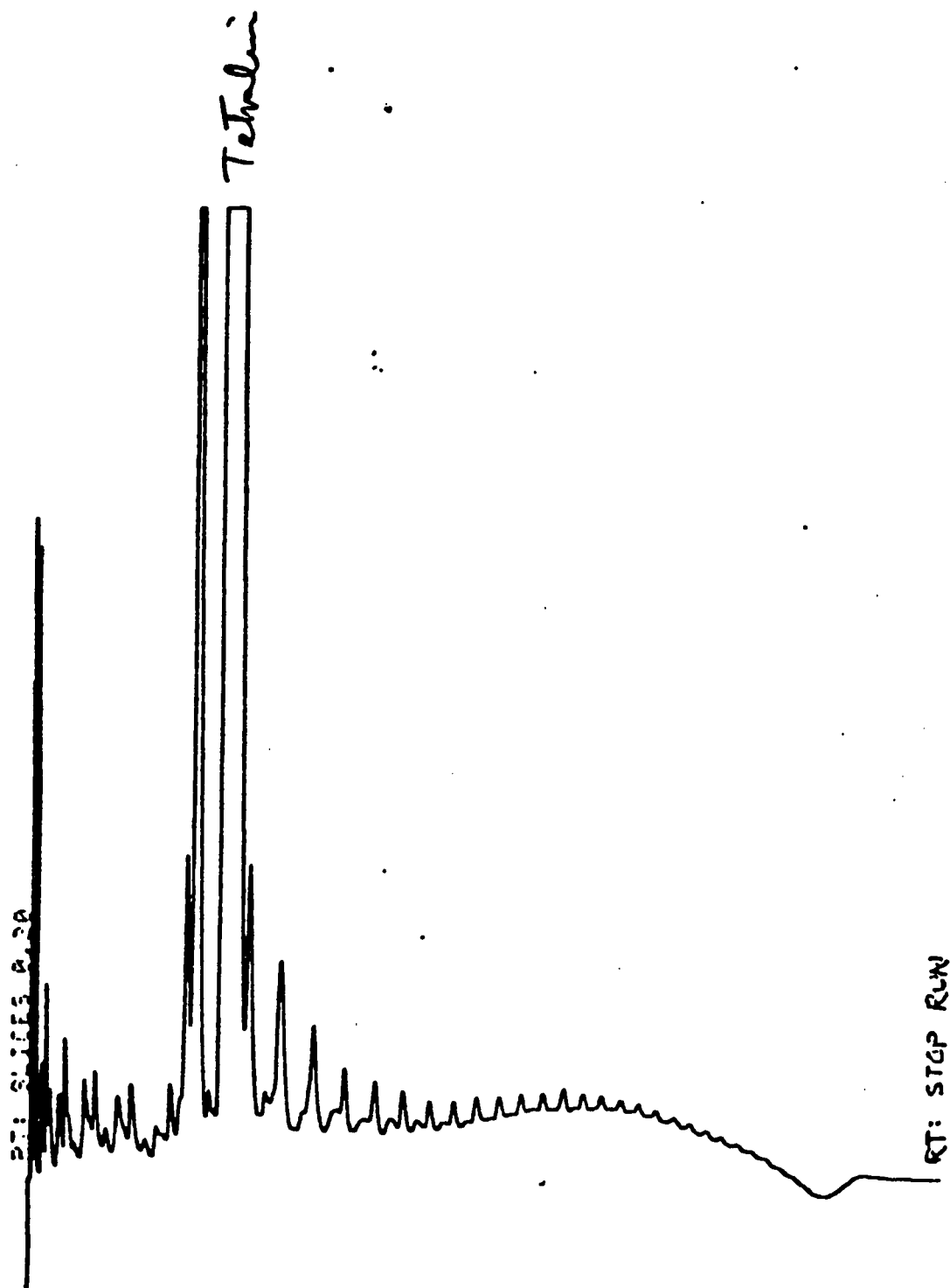


Figure 5.9 : GC Chromatogram of Products of Residuum # 2  
in Tetralin at 435°C



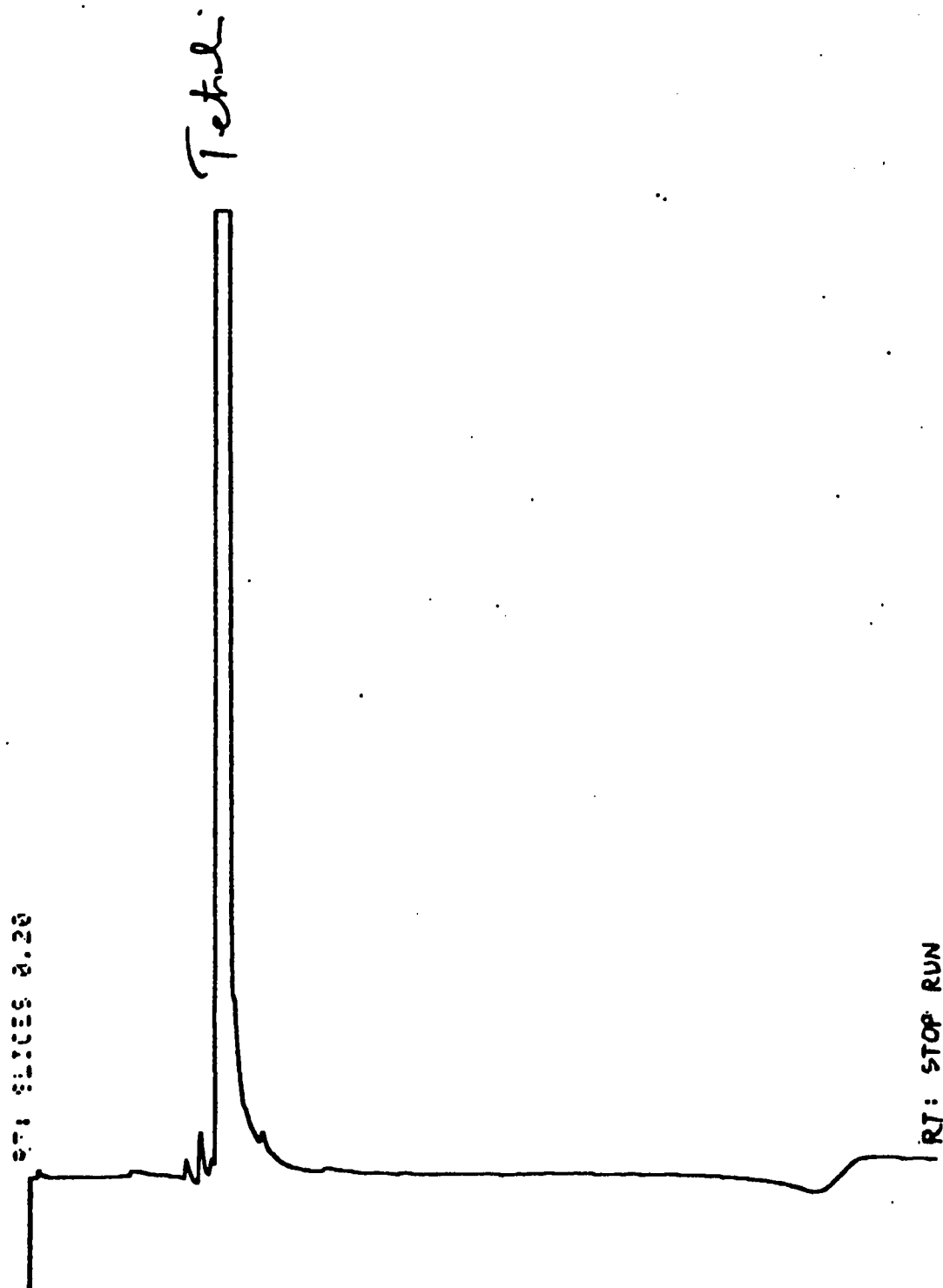


Figure 5.10 : GC Chromatogram of Residuum # 3 in Tetralin.

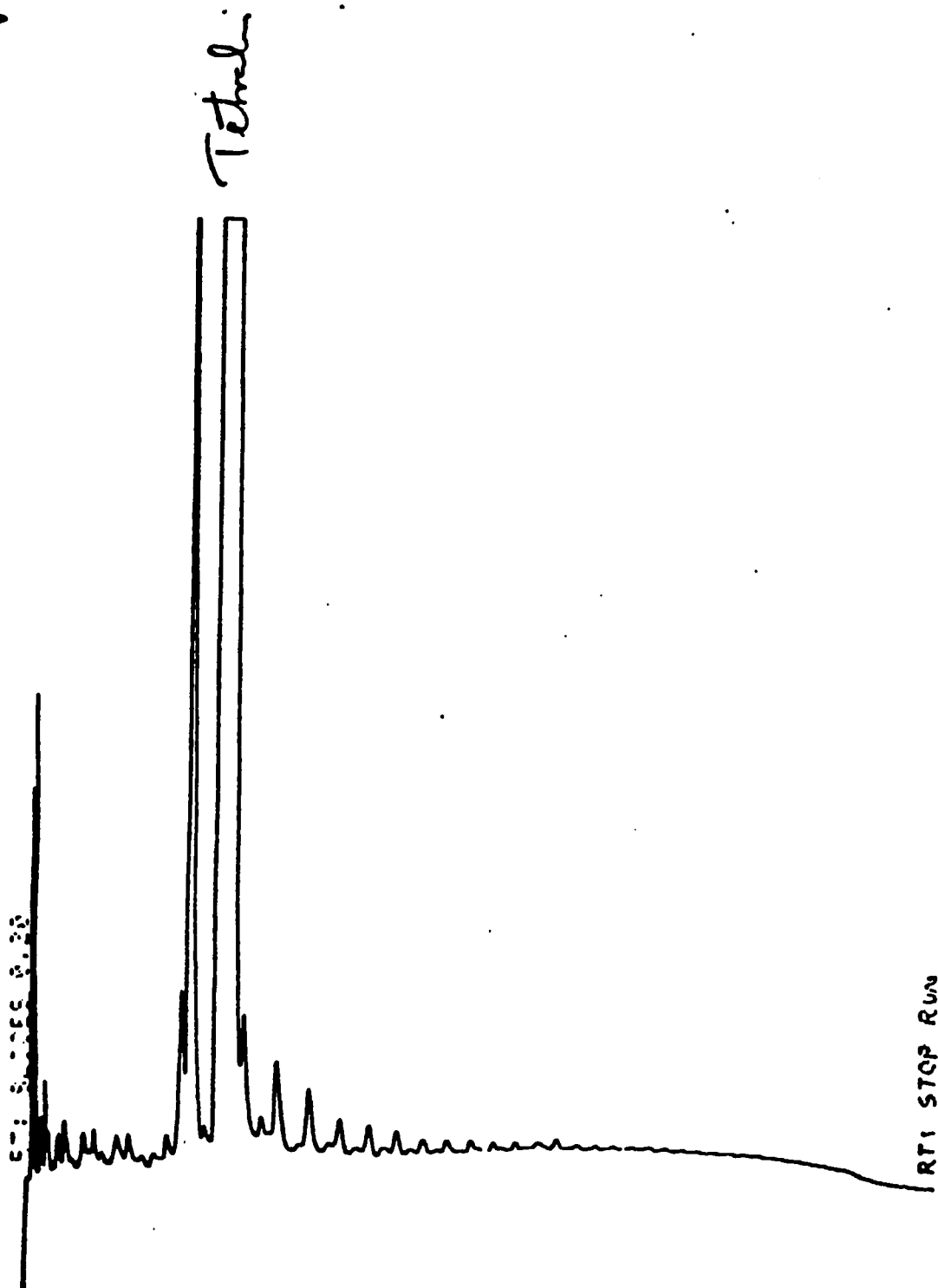


Figure 5. 11 : GC Chromatogram of Products of Residuum # 3  
in Tetralin at 425 °C

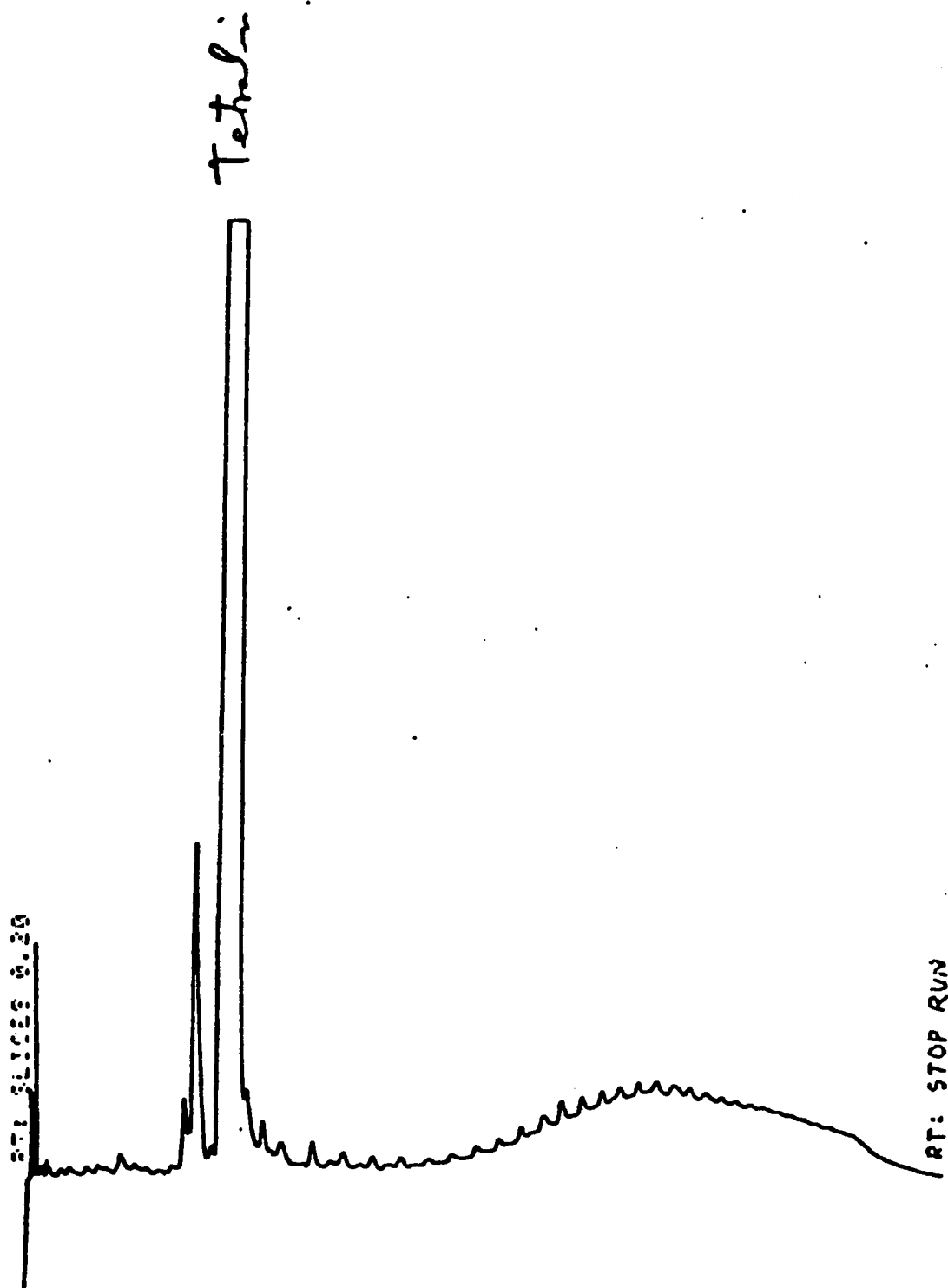


Figure 5.12 : GC Chromatogram of Products of Residuum # 2  
in Tetralin at 400°C and 1.5 MPa.

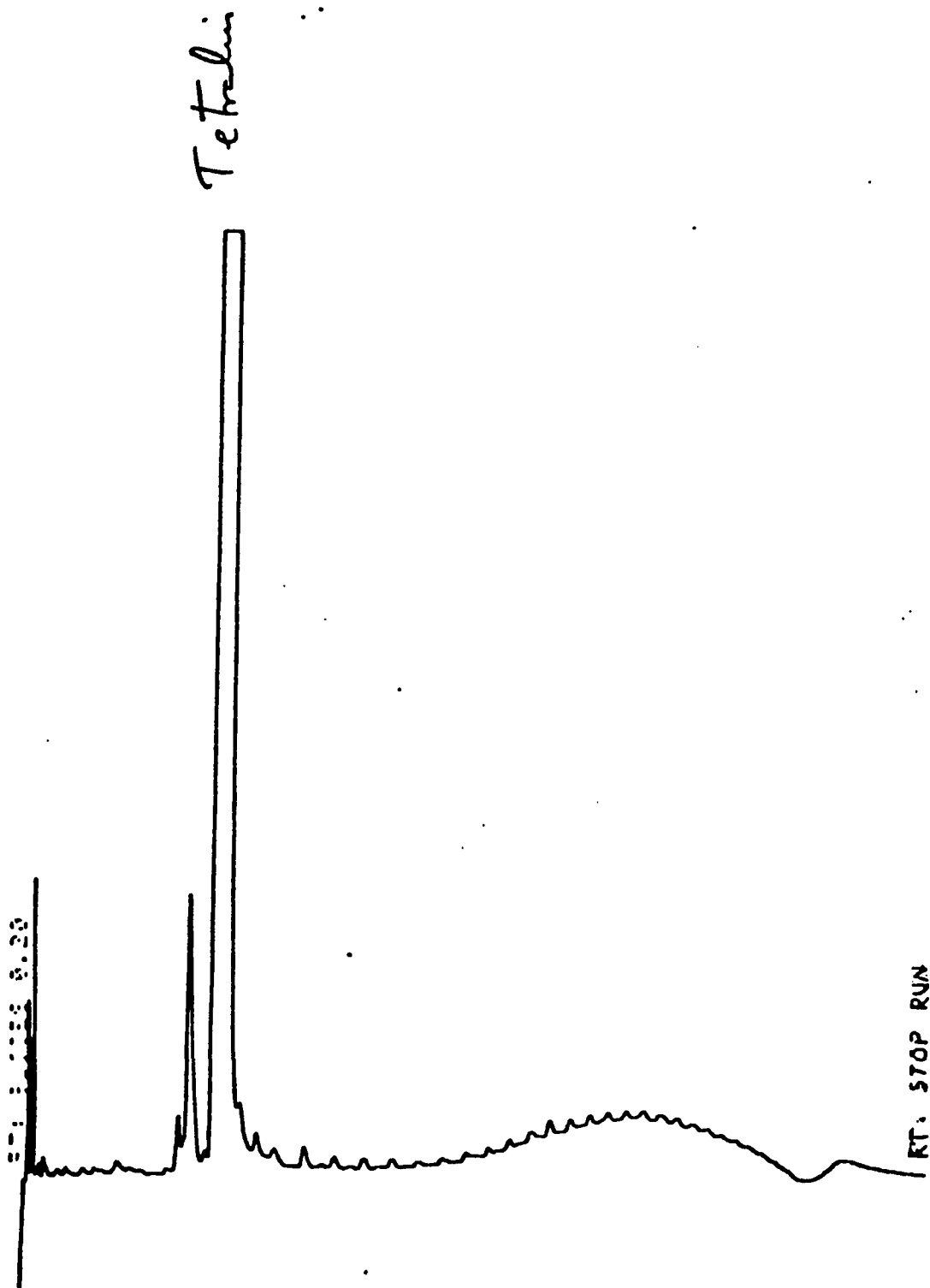


Figure 5.13 : GC Chromatogram of Products of Residuum # 2  
in Tetralin at 400°C and 2.5 MPa.

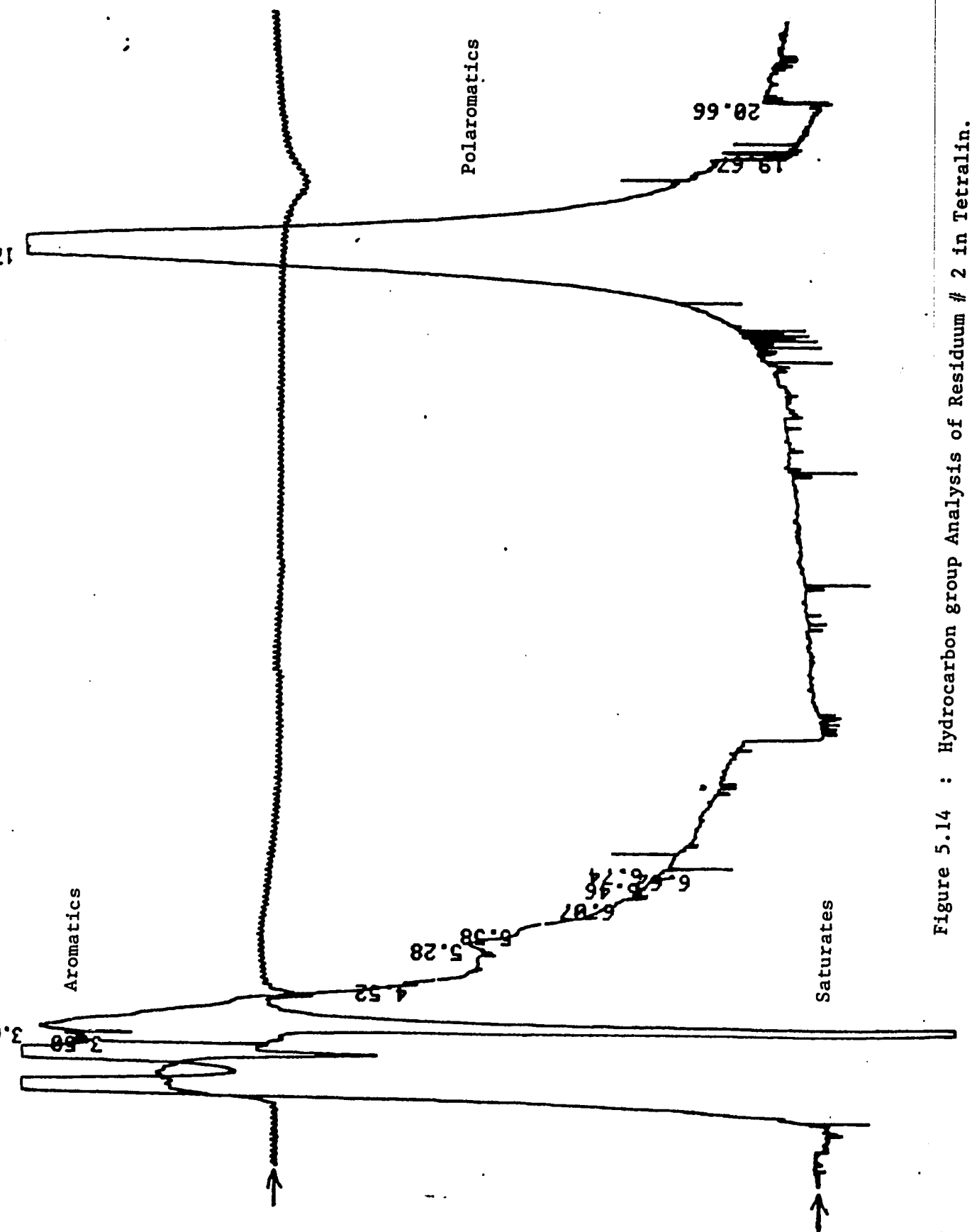


Figure 5.14 : Hydrocarbon group Analysis of Residuum # 2 in Tetralin.  
(2/1 ratio; asphaltene-free basis)

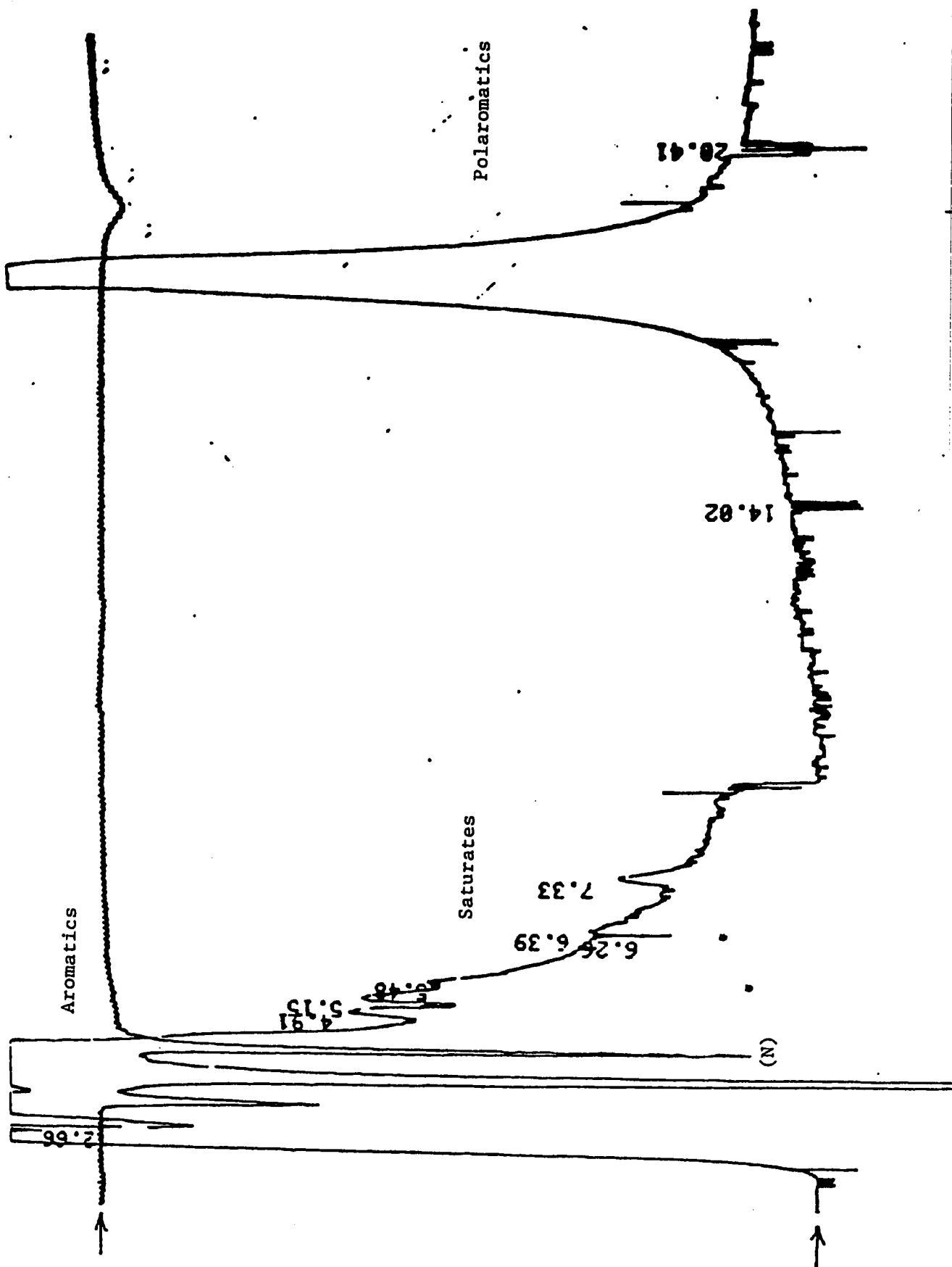


Figure 5.15 : Hydrocarbon group Analysis of Products of Residue # 2 in Tetralin at 425°C.

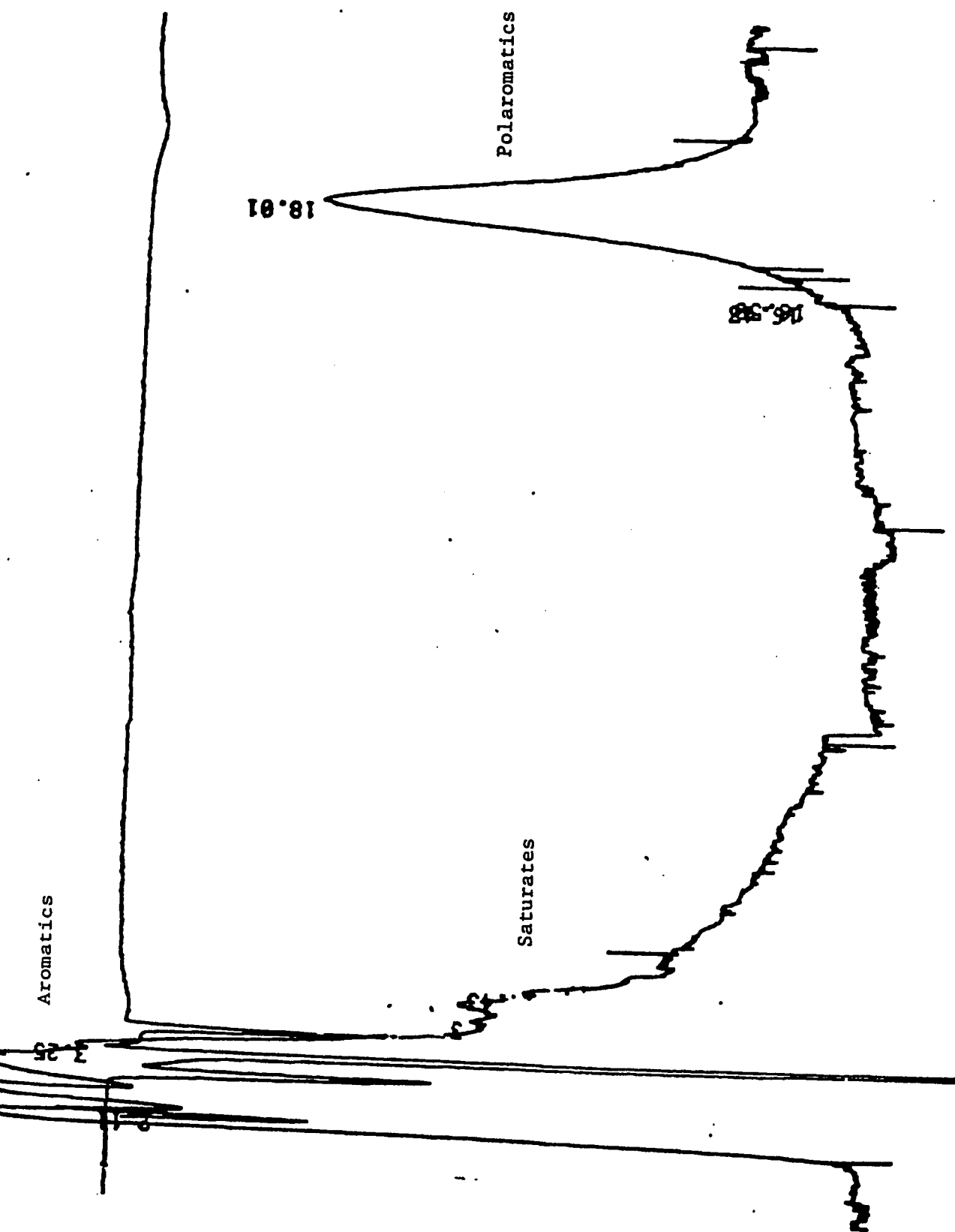


Figure 5.16: Hydrocarbon group Analysis of Products of Residuum # 2 in Tetralin at 400°C (1/1 ratio)

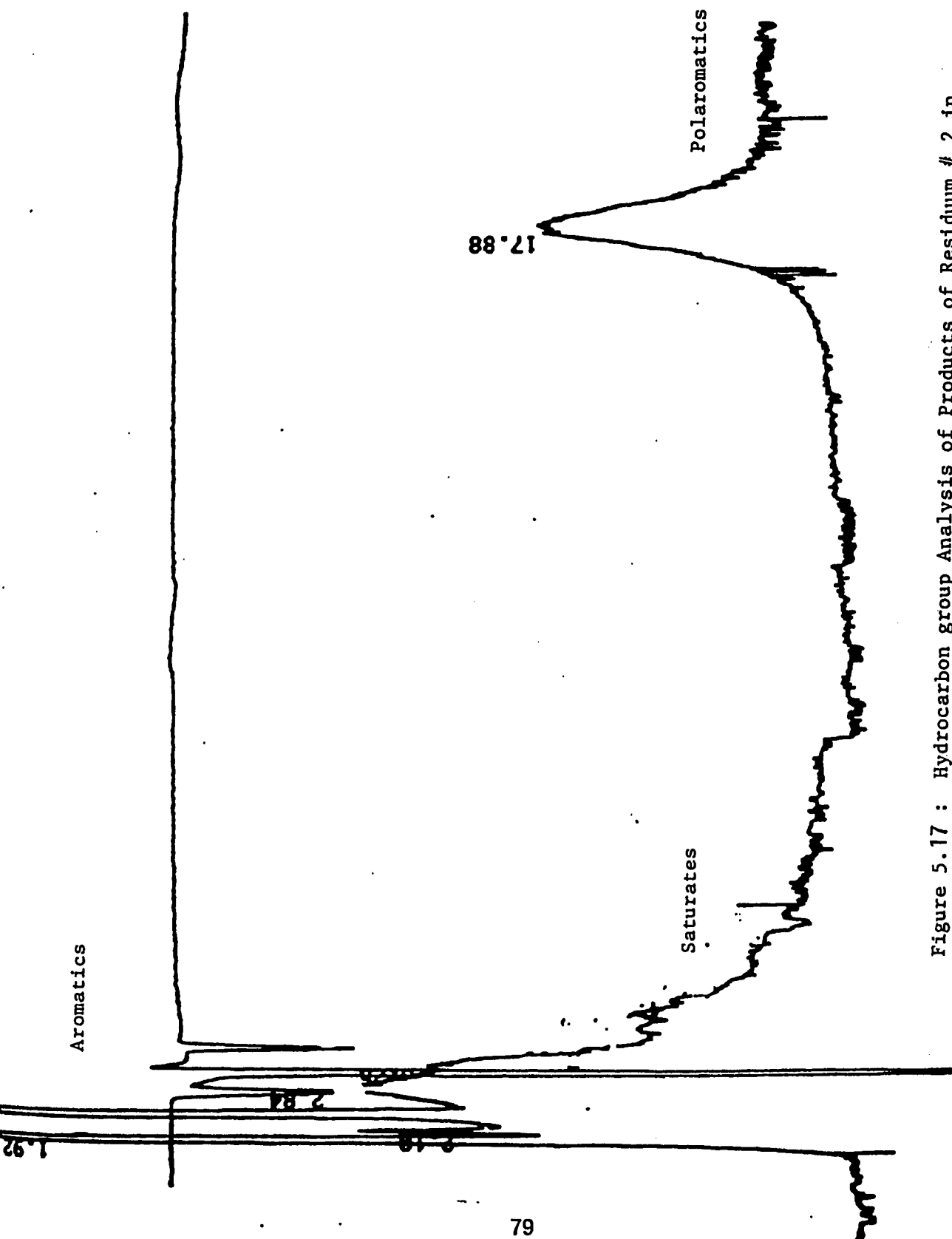


Figure 5.17 : Hydrocarbon group Analysis of Products of Residuum # 2 in Tetralin at 400°C (2/1 ratio).



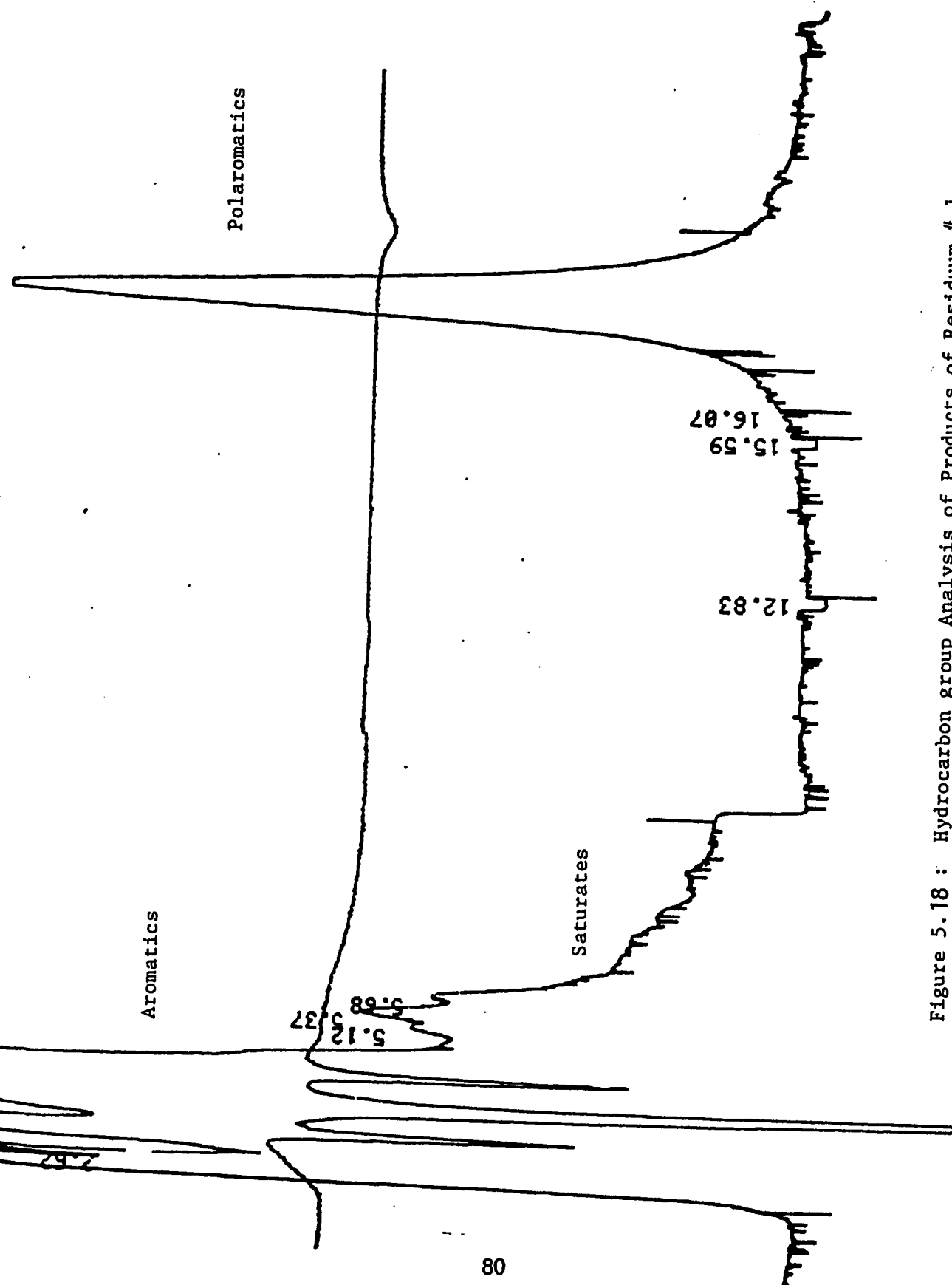


Figure 5.18 : Hydrocarbon group Analysis of Products of Residuum # 1 in Tetralin at 425°C.

comparison that a new peak in the saturates domain appeared (labeled N). Also many new peaks appeared in the aromatic domain. This is strong evidence of the conversion of the heavy fractions (asphaltenes and resins) into lighter ones. Figure 5.16 shows the peaks of the products at 400°C and an initial pressure of 1.5 MPa and a ratio of reactants of 1/1. Figure 5.17 shows the peaks at the same conditions but at a ratio of 2/1. Figure 5.18 shows the peaks of residuum #1 at 425°C.

### **5.6 Reactants Ratio**

The ratio of reactants is an important factor. It determines which reactant should be in excess. In thermal hydrogenation a special feature is the formation of coke. Reactants ratio determines whether coke is formed.

The changes of ratio studies were conducted at a temperature of 400°C and at an initial pressure of nitrogen of 4.0 MPa. Residuum # 2 was used in all of the runs. Products were analysed in terms of sulfur content. Table 5.5 indicates the results. This table shows that coke is formed whenever a ratio of tetralin/residuum  $< 2/1$  is used. It was also noted that traces of coke were formed when a ratio of 1/1 has been used. Thus the best choice on this basis is a ratio of reactants of 2/1. This ratio inhibits coke formation and guarantees an excess of tetralin for hydrogen consumption.

The sulfur content values presented give an indication that tetralin

**TABLE 5.5**

***Effect of Ratio on Sulfur and  
Coke Formation for Residuum # 2***

Ratio	Coke	Sulfur wt%	
		Feed	Product
1/0.5	No	1.50	1.45
1/1	Traces	2.25	2.06
1/2	Yes	3.00	2.76
1/5	Yes	3.75	3.39
ASTM METHOD		D1551	
Runs 1, 2, 3, 4 Temperature = 400 °C Reaction Time = 90 min. Initial Pressure = 4.0 MPa Ratio = Tetralin/Residuum (wt/wt)			

is an effective hydrogen donor.

### ***5.7 Pressure Effect***

Pressure can have an effect in thermal decomposition. Usually, increased pressure promotes reactions involving volume reduction: it suppresses dehydrogenation, but does not affect chain splitting. The marked effect here is to keep reactants in liquid form, thus preventing the solvent from evaporation. Homogeneous contact is essential for effective reactions. Also chemical forces are short range, making it necessary to keep reactants in the liquid form.

Pressure can have an effect on the rate of reaction although this is usually masked by the effect of temperature. This pressure effect is represented by the orientation factor in the collision theory. Chemical forces are known to be of short range and hence the effect of pressure. Thus it is important to keep the solvent in liquid form as the constituents of the residuum are already in the liquid form for purposes of better contact and reaction.

Several values of pressure were tried during preliminary stages. The role of pressure is to keep reactants in the liquid state, especially the donor solvent. The boiling point of the solvent is 207°C, and in the case of residuum # 2 the true initial boiling point is 350°C. So the effect of pressure is more obvious for the solvent. Being in a mixture there is a boiling point elevation of the solvent.

**TABLE 5.6**  
***Pressure Effect***

Pressure bar	API	Sulfur wt%	Asphaltene wt%
5	13.5	1.45	4.88
15	13.4	1.46	4.90
25	13.4	1.46	4.90
ASTM METHOD	D941	D1551	D2007
Residuum # 2 Runs # 19, 22, 24 Temperature = 400 °C Reaction Time = 90 min. Ratio of Tetralin/Residuum = 2/1 (wt/wt)			

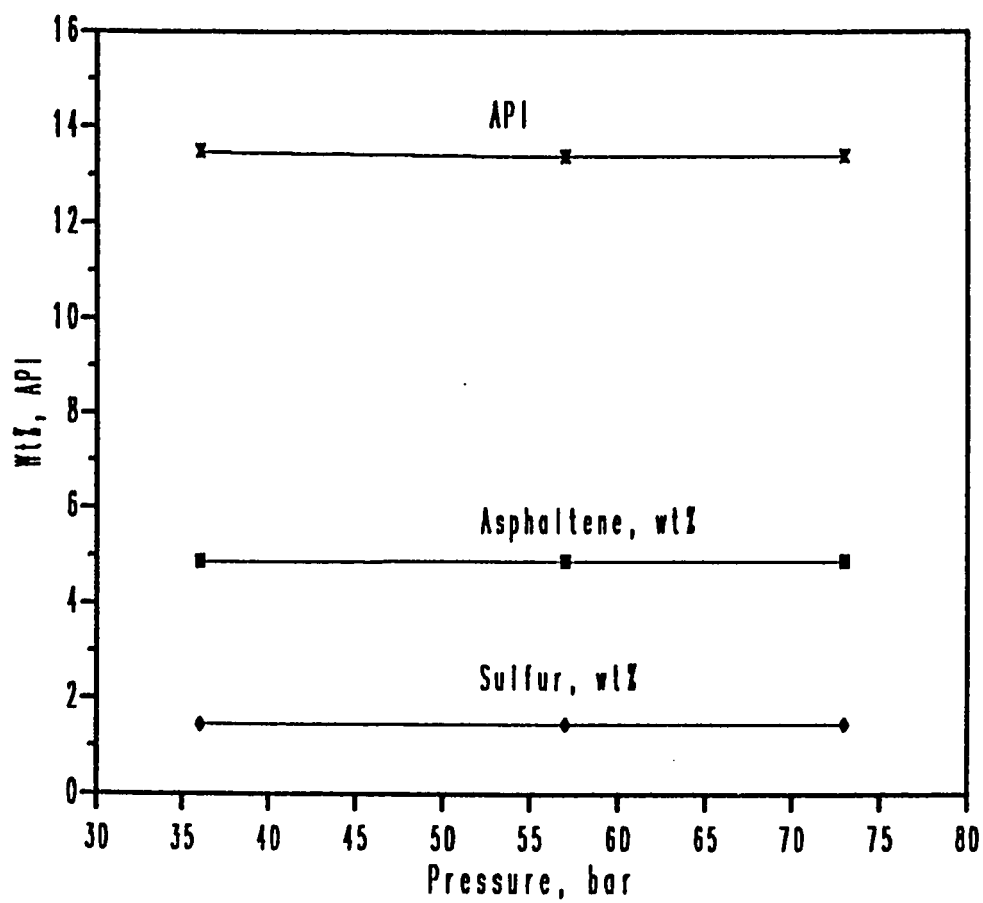


Figure 5.19 Variation of API and sulfur and asphaltene removal with pressure for residue # 2. (Table 5.6)

It has been found that an initial pressure of nitrogen of 0.5 MPa is sufficient for this purpose. This can be seen from Table 5.6 and Figure 5.19. There is no effect of pressures higher than 0.5 MPa on the API gravity, sulfur content or asphaltene content. It wasn't possible to try higher values of pressure without exceeding the pressure set point (10 MPa) and thus losing gaseous products. All of the runs were done at 400°C. The use of higher temperatures will be difficult for pressures higher than 1 MPa for the reasons mentioned above.

The same argument is true for hydrogen gas. The expected role of hydrogen gas is to hydrogenate naphthalene formed to tetralin, and to suppress the formation of hydrogen gas as a result of tetralin dehydrogenation to molecular hydrogen gas. This is true in case of catalytic reactions because hydrogenation of naphthalene is catalytic, and in this case the reaction of tetralin is in equilibrium. In noncatalytic hydrogenation the reaction is not an equilibrium reaction, so hydrogen gas is not expected to have any such effect.

### ***5.8 Temperature Effect***

The temperature of thermal decomposition not only affects the rate of reaction, but also determines the thermodynamically possible processes. Cracking is an endothermic process and so requires heat to release free radicals from the residuum constituents. On the other hand, hydrogenation of these radicals is exothermic. There is also a possibility of other reactions e.g., isomerization which is of negligible

heat of reaction, or in some instances is only slightly exothermic. The situation is complex; we don't have single reactions but rather a host of complex competing reactions including desulfurization and denitrogenation and others. The use of a high temperature is essential in order to release free radicals. This also increases the free energy and the rate of reaction.

In preliminary studies a temperature of 400°C was used at the beginning. Conversion at this temperature is not substantial. This can be seen from the results of sulfur change (Table 5.5, 5.6, 5.7 and 5.8). The relative percentage change at this temperature for residuum # 2 is only 3.4%. A change in Ramsbottom Carbon Residue of 8.5 % was observed (Table 5.9), and a change in asphaltene content of 23.7% was observed (Table 5.10). The results of Tables 5.9 and 5.10 are plotted in Figures 5.20a , 5.20b and 5.21a, 5.21b respectively.

Increasing the temperature increases the rate of reaction, so it was decided to raise the temperature to 425°C. An increased change in the asphaltene and carbon residue was noticed. This is obvious from Table 5.10 where the relative change at this temperature is 45%. The change in carbon residue is 21.3% (Table 5.9). The change on desulfurization is not significant. It is only 8.1% (Table 5.7). Increasing the temperature beyond this causes gas venting, and thus a loss of gaseous products. Although this was the case, a temperature of 435°C was tried. An increased change in asphaltenes and carbon residue was noticed. This can be seen from Tables 5.9 and 5.10 and Figures 5.20



and 5.21. Thus operation at higher temperatures increases conversion. A modification in the system is needed in order to allow work at higher temperatures. It was found that a temperature of 425°C is suitable, and produces considerable conversion.

The results obtained indicate that an increase in temperature will lead to an increase in the API gravity (a decrease in the specific gravity) of products. This can be seen from Table 5.11 and Figure 5.22. An approximately linear behavior of Ramsbottom residue is observed as is shown in Figure 5.20. This Figure also shows the percentage change relative to the feed value at each temperature. A similar trend is also observed for the change in asphaltenes as it is clear in Figure 5.21 and Table 5.10.

Gas produced at 425°C for residuum # 2 amounts approximately to 2 wt%. Refinery gas analysis show that among the gaseous products are: hydrogen, carbon dioxide, propane, propylene, i-butane, n-butane, hydrogen sulfide, ethylene, ethane and methane. These were the gaseous products for residuum # 2 at 425°C (Figure 5.23), and also at 400°C (Figure 5.24) with different proportions. The same products were also observed for residuum # 3 at 425°C (Figure 5.25). Hydrogen could be a hydrocracking product or a dehydrogenation product of tetralin. Oxygen which is not a gaseous product probably has entered during the sampling process. Carbon dioxide might be a product of indirect combustion especially with low olefinics. In this case water and carbon dioxide are the products. A probable source is air during sampling or

**TABLE 5.7**

***Sulfur Content (wt%) for  
Residua and their Products @ 425 °C***

Residue #	Feed wt%	Product wt%	Relative Change %
1	0.93	0.90	4.5
2	1.49	1.37	8.1
3	1.94	1.71	11.9
Runs # 16, 20, 23 Initial Pressure = 5 bar Reaction Time = 90 min. Ratio of Tetralin/Residuum = 2/1 (wt/wt) ASTM METHOD D1551			

**TABLE 5.8**

***Temperature and Pressure Effects on  
Sulfur content of Residuum # 2 Products***

Product Temperature °C	Pressure bar	Sulfur wt%
410	25	2.67
420	25	2.59
420	40	2.58
Feed	--	3.00
Reaction Time = 90 min. Ratio of Tetralin/Residue = 1/2 (wt/wt) ASTM METHOD D1551		

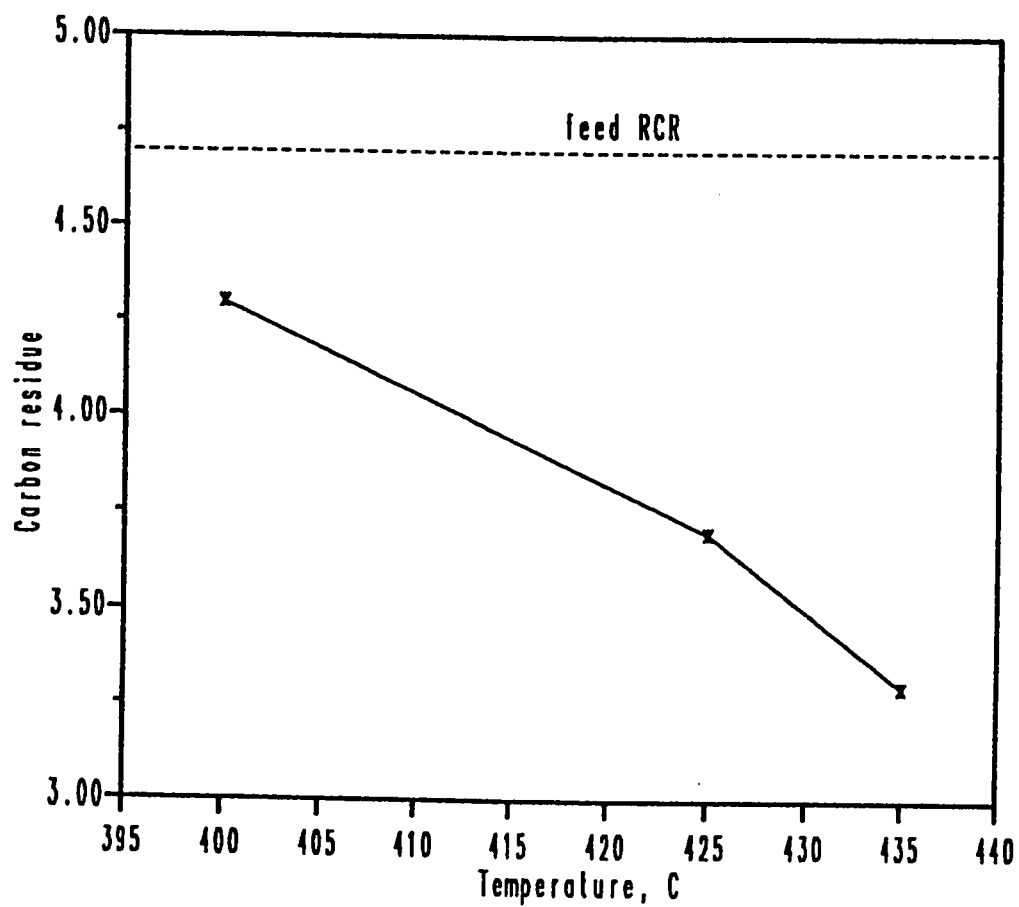
**TABLE 5.9**

***Ramsbottom Carbon Residue  
for Residuum # 2 and its Products***

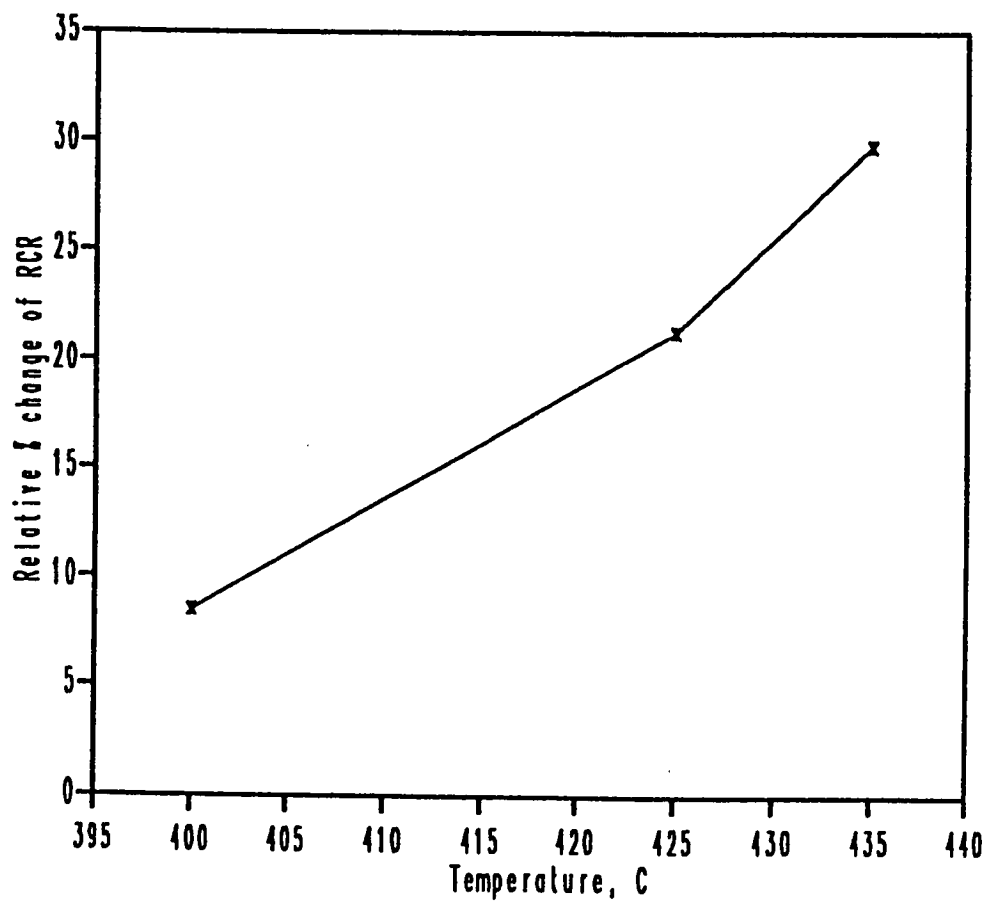
Product Temperature °C	Carbon Residue wt%	Relative Change %
400	4.3	8.5
425	3.7	21.3
435	3.3	29.8
Feed	4.7	
Runs # 19, 20, 21 Initial Pressure = 5 bar Reaction Time = 90 min. Ratio of Tetralin/Residue = 2/1 (wt/wt) ASTM METHOD D524		

**TABLE 5.10****Asphaltene Content for  
Residuum # 2 and its Products**

Product Temperature °C	Asphaltene wt%	Relative Change %
400	4.9	23.7
425	3.5	45.2
435	2.5	60.0
Feed	6.4	
Runs # 19, 20, 21 Initial Pressure = 5 bar Reaction Time = 90 min. Ratio of Tetralin/Residue = 2/1 (wt/wt) ASTM METHOD D2007		



*Figure 5.20a Variation of carbon residue with temperature  
(Table 5.9)*



*Figure 5.20b Relative percentage change of  
the carbon residue with temperature*

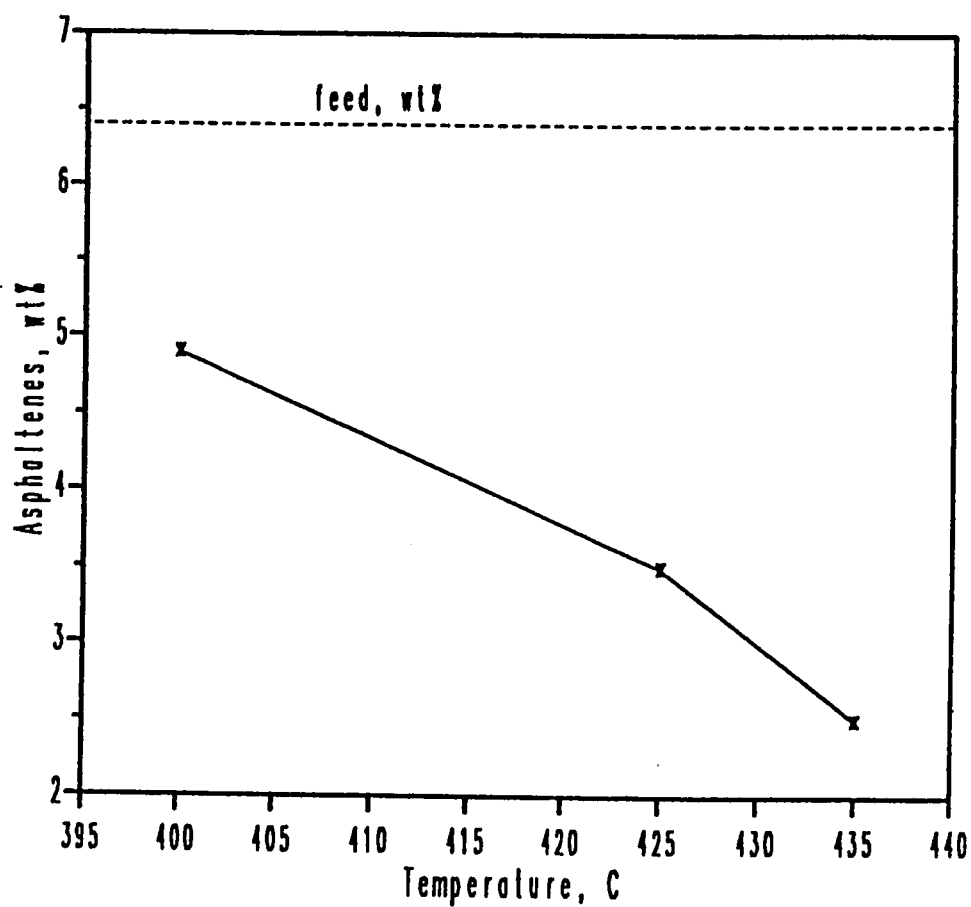
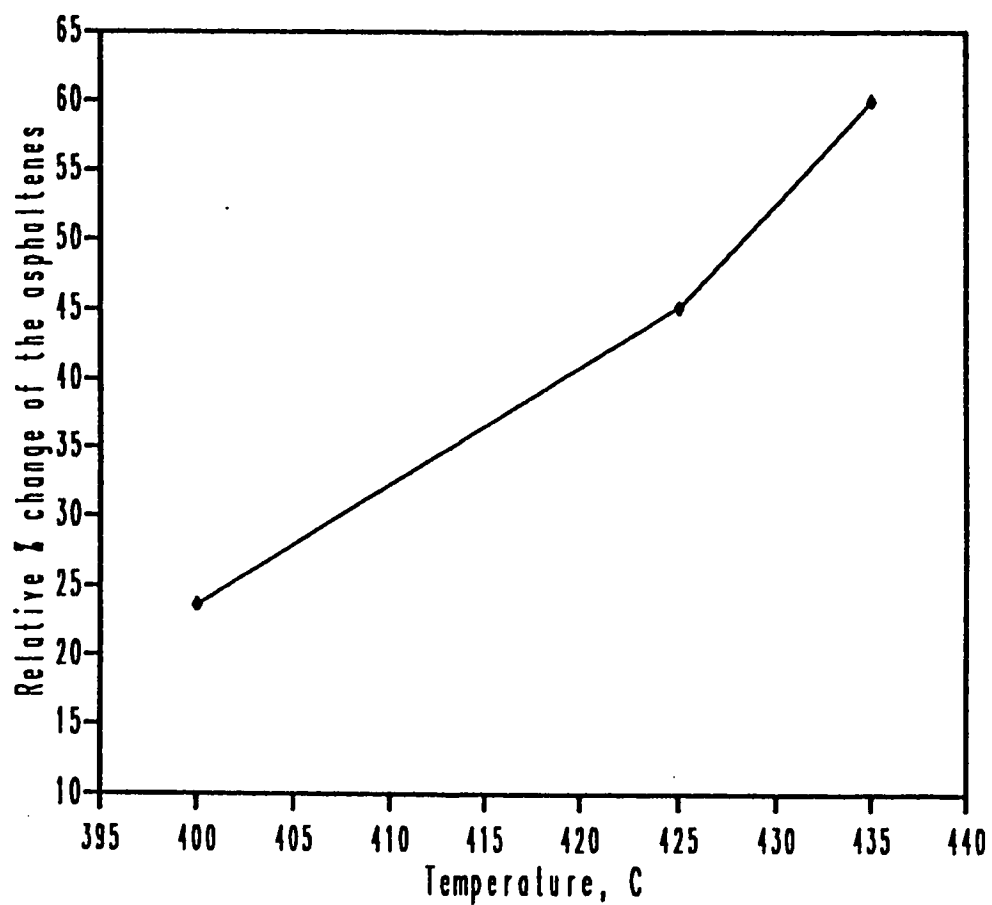


Figure 5.2/a Variation of asphaltenes with temperature  
(Table 5.10)



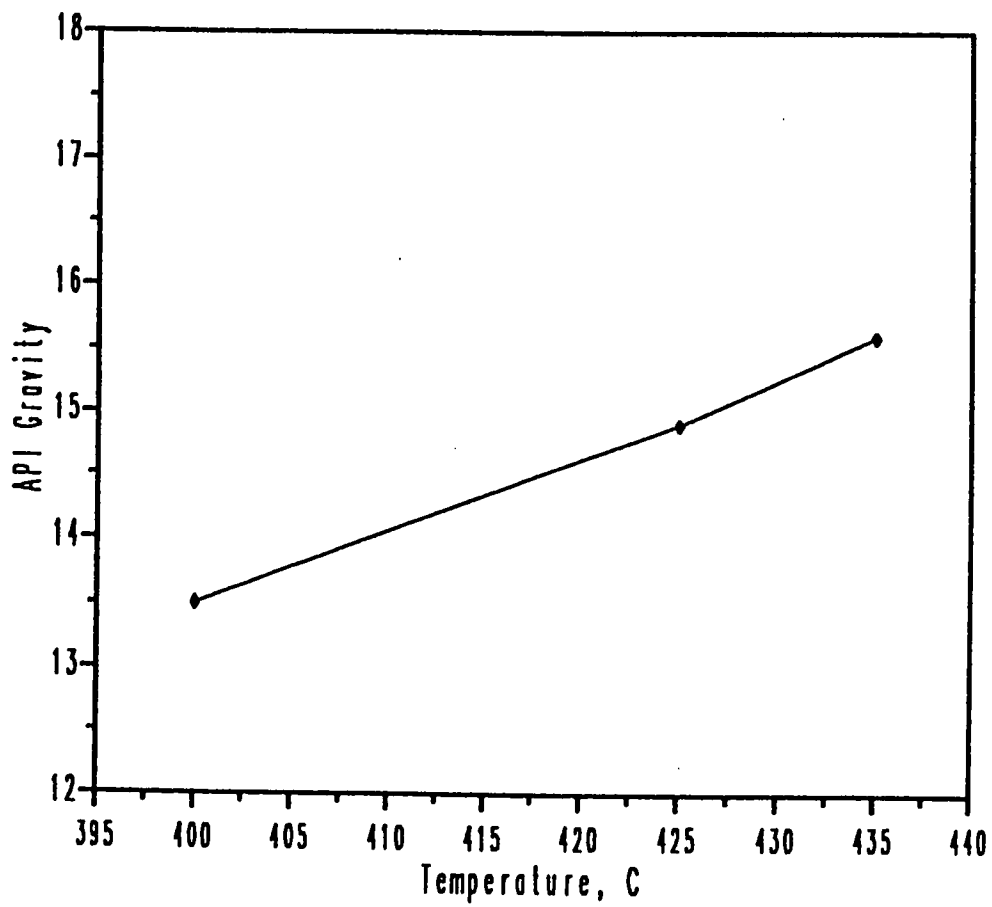


*Figure 5.21b Relative percentage change of the asphaltenes with temperature for residuum #2*

**TABLE 5.11**

**API And Specific Gravity @ 60/60°F  
for Residuum # 2 and its Products**

Product Temperature, °C	API	S.G.
400	13.5	.975
425	14.9	.966
435	15.9	.961
Feed	12.6	.982
Runs # 19, 20, 21 Initial Pressure = 5 bar Reaction Time = 90 min. Ratio of Tetralin/Residue = 2/1 (wt/wt)		



*Figure 5.22 Variation of API with temperature (Table 5.11)*

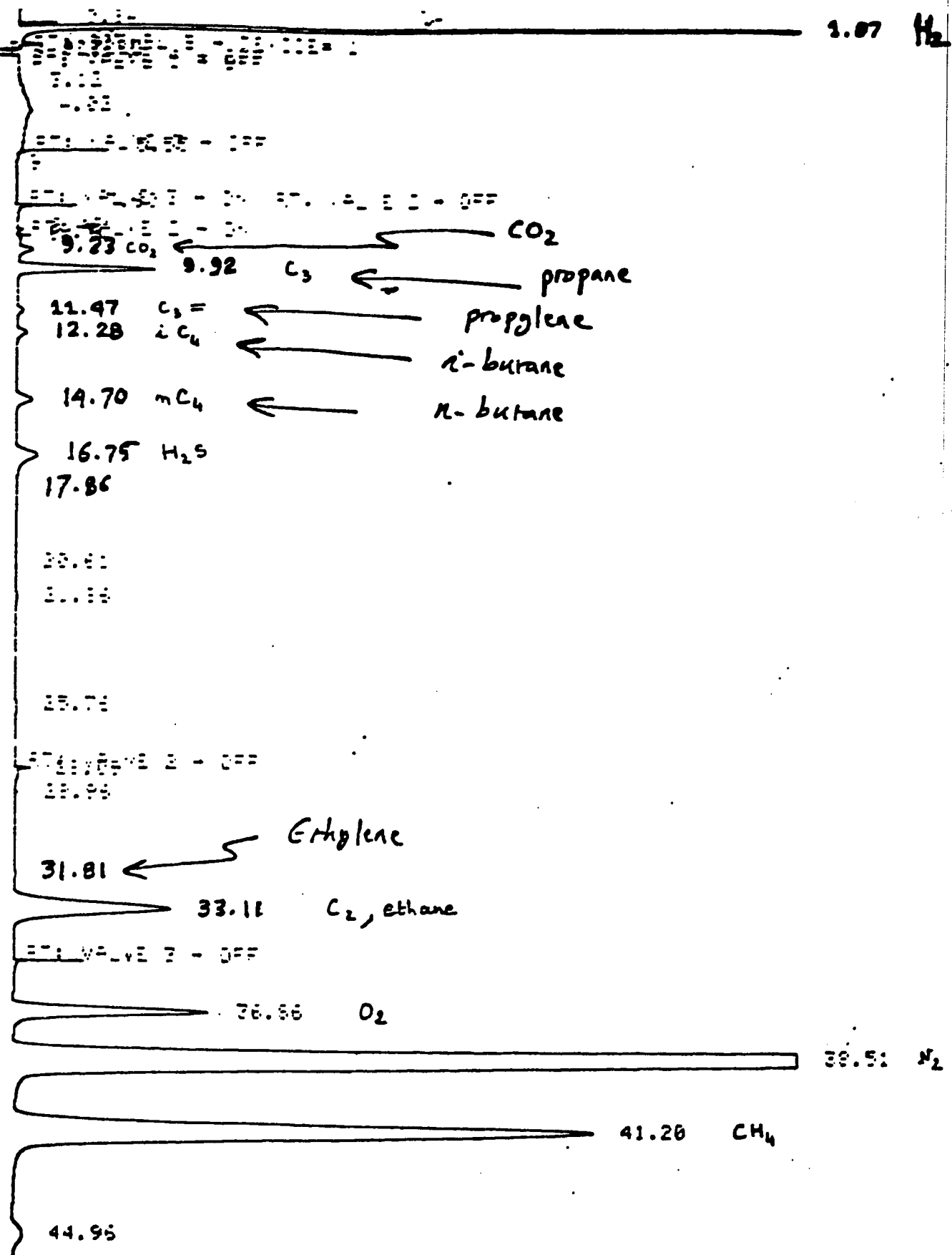


Figure 5.23 : GC chromatogram of gaseous products of residuum # 2 in tetralin at 425°C.

VALVE 3 → ON VALVE 2 → ON

1.02 H<sub>2</sub>

VALVE 3 → ON

VALVE 2 → ON

9.23 ← CO<sub>2</sub>

9.92 ← C<sub>3</sub>H<sub>8</sub>, propane

11.46 ← Propylene

12.29 ← isobutane

14.70 ← n-butane

16.74 ← H<sub>2</sub>S

21.85 ← n-pentane

VALVE 2 → OFF

31.79 ← Ethylene

33.19 ← Ethane

VALVE 3 → OFF

36.85 O<sub>2</sub>

38.44 N<sub>2</sub>

41.22 CH<sub>4</sub>

44.97

Figure 5.24 : GC Chromatogram of gaseous products of residuum # 2 in tetralin at 400°C.

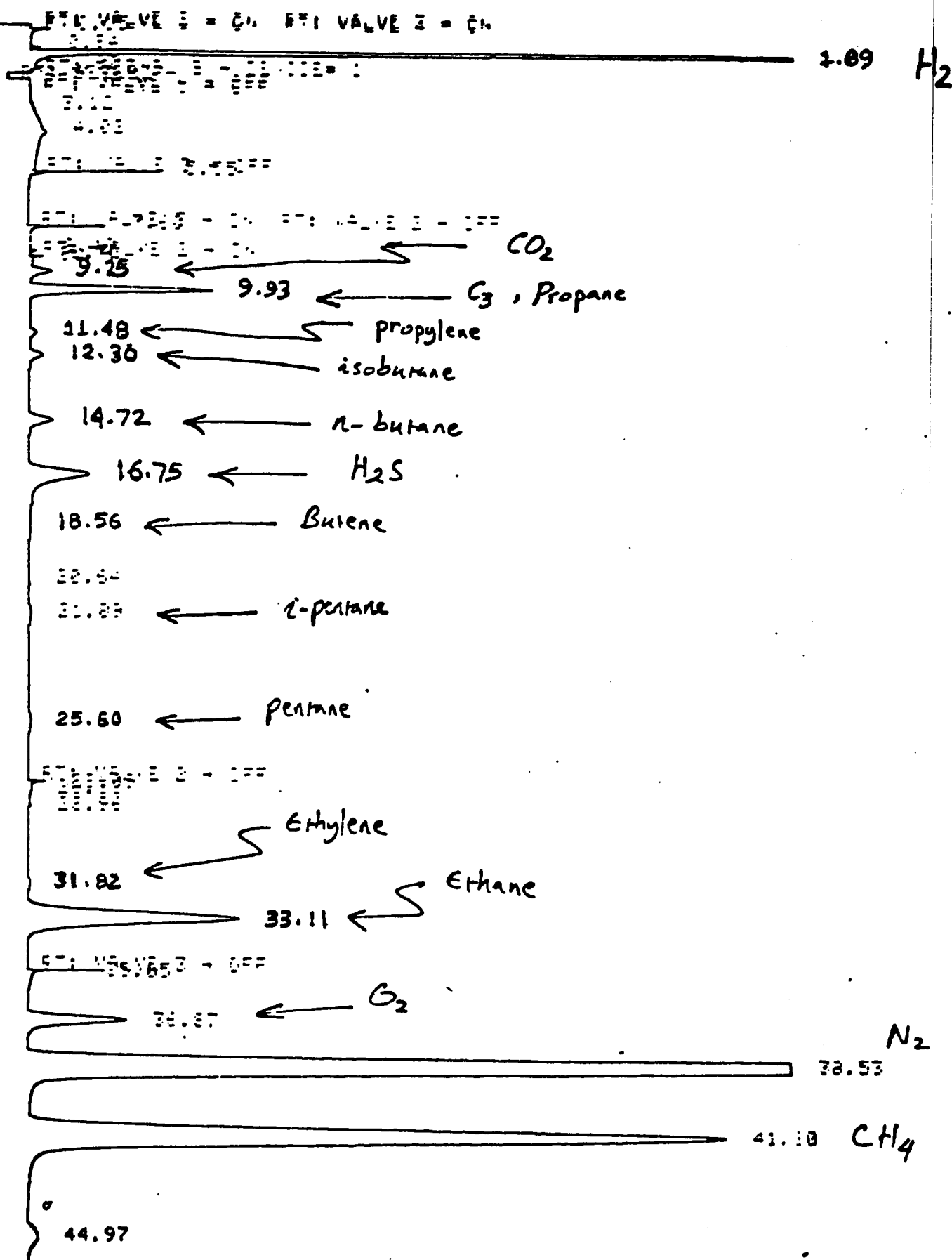


Figure 5.25 : GC chromatogram of gaseous products of residuum # 3 in tetralin at 425°C.

nitrogen.

A rough estimate of the contribution of gases show that hydrogen is approximately 35 % by volume while methane is 28 % by volume. Hydrogen sulfide amounts to 5 %.

Ramsbottom residue values at 425°C and the relative change for the three types of residua is shown in Figures 5.26, 5.26a and Table 5.12. It was found that as the API decreases, the carbon residue increases. The relative percentage change for residuum # 2 is slightly higher than that of residuum # 3. The same is observed with the asphaltene change (Figure 5.27 and 5.27a and Table 5.13). It seems that residuum # 3 needs more tetralin. The change for residuum # 1 is lower. It seems that free radicals for heavier fractions are more stable and that radicals of light fractions are less stable. The same can be said for sulfur change as can be seen in Figure 5.28 and Table 5.14, where the sulfur change increases as API decreases.

### *5.9 Pyrolysis of Tetralin*

In order to know what happens to tetralin under similar conditions of residua, a sample of tetralin was subjected to the same experimental conditions of the residua. 100 g of tetralin were heated to 425°C for 90 minutes under an initial pressure of Nitrogen of 0.5 MPa. Table 5.15 summarizes the conditions and results observed (see also section 3.4).

An extra pressure of 0.25 MPa of gases was observed upon cooling. The gaseous product was analysed by a refinery gas analyzer. Results

**TABLE 5.12**

***Ramsbottom Carbon Residue (wt%) for  
Residua and their Products @ 425 °C***

Residue #	Feed wt%	Product wt%	Relative Change %
1	2.1	1.9	9.5
2	4.7	3.7	21.3
3	8.6	6.8	20.9
Runs # 16, 20, 23 Initial Pressure = 5 bar Reaction Time = 90 min. Ratio of Tetralin/Residue = 2/1 (wt/wt) ASTM METHOD D524			



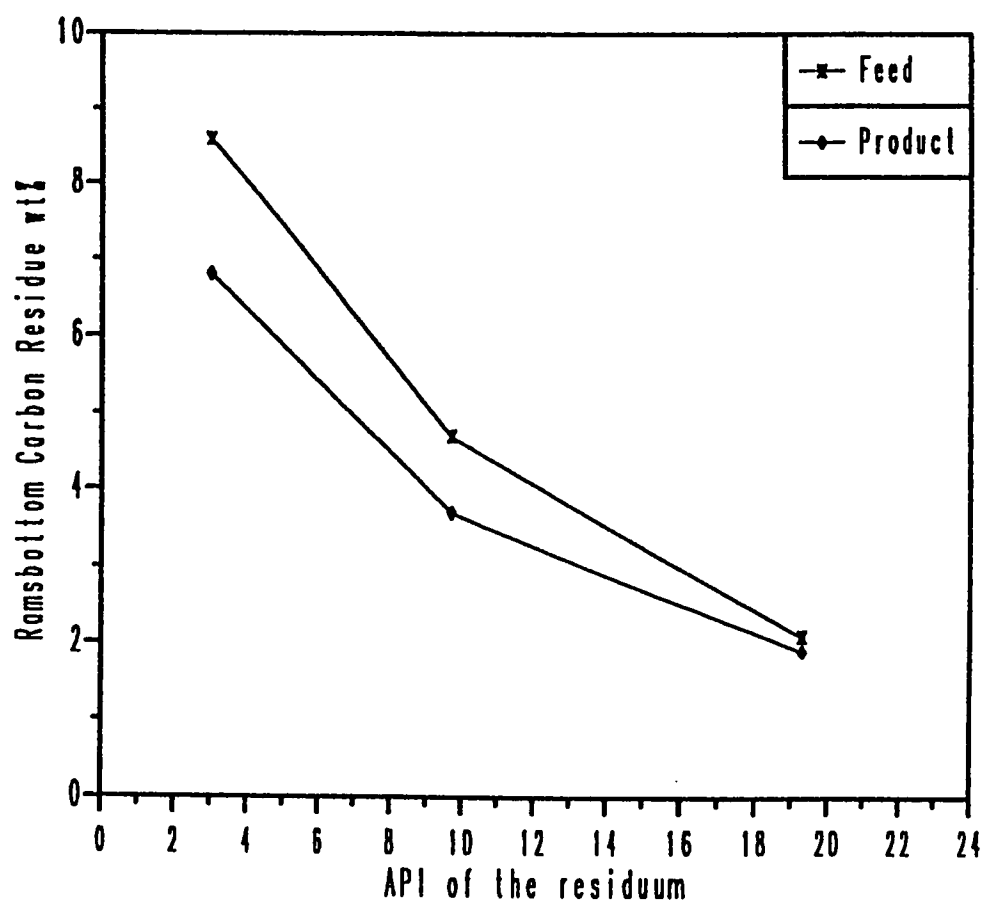
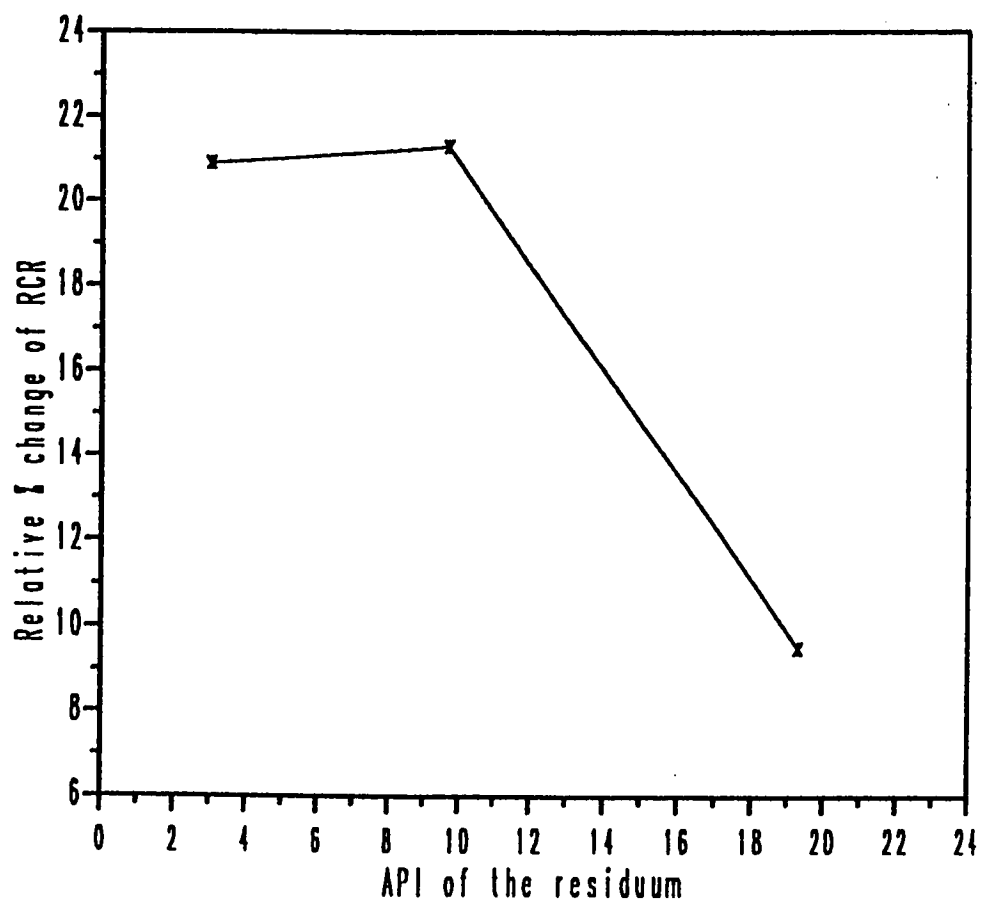


Figure 5.26 Variation, with API, of the carbon residue of the feed and products at 425 C. (Table 5.12)



*Figure 5.26a Relative percentage change of the carbon residue with API*

**TABLE 5.13**

***Asphaltene Content (wt%) for  
Residua and their Products @ 425 °C***

Residue #	Feed wt%	Product wt%	Relative Change %
1	2.5	1.6	36.0
2	6.4	3.5	45.0
3	11.2	6.2	44.6
Runs # 16, 20, 23 Initial Pressure = 5 bar Reaction Time = 90 min. Ratio of Tetralin/Residue = 2/1 (wt/wt) ASTM METHOD D2007			

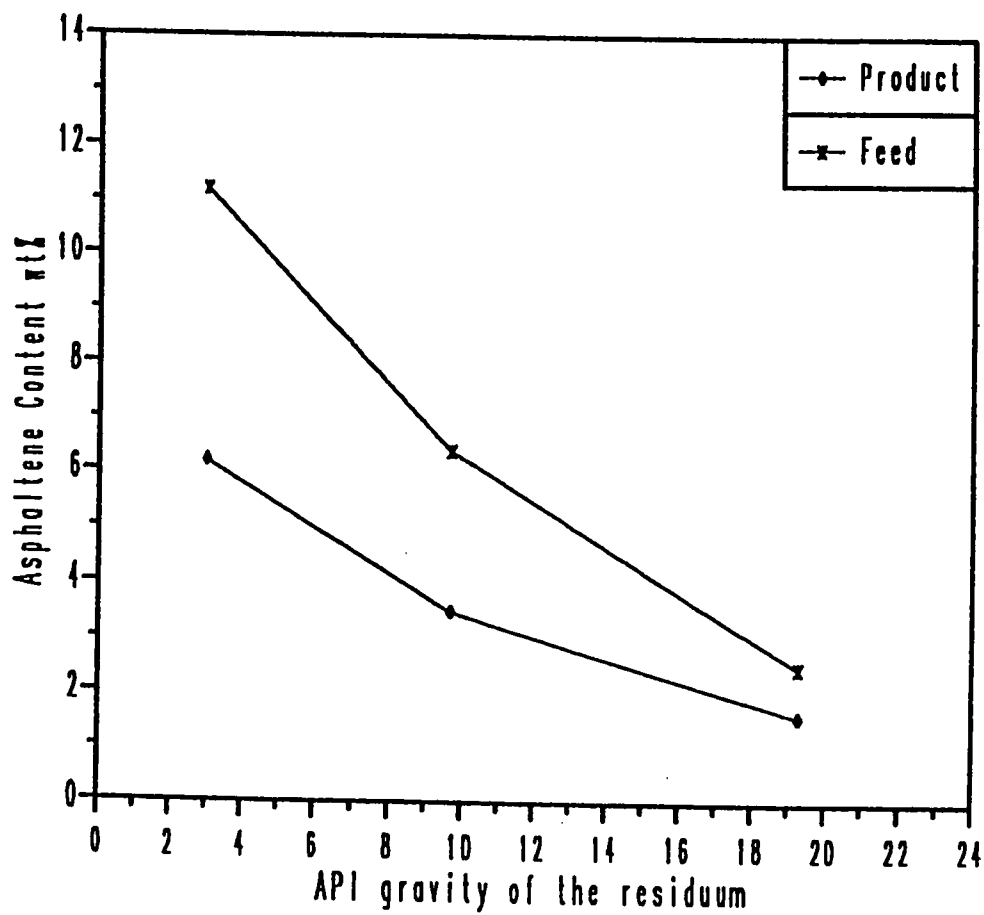


Figure 5.27 Variation, with, API, of the asphaltenes of the feeds and products of the residua at 425 C (Table 5.13)

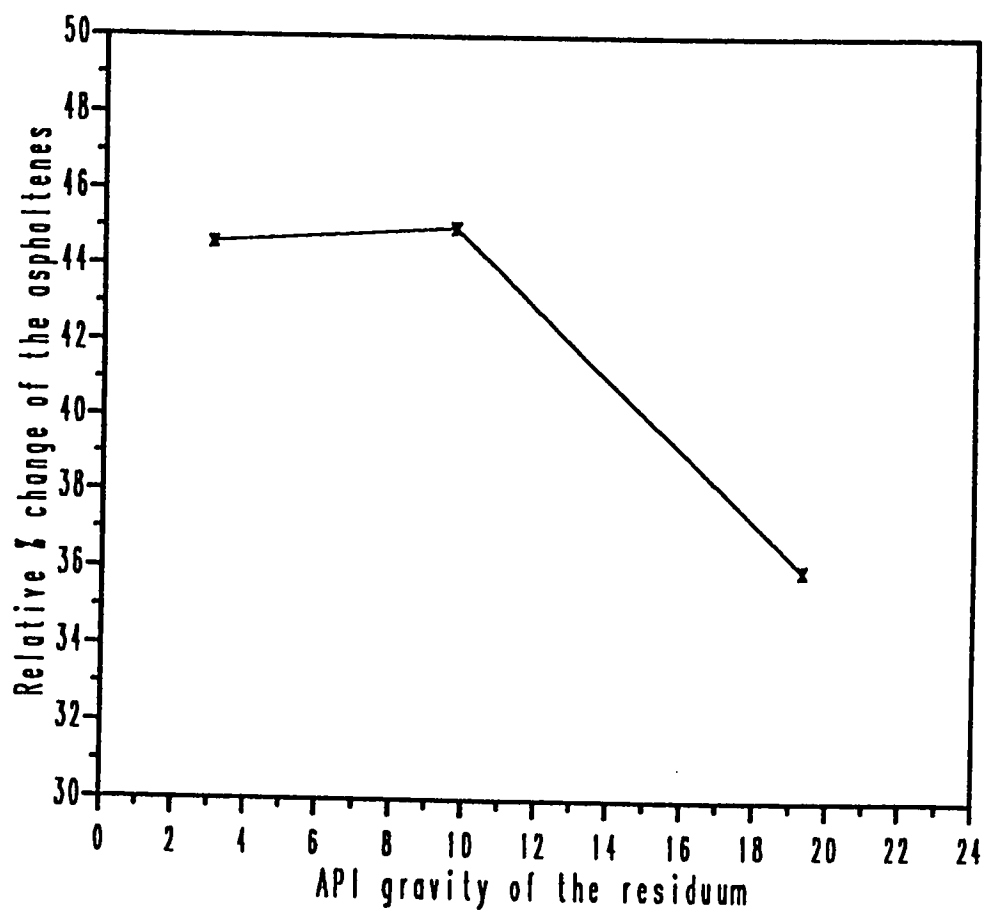
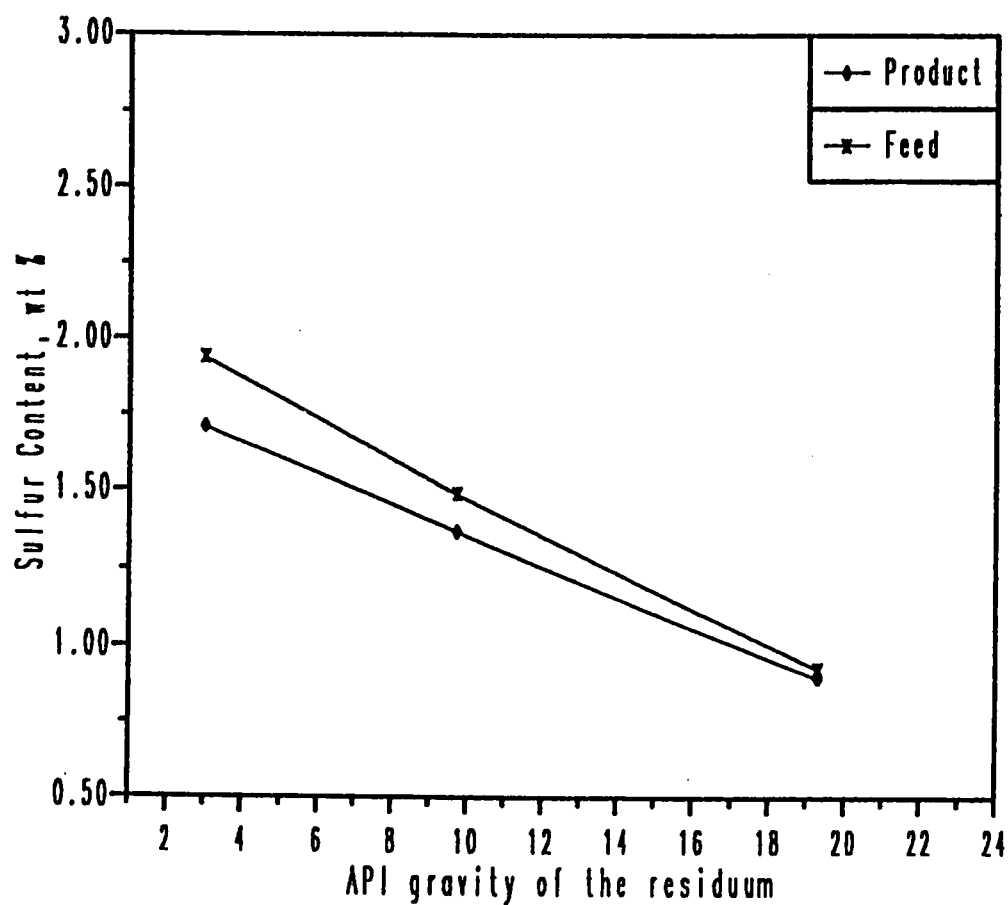


Figure 5.27a Relative percentage change of the asphaltenes with API



*Figure 5.28 Variation, with API, of sulfur removal of the feeds and products of residua at 425 C (Table 5.7)*

**TABLE 5.14**  
***Pyrolysis of Tetralin***

Runs # 25, 26, 27	
Initial Pressure of Nitrogen	0.5 MPa
Final Pressure	3.6 MPa
Temperature	425°C
Pyrolysis Time	90 min.
Weight of sample pyrolysed	100 g
Pressure after cooling	0.75 MPa

are shown in Figure 5.29. Hydrogen is the only gaseous product observed (retention time = 1.04). A very small peak of  $\text{CH}_4$  is also observed (retention time = 42.2). Tetralin is not liable to crack under these conditions as is stated in the literature. Methane could be a product of the disproportionation of Tetralin to methylindane and subsequently to indane, a reaction which has been observed in the temperature range of 400- 500°C. Oxygen (retention time = 36.85) is not a gaseous product. It might have come from Nitrogen or from air during sampling of the gases in the rubber balloon when it was subjected to evacuation. It might have entered during closing of the balloon or originally from reactor outlet lines. Hydrogen represents approximately 7% by volume of the gaseous product. The total gas produced is estimated to be 0.1 % by weight of the total sample.

The liquid portion was analysed by HPLC. Results are presented in Figure 5.30. Four peaks with retention times 1.93, 2.14, 2.47 and 2.98 were observed, which indicate the presence of aromatics. One saturate peak was also observed. Saturates are resolved according to refractive index.

In order to get a gross identification of the peaks, a sample of tetralin alone, a sample of naphthalene alone and a sample of an equal mixture of them were injected in to the HPLC. Results are shown in Figures 5.31, 5.32, and 5.33 respectively. Tetralin has one aromatic ring, whereas naphthalene has two rings. Figure 5.33 shows two major peaks of retention times 1.92 and 2.29. Figure 5.32 for naphthalene



alone shows a major peak of 2.29 and a small peak of 1.94 which is probably a trace of tetralin. Figure 5.31 shows two peaks with retention times 1.92 and 2.43. Obviously, by comparison, tetralin has a retention time 1.92 and naphthalene 2.29. The peak 2.43 in Figure 5.31 is not known. It doesn't appear in Figure 5.33 or is embedded under naphthalene peak. Figure 5.33 which shows the peaks of the heated tetralin shows a peak of 1.93 which is due to tetralin. A peak in the saturates domain is still there. Saturated peaks also appeared with naphthalene and with the mixture. These peaks could be attributed to some impurities due to their large size compared to tetralin and naphthalene peaks. Refractive index is a universal detector. Thus they could be peaks of this type. The peak with retention time of 2.14 in Figure 5.33 seems to be naphthalene (retention time 2.29 in Figures 5.32 and 5.33). If this is the case, then there is some dehydrogenation of tetralin to molecular hydrogen although not significant. If this peak wasn't considered as naphthalene, it must be other products of tetralin pyrolysis.

Studies on the pyrolysis of tetralin shows that the following processes may occur when tetralin is heated: disproportionation, dehydrogenation to naphthalene, and cracking. Extensive decomposition is observed only beyond 500°C. At 400°C ethylbenzene, propylbenzene, toluene and indane are formed. The first three may be regarded as products of the side chain cracking of butylbenzene which itself is formed from the  $\alpha$ -ring opening of tetralin [10]. The small peaks in Figure 5.33 could be methylindane or indane. Further investigation of

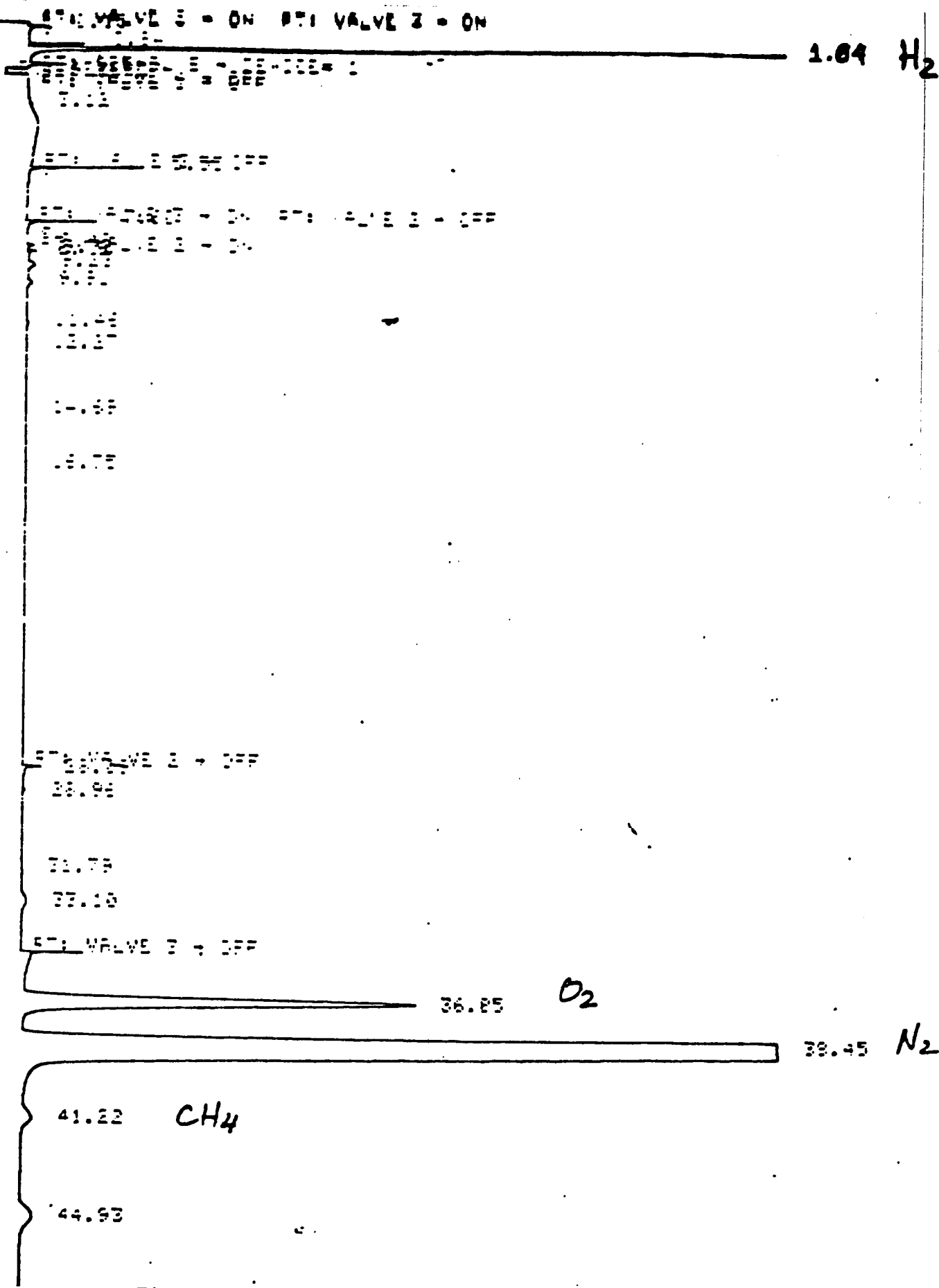


Figure 5.29 : GC Chromatogram of gases of Tetralin heated at 425°C.

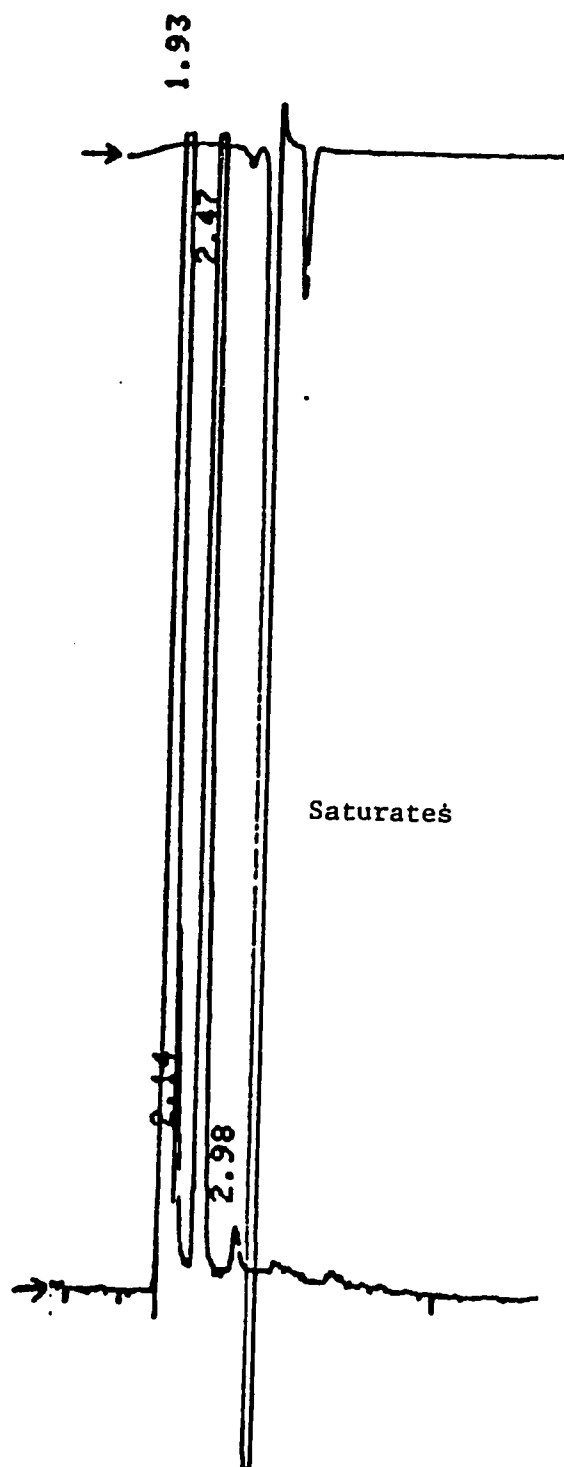


Figure 5. 30 : Hydrocarbon group Analysis of Heated Tetralin at 425°C.

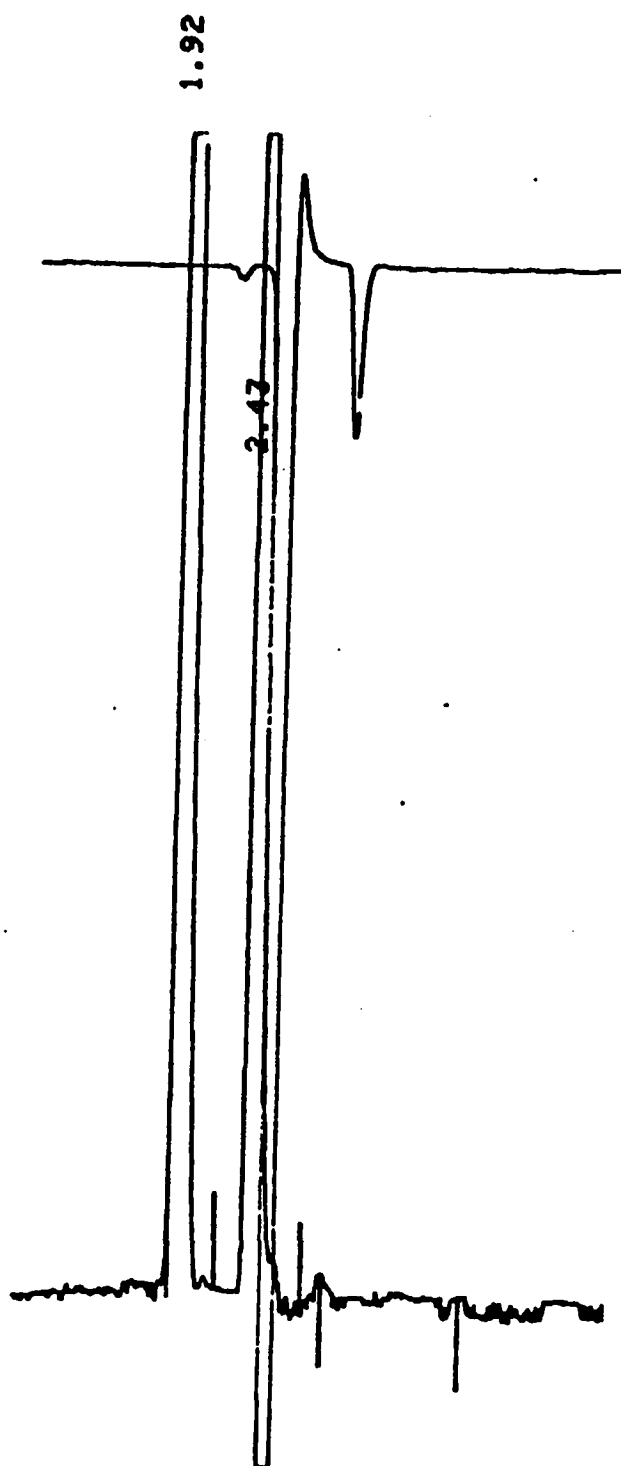


Figure 5.31 : Hydrocarbon group Analysis of Tetralin

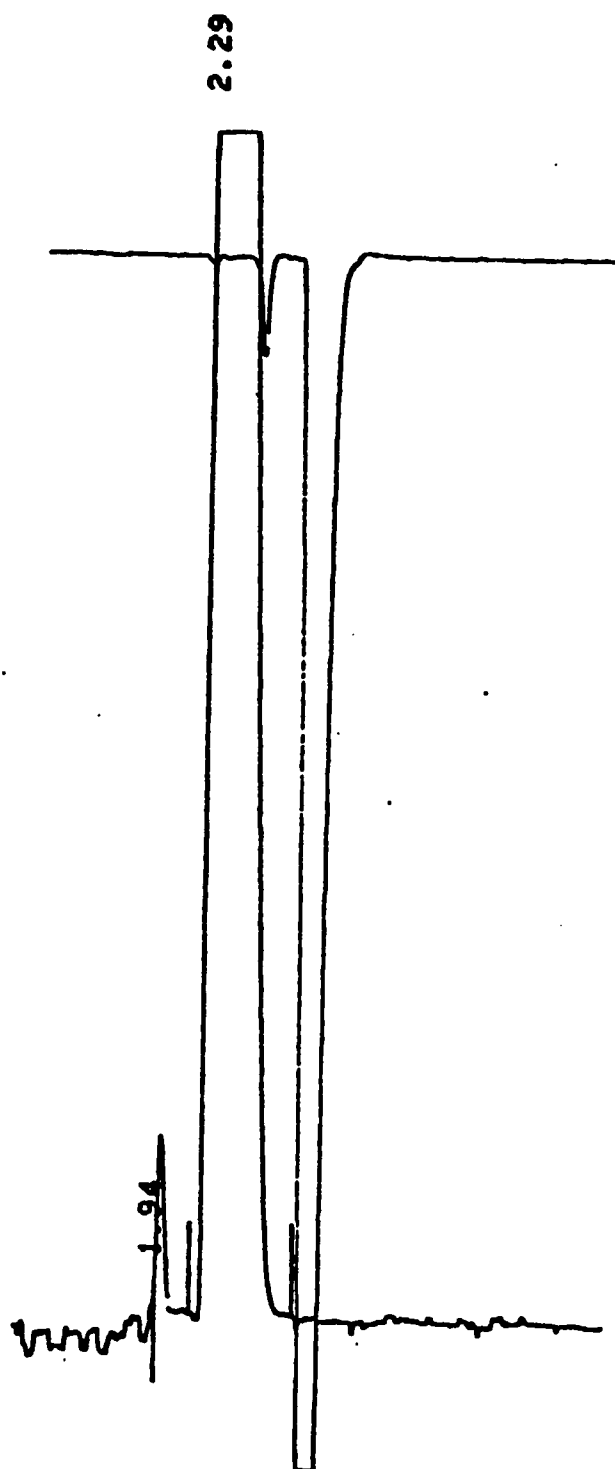


Figure 5.32 : Hydrocarbon group Analysis of Naphthalene.

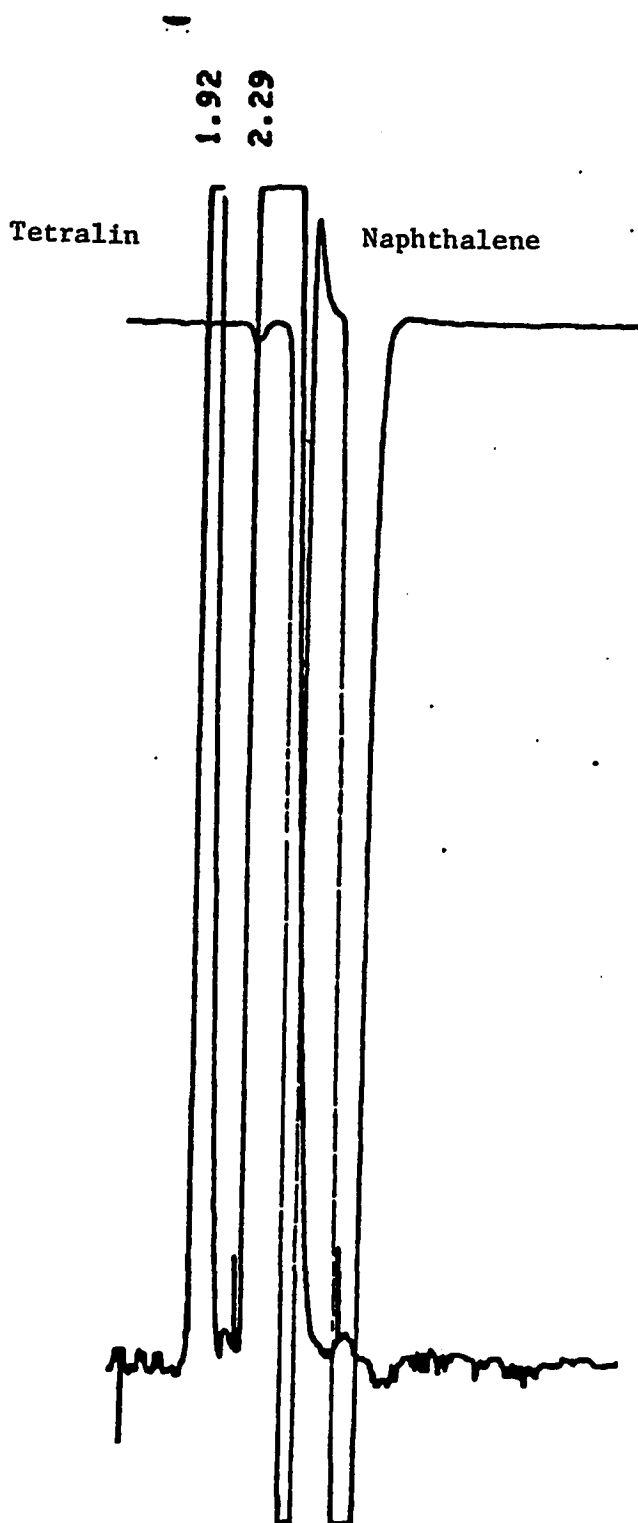


Figure 5.33 : Hydrocarbon Group Analysis of Tetralin and Naphthalene.

this point is recommended.

#### *5.10 Sulfur and Lumped Kinetics*

In hydrodesulfurization sulfur is removed as  $H_2S$  gas. If elemental sulfur is present in the oil, a reaction with the evolution of hydrogen sulfide begins at about  $220^{\circ}C$ , but organically bound sulfur is not released as hydrogen sulfide until higher temperatures are attained.

Removal of sulfur is complicated by the feedstock type, the presence of asphaltenes and the buildup of hydrogen sulfide. The residuum contains different kinds of sulfur compounds, nitrogen, oxygen and metallic compounds. Each reacts at a different rate due to the differences in structures and molecular weights. It has been shown that the sulfur removal increases after deasphalting, and that the buildup of  $H_2S$  gas decreases the rate of sulfur removal.

It was proposed to perform some lumped kinetic studies on total sulfur or asphaltenes. Sulfur removal is important because sulfur can deactivate the catalyst and has a bad pollutant effect. Sulfur change was not substantial as can be seen from Tables 5.7 and 5.8 and Figure 5.34. As temperature increases, percentage change of sulfur increases for residuum # 2. As the boiling range cut increases also the change of sulfur increases. It seems that the free radicals of the heavier fractions are more stable, thus they have the chance to hydrogenate. This seems not to be the case with residuum # 1. It seems also that in all cases, the formation of free radicals is a limiting step.

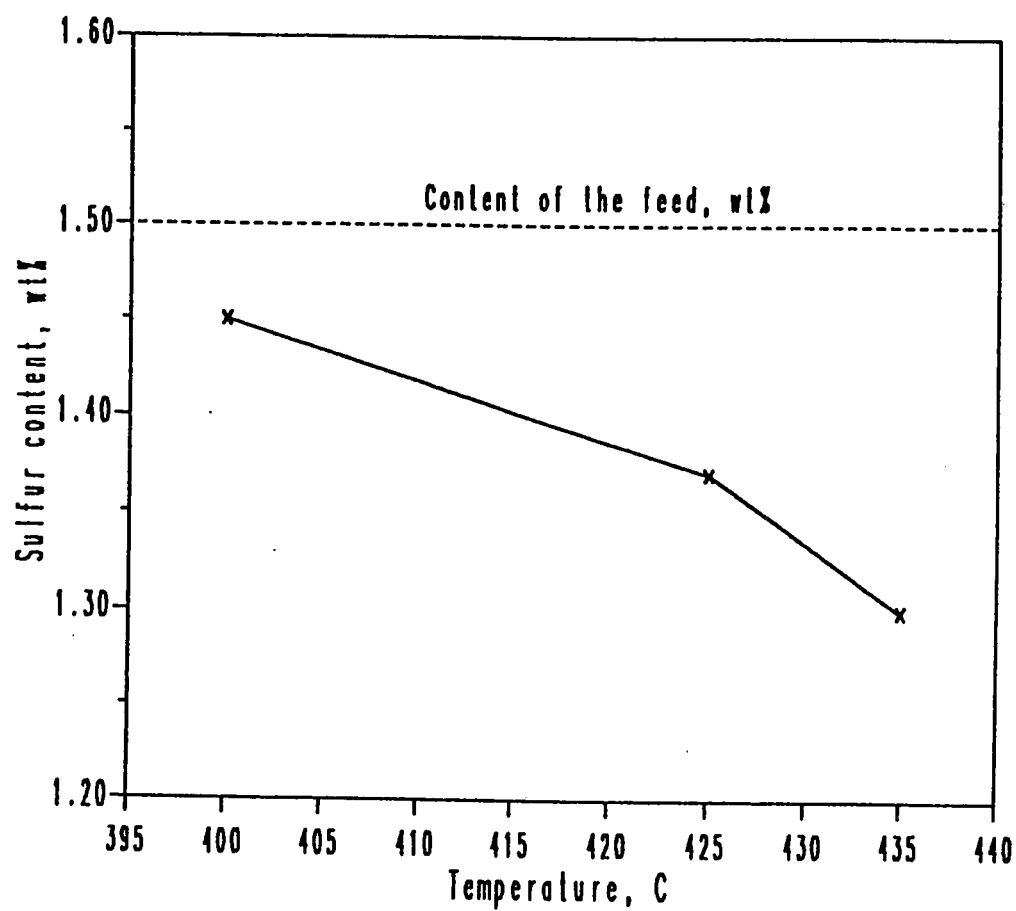


Figure 5.34 Variation of sulfur content with temperature for residuum #2



Heavy cuts mostly contain thiophenic sulfur structures. Once thiophenic structures are formed, it is very difficult to decompose or hydrogenate them. Thiophenes are very stable and do not decompose thermally even if heated to very high temperatures. Thiophene itself is stable up to 450°C even in the presence of alumina. Alkyl thiophenes lose the alkyl groups around 500°C. Substantial decomposition of the thiophenic ring occurs only around 800°C. Dibenzothiophene is stable up to at least 550°C. Decomposition of dibenzothiophene is catalysed by alumina or aluminosilicates. The sulfur takes part in the resonance of the hetero-ring and thus stabilizes the carbon-sulfur bonds. Hydrodesulfurization is in general a thermodynamically favorable reaction where the sulfur is not associated with an aromatic ring [49].

On the other hand, aryl sulphides are difficult to hydrodesulfurize because they are very stable and the sulfur is adjacent to an aromatic ring and takes part in the ring resonance. Thiols and disulfides are unstable and tend to decompose easily to  $H_2S$  and to unsaturated compounds.

Analysis of sulfur using the quartz tube method is time consuming. Also sampling for sulfur analysis during experimentation is not possible with the present setup. It needs to be modified. Each run of analysis takes 90 minutes and needs about 0.25 grams of sample. Also the long heating and cooling periods during reaction makes it difficult to consider this option. There must be a point of contact between reactants at similar conditions. A modification as shown in Figure 5.35

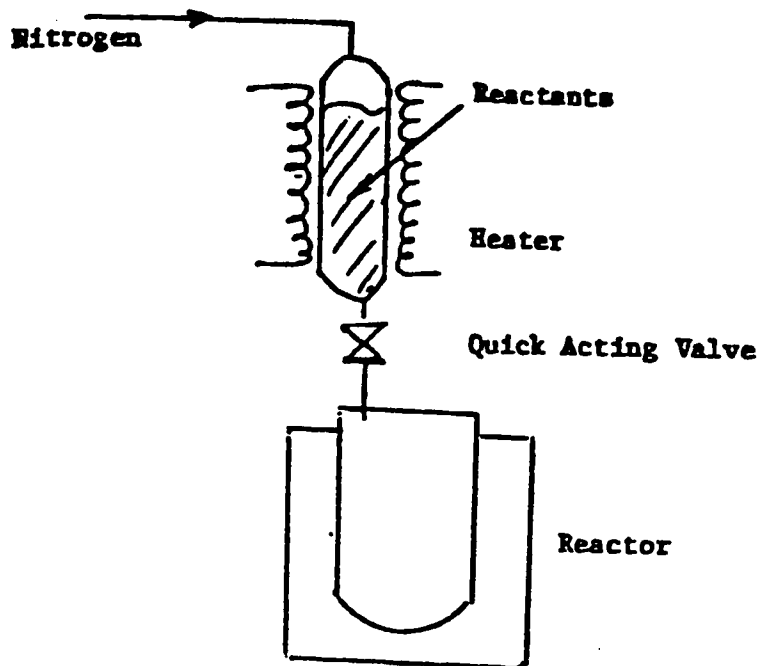


Figure 5.35: Arrangements for rapid injection of reactants (relevant parts only)

may solve this problem, where one of the reactants may be injected under pressure after preheating and mixed with the other one.

Thus lumped kinetic studies in terms of total sulfur change is not useful without the separation of solvent and products, because this kind of study is specific. Also the change in sulfur is not significant.

#### *5.11 Advantages of the Hydrogen Donor Process*

The main advantage of hydrogenation by a donor solvent is the complete absence of the catalyst. There is little or no coke formation. This is clear from Table 5.5 where the best choice of tetralin to residuum ratio is 2/1 wt/wt. In this case coke has not formed at all. Using a ratio of 1/1 produces little coke, and if a lower ratio is used more coke will be formed. Thus the problem of catalyst deactivation is of no significance here, partly because no catalyst is used in this process and if it was used there would be no coke deposition on the catalyst.

Catalyst deactivation in upgrading processes is caused by two things: coke formation and deposition of organometallic compounds of ash-forming constituents with nickel and vanadium being the predominant metals. The exact mechanism of deactivation by metals deposition is subject to speculation. However, nickel tends to be deposited throughout the catalyst, whereas vanadium is more concentrated in the outer layers of the catalyst.

The deposition of coke is believed to be due to the condensation reactions that are an integral part of any thermal (even hydrocracking) process in which heavy feedstocks are involved as explained in detail in chapter two. Heavy oils and residua contain large molecules in their original state (also tend to form during processing); these large molecules are not sufficiently mobile (or are too strongly adsorbed by the catalyst) to be saturated by the hydrogenation components and, hence, continue to condense and eventually degrade to coke. This will deactivate the catalyst. This will be the case even with a deasphalted feedstock, i.e., a heavy feedstock from which the asphaltenes have previously been removed. Resins almost play a similar role to asphaltenes.

In hydrogenation donor processes, no coke is formed at all provided that a proper ratio is chosen. Thus the problems arising from coke formation are eliminated. When coke is formed it must be discarded or desulfurized and burned. This lowers the yield of useful hydrocarbons. When coke is deposited in the reactor, insulator layers are formed. These resist heat transfer, thus requiring more heat load, and this causes overheating leading to more coke formation.

In summary deposition of coke and organometallic compounds causes catalyst deactivation and requires a greater heat load causing overheating. These effects are partly eliminated because coke formation is inhibited and hydrotreating is possible, although not substantial as can be seen from sulfur removal (Table 5.7). Frequent regeneration or

replacement of the catalyst is completely avoided. However, sulfur is expected to be distributed throughout the boiling range of the cracked products, and if conventional methods of desulfurization are used then the contamination with the catalyst is avoided.

Hydrogen donor cracking can work at substantially lower pressures than are necessary with the use of molecular hydrogen in hydrocracking. The consumption of hydrogen in hydrogen donor cracking may be comparable to that of hydrocracking. It is estimated that when a ratio of tetralin to residuum of 2/1 is used, 1340 ft<sup>3</sup> (STP) per barrel will be consumed if 35% of tetralin is converted to naphthalene; and 670 ft<sup>3</sup> if a ratio of 1/1 is used.

Hydrogen donor may be needed only in the initial stages because part of the hydrocracked liquid may be used as a source of hydrogen after hydrogenation by conventional methods. This stream also dilutes the highly viscous stream and reduces pumping problems.

Gases produced can be used as a source of molecular hydrogen after steam reforming or as fuel gas because it has high heating value.

## **CHAPTER SIX**

### **6.1 Conclusions**

- (1) Tetralin is an effective hydrogen donor for Arabian residua.
- (2) A ratio  $> 1/1$  (wt/wt) of tetralin to residuum inhibits coke formation and provides an excess of tetralin. Ratios  $< 1/1$  produce coke in amounts proportional to the ratio.
- (3) As the temperature increases the conversion to lighter products increases. About 50% change of the asphaltenes is observed at 425°C.
- (4) Higher conversion is achieved with heavier residua.
- (5) Degree of desulfurization increases with temperature.
- (6) An initial pressure of nitrogen of 0.5 MPa is sufficient to keep reactants in the liquid state. Otherwise, the pressure has no effect.

## 6.2 Recommendations

The analysis of the products turned out to be a difficult job, and in some cases misleading. This is mainly due to the inhomogeneity of the products. Therefore, it is recommended that the products be separated into fractions, and each fraction can then be analysed separately. The percentage of each fraction can be determined along with other physical and chemical properties. Comparison on this basis is better and obvious i.e., at different operating conditions of temperatures and pressures. It is also recommended that among the fractions to be separated is the fraction including tetralin and derivatives, so that the spent donor can be rehydrogenated.

The rehydrogenation of the spent donor is important; this means that the solvent will be used at the initial stage only. The process of rehydrogenation of the spent donor needs to be studied.

The conversion on the basis of asphaltenes does not exceed 50% at 425°C. It is believed that conversion will increase if cycling is used, i.e., after separation into fractions, the heavier one to be treated again until a considerable conversion is obtained.

In this study, tetralin alone was used as a hydrogen donor solvent. Other solvents may be used provided they are of fused naphthenic-aromatic type. Also petroleum fractions such as light cycle oil may be used as donors.

Separation into fractions enables one to study lumped kinetics in terms of certain variables e.g., sulfur or asphaltene. However, the system need to be modified for rapid injection. Model compounds can be used to study hydrodesulfurization with donor solvents.



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