EVALUATION OF THE ENGINEERING PROPERTIES OF FRACTIONATED AND RECOMBINED ASPHALT CEMENT

By

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1988

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May, 1992

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ACKNOWLEDGMENTS

With profound appreciation, I wish to express my sincere thanks to my major adviser, Dr. Michael E. Ayers, for his interest, timely professional advices, continous encouragement and friendship, and to the Oklahoma Department of Transportation for providing the necessary funding.

Appreciation is also extended to Dr. Samir Ahmed and Dr. Oberlender for serving on my committee.

I would like to offer special thanks to my parents and other family members for their encouragement and support.

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INTRODUCTION

Problem Statement

It is claimed by many pavement technologists that the quality of much of the asphalt cement currently being produced is inferior and its properties are not comparable to those produced 20 or more years ago. The 1973 oil embargo is generally cited as the basis for these claims. The shortage of crude oil and the variability in the sources of crude oil available to many refineries is thought to be the cause. Crude oil sources are known to have a dramatic effect on the properties of refined asphalt cement. Another reason for the changes in the properties of asphalt cement are new refining and manufacturing techniques. It has been observed that asphalt cements from different sources meeting the same specification criteria often produce pavements with widely different performance and servicability characteristics.

The incompatibility of various asphalt cements is problematic for producers of asphalt products and end users. The composition of asphalt cement determines both its engineering properties and performance. Therefore, this study was undertaken to determine correlations between the composition and engineering properties of asphalt cement. These correlations may be used for blending asphalt cements to achieve specific material properties.

Objective of the Study

The objective of the study is to gain a basic understanding of the relationship between selected asphalt cement fractions and their effect on the engineering properties.

Scope of Work

The scope of work includes:

1. Literature Review
2. Fractionation of asphalt cement into four constituent fractions:
    a. Asphaltenes
    b. Saturates
    c. Naphthene Aromatics
    d. Polar Aromatics
3. Determination of the weight percentage of each fraction.
4. Preparation of recombined samples by blending individual fractions into the non-fractionated or reference asphalt cement (125, 150, 175, 200, 250 and 300% of the weight percentage of the each fraction was evaluated).

5. Assess changes in material properties by performing the following tests:
    a. Penetration Test
    b. Absolute Viscosity Test
    c. Kinematic Viscosity Test
    d. Thin Film Oven Test

CHAPTER II

LITERATURE REVIEW

The American Society for Testing Materials established the following definition [1]:

Asphalt - A dark brown to black cementitious material, in which the predominating constituents are bitumens, which occur in nature, or are obtained in petroleum processing.

Asphalt is one of man's oldest engineering materials. Its adhesive and waterproofing properties were utilized as early as 6000 B.C. in Sumeria where it was used in the ship building industry. The area between the Euphrates and Tigris Rivers in Iraq contained the earliest documented deposits of asphalt and heavy liquid petroleum. It was also used by the Egyptian's as a waterproofing material as early as 2600 B.C.[2].

These early asphalts occured naturally. They were found in geological strata both as soft, readily workable mortar and also as hard, friable rock. These soft asphalt products are referred to as natural asphalts and were used extensively until the early part of this century.

In the early 1900's, the process of obtaining asphalt cement from the refining of crude petroleum created a fast growing industry. The popularity of the automobile was largely responsible for the increased demand for asphalt cement to be used in pavements. Asphalt cement appeared to be an inexpensive and inexhaustible resource that could be used to construct smooth, modern roads and in numerous other applications.

As the asphalt paving industry developed, the properties and characteristics of asphalt cement needed to be determined. It was recognized that the behavior and engineering properties of asphalt cement were dependent on its chemical composition.

Asphalt cement is a heterogeneous mixture of complex compounds. The various types of hydrocarbon molecules and the different molecular sizes found in asphalt cement make it a complex material. Asphalt cement contains oxygen, nitrogen, sulfur, and certain metals such as vanadium and nickel. Its molecular structure ranges from straight chain to cyclic molecules, thereby complicating the interactive structure [2].

Asphalt Composition as Defined by Fractionation

Asphalt cement is so complex that chemists have encountered numerous problems in studying its composition. However, during the past several decades new equipment and techniques have been developed for the fractionation of asphalt materials, and evaluation and analysis of the resulting fractions.

Fractional separation has been the basis for most asphalt cement compositional analysis for approximately 30 years. A variety of procedures have been employed in an attempt to fractionate asphalt into less complex and more homogeneous fractions. Many of these techniques are specialized and unique to a given area of research. Several, however, have found more general use for characterizing and classifying asphalt cements.

Since the fractionation of asphalt cement was one of the primary tasks of this study, numerous fractionation techniques were reviewed in order to select the most feasible technique. A brief outline of the different compositional analysis techniques, including fractionation are presented below:

The various techniques can be categorized into two primary groups.

I. Fractionation Techniques
    1. Fractionation by precipitation.
    2. Fractionation by distillation.
    3. Chromatographic separation.

II. Analysis Techniques
    1. Chemical analysis
    2. Molecular weight analysis by mass spectroscopy, vapor pressure osmometry, size exclusion chromatography.
    3. Indirect compositional analysis by internal dispersion stability technique.

Fractionation Techniques

Fractionation by Precipitation

This fractionation technique includes separation by solvent precipitation and chemical precipitation.

Solvent Precipitation. Solvent precipitation is sequentially treating the asphalt cement with increasingly polar solvents. Which causes a series of fractions with decreasing polarity. This technique has not been widely used. Although it avoids contact with reactive adsorbants and chemicals that might irreversibly adsorb or alter asphalt cement fractions, the fractions obtained are usually not as distinctively different as with other separation techniques.

a. Richardson Method [3,4]. This method uses naptha to separate asphalt into asphaltenes and maltenes.

b. Hoiberg Method [5]. This method uses polar solvents for the separation of asphalt cement into five fractions including:

-asphaltenes insoluble in hexane

-hard resins insoluble in 80:20 isobutyl alcohol:cyclohexane mixture

-waxes insoluble in 1:2 mixture of acetone and methylene chloride at 32 degree Fahrenheit.

-Soft resins insoluble in isobutyl alcohol

-Oils soluble in isobutyl alcohol

c. Traxler and Schweyer Method [6]. This method uses n-butanol to precipitate asphaltenes from asphalt cement. Then n-butanol solubles are dissolved in acetone and this acetone solution is chilled to precipitate paraffinics.

d. Knowles, Mcloy, and Eckert Method [7]. The following steps are involved in this process:

- Separation of asphaltenes by precipitation with pentane.
- Separation of resins by precipitation with propane, followed by fractionation with aniline into soft resins and hard resins.
- Precipitation of wax with methyl isobutyl ketone (Hexone).
- Separation of the remaining oil fraction into paraffinic oil and naphthenic oil with acetone.

Chemical Precipitation. In this method, after separation of asphaltenes by solvent precipitation, the remaining components are sequentially separated into fractions based on their reactivity with sulfuric acid of increasing acid strengths (decreasing degree of hydration).

a. Marcusson Eickmann Method [8]. Naptha and sulfuric acid are used to precipitate asphaltenes.

b. Rostler and Sternberg Method [9]. Asphalt cement is separated into asphaltenes, nitrogen bases, 1st acidifins, 2nd acidifins and paraffins. N-pentane is used to precipitate asphaltenes and 85% sulfuric acid is used to separate the remaining fractions. Polar compounds are determined by measuring the percentage of material that does not react with 85% sulfuric acid. First acidaffins are those that do not react with cold 85% sulfuric acid but react with cold concentrated sulfuric acid. Second acidaffins are those that do not react with cold concentrated sulfuric acid but with cold fumming sulfuric acid. The percentage of the material not adsorbed on silica gel under specified conditions are saturated hydrocarbons. The chemical precipitation has been exclusively used in analyzing and defining the asphalts used in the highway construction.

Fractionation by Distillation

Fractionation by distillation is the first step in determining the fractional composition. These methods are insufficient to obtain any chemical sub-division of asphalt cement.

Short-Path, High Vacuum Distillation [10]. Fractionation by heating and condensing to separate various fractions according to their volatilization temperature. This method permits fractionation up to approximately 1300 degree Fahrenheit. Thus a large portion of asphalt cement can be fractionated for further analysis.

Chromatographic Separation

A separation procedure that depends on the separation of the fractions between a stationary phase and moving phase. Chromatographic separations are usually performed for the purpose of determining the composition of asphalt cement.

Liquid Chromatography - Adsorption [11]. Chromatography in which the stationary phase, the absorbent, is a solid. Separation of the fractions depends on their relative affinities toward the absorbent. In column chromatography, the stationary phase is placed in a column and substance to be separated is placed into the column. Various solvents are then passed through the column. The fractions become distributed between the stationary phase and the solvent phase by a combination of adsorption and desorption processes. First, the least strongly adsorbed and most easily desorbed fraction gets eluted from the column.

a. Corbett Method [12]. This method uses a column packed with alumina to separate asphalt cement into asphaltenes, n-hexane petrolenes, polar aromatics, naphthene aromatics and saturates. The asphaltenes and the maltenes are separated using normal heptane. Maltenes, the soluble portion, is further separated by chromatography on alumina to produce three generic fractions using solvents of increasing elution strength.

b. Clay Gel [13]. This method uses a column packed with clay in the upper section and silica gel in the lower section to separate asphalt cement into asphaltenes, polar compounds, aromatics and saturates. The n-pentane is charged to the double column until a definite quantity of the effluent has been collected. Then the upper section is removed from the lower section and washed further with n-pentane. Then toluene-acetone mixture is poured into the clay section. The solvents are removed from the recovered pentane and toluene-acetone fractions. The residual material consists of saturates and polar compounds.

High Pressure Liquid Chromatography [14]. This method uses nine solvents or solvent mixtures across a silica gel column. Asphalt cement is separated into saturates, aromatics, polar aromatics, basic nitrogen heterocyclics, polyphenols and highly functional molecules. Following are the solvents used and the portion separated by using each solvent.

	SOLVENT	FRACTIONS SEPARATED
1.	n-hexane	saturates
2.	n-hexane:15% benzene	aromatics
3.	chloroform(ethanol free)	polar aromatics non-basic
4.	chloroform:10% diehtyl ether	monophenols
5.	diethyl ether:3% ethanol	basic nitrogen heterocyclics
6.	methanol	highly functional molecules

7.	chloroform:3% ethanol	polyphenols
8.	tetrahydrofuran:3% ethanol	polyphenols with high oxygen content
9.	pyridine:3% ethanol	like 8 but of higher molecular mass.

Liquid Chromatography - Ion Exchange. Ion-Exchange chromatography is widely used in sophisticated analysis of asphalt cement for the separation of acidic and basic fractions. This has the advantage of greatly improving the quality of a complex operation; a disadvantage is the very time consuming nature of the separation.

Anion-exchange Chromatography [15,16]. This method separates the acidic components into four solvent defined fractions. Asphalt cement is dissolved in cyclohexane and charged into an anion resin column, which is wet packed in cyclohexane. The material retained on the resin is recovered. A mixture of methylenechloride(50%), toluene(25%), and methanol(25%) saturated with carbon dioxide is used to recover the compounds bonded with the anion resin.

Cation-exchange Chromatography [15,16]. This method separates the basic components into four solvent defined fractions. Asphalt cement is dissolved in cyclohexane and charged into a cation resin column, which is wetted with cyclohexane. The material retained on the resin is recovered. Compounds hydrogen bonded with the cation resin (bases) are recovered by elution with 2000ml of the mixture of methylene chloride(40%), toluene(25%), methanol(25%) and isopropylamine (10%).

Liquid Chromatography - Coordination [15,16]. This method separates the neutral Lewis bases from the acid and base free asphalt cement. The coordination chromatography system consists of two columns. The first column is wetted with cyclohexane and Attapulgus clay coated with ferric chloride. The second column is wet packed with 200g of Amberlite IRA-904 anion resin. The solvent is delivered by a pump. The acid and base free asphalt cement is dissolved in cyclohexane and charged into the first column. The hydrocarbon fraction is separated by feeding cyclohexane at 3ml/min. flow rate. The neutral Lewis bases-ferric chloride complexes are separated with dichloroethane (fraction 1) followed by a mixture of methylene chloride (50%), toluene (25%), and methanol(25%) (fraction 2). Both fractions are passed through the anion resin column where complexes are broken. The ferric chloride salt is retained on the resin and the neutral Lewis bases are recovered in the eluate as two fractions. The solvents are removed, and the fractions are redissolved in benzene and passed over the anion resin to remove the remaining ferric chloride.

Analysis Techniques

Chemical Analysis

Chemical analysis of asphalt cement composition includes spectroscopy, atomic absorption and elemental analysis.

Infrared Spectroscopy [17]. This method qualitatively measures the types of polar compounds in asphalt cement which absorb in the carbonyl region. Asphalt cement is separated into five major compound types including: carboxylic acids, ketones, dicarboxylic anhydrides,2-quinolone.

Nuclear Magnetic Resonance Spectroscopy [18]. This method uses the proton and carbon-13 NMR to estimate saturate/aromatic carbon ratios. It provides a spectrum of protons according to their effective moments as observed in a strong magnetic field. Two partially resolved peaks are exhibited by the paraffin fraction. The peak:height ratio is refered as the branchiness index. It is a measure of the relative number of methyl hydrogens to the other types. A spectrum of the aromatic hydrocarbons exhibit a peak for the hydrogens attached to the aromatic ring, and a pair of partially resolved peaks for the other types of hydrogen. The areas under the various peaks give the relative number of the respective hydrogen types.

X-ray Flourescence Spectroscopy [19,20]. Used to determine heavy metal content including nickel and vanadium.

Neutron Activation Analysis [19,20]. Provides elemental analysis. Elements measured include hydrogen, carbon, nitrogen, sulfur and oxygen.

Atomic Absorption [21]. Used to determine heavy metal content of asphalt cements and asphaltenes. There are various methods, such as inductively coupled plasma atomic absorption(ICPAA) and graphic furnace absorption(GFAA).

Elemental Analysis [21,22]. A variety of techniques are used to determine the element analysis of asphalt cement. Elements most often measured include hydrogen, carbon, nitrogen, sulfur and oxygen. This method involves the pyrolysis(combustion or reduction) and the purification of the resultant gases and detection by IR, coulometric titration, etc.

Molecular Weight Analysis

Mass Spectrometry [23]. Mass spectrometry is used to determine the mass of individual molecules and ionized fragments resulting from bombardment of a sample with electrons.

Vapor Pressure Osmometry [19]. The heat of absorption of solvent vapor into a solution of asphalt cement in the same solvent is used to estimate the molecular weight.

Size Exclusion Chromatography [24]. Asphalt cements are separated based on their associated molecule sizes in dilute solutions. In this technique a solution of asphalt cement is injected into a chromotographic column packed with a solid, porous substrate. The size separated molecules are detected and recorded according to their concentration.

Indirect Compositional Analysis

This analysis is done on the basis that properties of asphalt cements depend not only on the relative quantity and the physical properties of asphaltenes and maltenes present, but also on the solubility or dispersion of the asphaltenes in the solvent medium.

Heithaus Parameter,P [25]. Measures the intercompatibility of the components in asphalt cement by "state of peptization". This tests how good a dispersant the maltenes are for the asphaltenes and how readily the asphaltenes are dispersed.

Asphaltene Settling Test [26]. In this test a 2 grams sample of asphalt cement is digested in 50ml of n-hexane for 24 hours. The settlement of the asphaltenes in an undisturbed cylinder is then observed. Settling time is defined when the asphaltenes have settled to half the solution height. The asphaltene settling test attempts to quantify the compatibility of the asphalt cement fractions by upsetting their critical balance in the asphalt cement with hexane. The asphaltenes that exhibit the longer settling times are more finely or better dispersed in the hexane-maltene phase. The longer settling times indicate a more compatible asphalt cement.

Solubility Profiles [27]. This method describes the solubility characteristics of a substance. Solubility profiles describe the intermolecular relationship of asphalt cement molecules. They can be used to compare different asphalt cements, and can be related to asphalt cement quality.

Comparison of Fractionation Techniques

A comparison between the various fractionation techniques is difficult since the procedure chosen by the individual various investigator is usually for a specific purpose.

A comparison between the Marcusson and Eickmann, and Traxler and Schweyer methods showed a relatively good correlation in the separation of asphalt cement into three groups; asphaltenes, resins, and oils.

A comparison between chromatographic methods and the precipitation method indicated little difference in terms of the recovered fractions.

The Corbett technique is a selective adsorption-desorption chromatography procedure and has been widely used as a research separation technique. In this method asphaltenes are separated based on their insolubility in a non-polar paraffin solvent. The most polar and least soluble asphalt cement fraction is removed first, thereby facilitating further separation. The remaining petrolene fraction, which is dissolved in the paraffinic solvent, is then adsorbed in a calcined alumina chromatographic column and sequentially desorbed with solvents of increasing polarity. Even though this procedure is very labor intensive, it has many advantages including: it has been standardized by ASTM (ASTM D 4124), it is feasible to obtain small amounts of the fractions, and the recovered fractions are similar to those produced in the residuum oil supercritical extraction process. The Corbett procedure was selected as the sole fractionation technique used in this study.

Previous Studies Concerning the Composition of Asphalt Cement and its Properties

The study of asphalt cement composition has been widely investigated. Several studies have been undertaken to relate engineering properties of asphalt cement to its chemical composition.

Bransky, Horan and Spear [28] related the quality of asphalt cement to its composition in terms of asphaltenes, resins and oils. Asphalt cements, differing widely in composition, were produced by separating Mid-Continent, Wyoming and West Texas residue into asphaltenes, resin and oil fractions and then recombining the fractions in different ratios. Various engineering properties including; the effects of aging, penetration, ductility, etc. were correlated with asphalt cement composition and method of manufacture. It was found that an increase in either the resin or asphaltene fractions caused a decrease in penetration, the latter effecting a much greater change. The highest ductility values occured with high resin and low asphaltene contents. The ductility decreased significantly with increasing asphaltene content. It was also observed that asphalt concrete produced with the "Engineered" asphalt cements showed increasing Marshall Stability and Hveem cohesion values with increasing asphaltene and oil contents.

Asphalt cement composition and its rheological behavior were studied by Marvillet [22], Hughes and Hardman [29], Dukatz, Anderson and Rosenberger [30], Altgelt [31], and Rostler and White [32,33].

Simpson, Griffin and Miles [34] fractionated Venezuela asphalt cement into asphaltenes, saturates, aromatics and resins. The fractions were then reblended in various ratios, while holding the asphaltenes constant at 25% in order to produce asphalt cements with a broad range of properties. The asphalt cements were characterized by penetration tests, ring and ball softening point, and viscosity tests at 77 degrees Fahrenheit(25 degrees Centigrade) with sliding plate microviscometer and microcapillary viscometer. They concluded that an increase in resin content is associated with a decrease in penetration and an increase in viscosity. An increase in saturates increases the penetration and decreases the viscosity. An increase of the aromatic content produces virtually no change in either.

Evans, Hopson and Marschner [35] suggested in their research that the consistency of asphalt cements is basically a resin base thickened by asphaltenes and thinned by oils. The blending consistency of asphaltenes depends on the temperature and purity. Wax acts as an oil like thinner at high temperature but as an asphaltene like thickener at low temperatures. Consequently, wax is a major contributor to the differences in consistency among asphalt cements. Either asphaltenes or wax can be added to counteract the effect of the other in heated asphalt cement, but both lessen the concentration of resins and make the normal temperature asphalt cement less stable.

Lamb and Couper [36] related flow properties to chemical composition. They determined the chemical composition by separating the asphalt cement into five fractions by a modified Corbett-Swarbrick chromatographic method. Flow properties at 45, 77 and 120 degrees Fahrenheit were investigated by means of a sliding plate microviscometer for a total of nine paving grade asphalt cements. It was found that there is a significant relationship between the flow properties at 120 degrees Fahrenheit and the fractional composition of asphalt cements. However, at lower temperatures, the data indicated that there is a lessened correlation between the flow properties and chemical composition.

It was observed by Winniford [37] that microviscometer measurements on paving and industrial asphalt cements and on synthetic asphalt cements produced from asphalt cement fractions, show that viscosity is primarily a function of asphaltene content.

Griffin, Simpson and Miles [38], separated four representative asphalt cements according to molecular weight and chemical type. The viscosity, viscosity-temperature susceptibility and durability of the fractions were investigated. They concluded that as molecular weight increases, there is an increase in viscosity and a decrease in the viscosity temperature susceptibility.

To best utilize the compositional data of asphalt cements, more definitive correlations between composition and properties are needed. L.W. Corbett [39] related the composition of asphalt cement with physical tests conducted on paving grade asphalt cements. This was done by separating asphalt cement into four fractions (asphaltenes, saturates, naphthene aromatics and polar aromatics), preparing various two component reconstituted asphalt cements and observing the change in properties with respect to variation in composition. The main conclusions of this study were:

1. The physical properties of each of the four generic fractions are distinctly different from each other.
2. The fluidity of an asphalt increases by the effect of the liquid fractions(saturates and naphthene aromatics) on the solid fractions(polar aromatics and asphaltenes).

3. The combination of either the saturates or the naphthene aromatics with asphaltenes improves the temperature susceptibility. The combination of polar aromatics with asphaltenes makes the temperature susceptibility poorer.
4. Ductility is largely dependent upon the presence of polar aromatics while the other three fractions contribute very little if at all to ductility.
5. Flow resistance(softening point) is increased by the combination of saturates or naphthene aromatics with asphaltenes, and is decreased by the combination of saturates with polar aromatics.
6. High viscosity, relative to penetration, occurs when naphthene aromatics are combined with asphaltenes, whereas all other combinations tend to lower viscosity.
7. Each fraction or combination of fractions perform separate functions in respect to physical properties, and it is logical to assume that the overall physical properties of an asphalt cement are dependent upon the combined effect of these fractions and the proportions in which they are present.

Numerous studies have been conducted to relate age hardening to chemical compositional changes. Corbett and Swarbrick [40] made a comparison between an asphalt cement recovered from a 3 year old asphaltic concrete pavement and an original asphalt cement retained as a reference sample. They found that penetration dropped from 82 to 56 over this period, and the asphaltene content increased from 14.5 to 17.0 weight percent. They concluded that age hardening seems to be largely due to an increase in the concentration of asphaltenes.

In a separate study, Corbett and Swarbrick [18] found that paraffinic plus naphthene fractions remain relatively constant in quantity and character when an asphalt cement is subjected to the thin film oven test. The aromatic oil fraction has a relatively high reactivity as demonstrated by its conversion to asphaltenes.

Knowles, McCoy, Weetman and Eckert [7], in a report concerning the relationship of asphalt cement composition to its durability in service, concluded that the rate of weathering of roofing asphalt cements is decreased with increasing resin content and that the hardening that occurs is apparently the result of the conversion of part of the resins to asphaltenes and the oil to resins. For paving asphalt cements, surface hardening may vary appreciably with crude source. Enrichment of paving asphalt cement with naphthenic oil reduces the tendency toward to surface hardening. Hard resins may have an unfavorable effect on surface hardening.

Traxler [41] concluded that "The susceptibility of an asphalt to hardening by heat and oxidation is related to its colloidal nature (degree of dispersion), which in turn is governed by its chemical composition". Six asphalt cements analyzed for chemical composition and susceptibility to hardening by heat in the presence of air. The thin film oven test and microviscometer techniques were used to assess aging and viscosity respectively.

Kinnaird, Jr.[42] suggested that there is a factor correlating softening point and penetration tests; termed the characterizing factor. He determined a relationship existed between the characterizing factor and the composition of asphalt cement. Asphalt cements were separated into paraffinic fractions, aromatic oils, alcohol resins, and asphaltenes by chromatographic separation. Penetration and softening point tests were performed before and after aging. It was concluded that the changes that occur in asphalt cement due to oxidation, do not exhibit a change in the percentage of paraffinic fractions or in the characterizing factor. Conversely, there is a large increase in the asphaltene and a decrease in both aromatic oils and the alcohol resins.

Corbett and Schweyer [43] pointed out that age hardening is the result of a change in the asphalt cement composition in which naphthene aromatics are converted to polar aromatics and ultimately to asphaltenes. These changes create an increase in viscosity and a reduction in penetration, which somewhat explains the development of stiffness in aged pavements.

A recent study, conducted by Tuffour,Ishai and Craus [44], evaluated the changes in asphalt cement composition during age hardening. Compositional analysis of unaged and laboratory aged samples by clay gel compositional analysis were conducted. The asphalt cements were fractionated into four fractions; asphaltenes, saturates, polar aromatics and naphthene aromatics. Absolute viscosity and penetration tests were conducted. They found that during aging, whether in the field or under accelerated laboratory conditions, the asphaltenes increase, the naphthene and polar aromatics decrease and the saturates remain unchanged. Perhaps increasing the saturates fraction to a predetermined level might be a way to limit the reactive components in an asphalt cement and thus improve the resistance of the material to aging.

In summary, the composition of asphalt cements determines both its engineering properties and its performance. The literature contains information relating asphalt cement composition to selected engineering properties, however, additional investigations are clearly required to obtain a complete understanding of these complex relationships.

CHAPTER III

RESEARCH METHODOLOGY

The research methodology is based on the following sequence:

1. Fractionation of asphalt cement into four fractions according to ASTM standard method D 4124.
2. Blending of a reference asphalt cement with variable percentages of each of the four fractions.
3. Determination of the absolute viscosity, kinematic viscosity and penetration values before and after the thin film oven test on each sample.

Fractionation of Asphalt Cement

The method of compositional analysis used in the present study is the Corbett Separation Technique [45], which is standardized as ASTM D 4124. This separation technique divides asphalt cement into four fractions - saturates, naphthene aromatics, polar aromatics, and asphaltenes. This separation method utilizes the difference in the solubility of chemical species in solvents with varying polarity.

Asphalt cement is first separated into asphaltenes and petrolenes using n-heptane. The insoluble component is refered to as asphaltenes and the soluble component is refered to as petrolenes. The petrolenes are then passed through calcined F-20 Alumina and further fractionated into the saturates, naphthene aromatics and polar aromatics fractions by downward solvent elution in a glass chromatographic column. The eluted (desorbed) fractions are recovered by solvent removal. The saturates are eluted by n-heptane and the naphthene aromatics are eluted from the column by toluene. The polar aromatics are eluted from the column by a mixture of toluene and methanol (50/50) followed by trichloroethylene. Detailed procedure is Shown in Appendix B.

Asphalt cement (AC-20) from the Kerr McGee refinery at Wynneword, OK was used for this research. Approximately 1000 grams of the asphalt cement was fractionated by the aforementioned method.

Sample Preparation

The purpose of blending asphalt cement fractions is to establish the compositional limits of the individual fractions to achieve specific material properties. The following procedure was used for blending:

1. The AC-20 without the addition of added fractions, is used as the "reference" AC.
2. The percentage of each fraction was then varied from its "normal" range. That is, blending individual fractions into the reference AC (125, 150, 175, 200,

250, and 300% of base percentage).

3. The calculations used in preparing the blends is as follows:

Sample I:

Objective of Blend Composition: 125% of Asphaltnes

The weight percentage of each fractions found in the reference asphalt cement was termed as "base percentage". This base percentage was increased by 25% to make it 125%. This was done by adding 25% of base percentage in the reference asphalt cement.

W1= Weight of empty dish = 200 gms

W2= Weight of empty dish + AC = 300 gms

W2 - W1 = Amount of reference asphalt=100 gms

Base percentage (7%) + Addition (25% of 7%)

For amount of reference asphalt=Base(7gms)+Addition(1.75gms)

Test Procedures

The principal objective of this study is to determine the engineering properties of fractionated and recombined asphalt cement. The following tests were conducted:

1. Consistency tests
    a. Absolute viscosity test
    b. Kinematic viscosity test
    c. Penetration test
2. Aging test
    a. Thin Film Oven test

Consistency tests

Consistency describes the degree of fluidity of asphalt cement at a particular temperature. Since asphalt cement is a thermoplastic material, its consistency varies with the temperature. Therefore it is necessary to measure the consistency of various asphalt cements at the same temperature and rate of shear if comparisons are to be made. The following consistency tests were performed on the reference and "blended" asphalt cement samples.

Absolute Viscosity Test. Viscosity can be defined as the resistance of fluid to flow. Viscosity grading of asphalt cements is based on viscosity measurements at 140 degrees Fahrenheit(60 degrees Centigrade). This temperature was selected because it approximates the maximum surface temperature of pavements.

The ASTM D-2171 [46] test method describes the test procedures for the asphalt institute viscometer. The viscometer is mounted in a thermostatically controlled constant temperature water bath which is maintained at 140 degrees Fahrenheit. The viscometer is filled with asphalt cement through the large tube until the level of asphalt cement reaches the fill line. The "filled" viscometer tube is kept in the temperature bath for 30 minutes to reach equilibrium. A partial vacuum is applied to the small side of the viscometer tube to cause the asphalt cement to flow. Application of partial vacuum is necessary because the asphalt cement is too viscous to flow at this temperature. A vacuum control manifold and a vacuum source are required as part of the testing equipment. After the asphalt cement begins to flow, the time (in seconds required for it to flow between two timing marks) is measured. The measured time in seconds is multiplied by the calibration factor for the viscometer tube to obtain the viscosity in poises. Poise is a standard unit for measuring viscosity. It is the result obtained by dividing the shearing stress in dynes per square centimeter by the rate of shear in reciprocal seconds.

Kinematic Viscosity Test. The 275 degrees Fahrenheit (135 degrees Centigrade) temperature was chosen as one that approximates mixing and laydown temperatures for asphalt pavements. Asphalt cements are sufficiently fluid at 275 degrees Fahrenheit to flow through capillary tubes under gravitational forces alone. Therefore, vacuum is not required, however, a different type of viscometer is used. The Cannon - Fenske Opaque Viscometer is used. The ASTM D 2170 [47] test method describes the test procedures. Since the Kinematic viscosity tests are conducted at 275 degrees Fahrenheit, a suitable clear oil is used as the bath medium. The asphalt cement is filled into the viscometer until it reaches the filling line. The viscometer is mounted in the bath and the system is then allowed to reach equilibrium temperature as before. The asphalt cement is then allowed to flow downward in the vertical section of the capillary tubing by gravitational forces. The timer is started when asphalt reaches the first timing mark and stopped when it reaches the second. The timer interval, multiplied by a calibration factor for the viscometer, gives the kinematic viscosity in centistokes. Gravity induces the flow in the kinematic viscosity test(result in centistokes), and density of the material affects the rate of flow through the capillary tube.

Penetration Test. The penetration test is an empirical test used to measure the consistency of asphalt cement. Penetration tests are performed at 77 degrees Fahrenheit(25 degrees Centigrade), which approximates the average service temperature of pavements.

A container of asphalt cement is brought to the standard temperature (77 degrees Fahrenheit) in a thermostatically controlled water bath. The sample is placed in the test apparatus and the penetration needle lowered until contact is made with the sample. The total weight including the needle is 100g and is allowed to penetrate the asphalt cement sample for 5 seconds. The depth of penetration is measured in units of 0.1 mm and is reported as penetration units. The penetration test is run in accordance with ASTM D5 [48].

Aging Test

Asphalt cements undergo substantial short term aging (hardening) when they are mixed with hot mineral aggregates in a mixing facility. Long term aging continues during the life of pavements which are subjected to environmental and other factors. No standard test method is currently available to approximate the long term aging of asphalt cements. However, the following test is used to approximate the short term hardening conditions which occur in normal mixing operations:

Thin Film Oven Test. The thin film oven test is conducted by placing a 50g sample of asphalt cement in a cylindrical flat bottom pan (5.5 inches inside diameter and 3/8 inch deep). The asphalt cement layer in the pan is approximately 1/8 inch deep. The pan containing the asphalt cement sample is transfered to a shelf in a ventilated oven maintained at 325 degrees Fahrenheit(163 degrees Centigrade). The shelf rotates at 5 to 6 revolutions per minute. The sample is kept in the oven for 5 hours, and then transfered to a container for measuring penetration and viscosity of the aged asphalt cement. This test method is described in ASTM D1754 [49]. The aged asphalt cement is usually required to meet specified minimum percentage retained penetration or maximum viscosity.

CHAPTER IV

RESULTS

This chapter summarizes the results of all experimental work performed in this study. The results are presented both in tabular as well as in graphical form. The chapter is organized as follows.

1. Results of compositional analysis (Fractionation) of asphalt cement.
2. Results of penetration tests performed on each sample of asphalt cement with varying percentage of each fraction.
3. Results of Absolute and Kinematic viscosity tests are summarized for each sample.

Fractionation of Asphalt Cement

As described in Chapter III, the Corbett fractionation technique(ASTM D4124) was used as the sole fractionation technique. Approximately 1000 grams of asphalt cement was fractionated. Four fractions were recovered including:

a. Asphaltenes
b. Saturates
c. Naphthene Aromatics
d. Polar Aromatics

The weight percentage of each fraction was determined and is presented in Table 2 and Figure 2.

Penetration Test Results

Penetration tests are one of the oldest methods used to characterize asphalt cements. Penetration tests are performed at 77 degrees Fahrenheit and provide an indication of the stiffness of an asphalt cement at a temperature comparable to inservice conditions in a pavement. Soft asphalt cements are typified by high penetration values.

Penetration tests were performed on the referenced asphalt cement, blended asphalt cement with the addition of 125, 150, 175, 200, 250 and 300% asphaltenes; 150, 175 and 200% saturates; 125, 150, 175 and 200% naphthene aromatics; 125, 150, 175 and 200% polar aromatics. Tests were also performed on comparible "aged" specimens resulting from thin film oven procedures. The results of the penetration tests are presented in Tables 3 through 10 and Figures 3 through 10.

Absolute Viscosity Tests Results

Absolute viscosity tests, performed at 140 degrees Fahrenheit(60 degrees Centigrade), are another method of characterizing asphalt cements. A high value of absolute viscosity, expressed in poise, is indicative of stiff asphalt cement. This test was performed on all samples as previously described. The results of the absolute viscosity tests are presented in Tables 11 through 18 and Figures 11 through 18.

Kinematic Viscosity Tests Results

Kinematic viscosity tests, are performed at 275 degrees Fahrenheit(135 degrees Centigrade). The adherence of asphalt cement to the aggregate particles in hot mix asphalt concrete is somewhat dependent on the viscosity of the asphalt cement at mixing temperature (generally 275-300 degrees Fahrenheit). A stiff asphalt cement is indicated by a large viscosity value expressed in centistokes. This test was performed on all samples except blended asphalt cement samples with the addition of 150, 175 and 200% saturates. The results are presented in Tables 19 through 25 and Figures 19 through 25.

CHAPTER V

DISCUSSION OF RESULTS AND CONCLUSIONS

This Chapter summarizes and interprets the results of the test data presented in Appendix A.

Discussion of Results

Asphaltenes

Asphaltenes are characterized as dark brown solid material. The type of non-polar solvent used to precipitate the asphaltenes affects the determination of its total amount in the asphalt cement. More asphaltenes are precipitated by the use n-pentane rather than n-heptane because the number of carbon atoms in n-pentane is less than that is n-heptane [50]. In this project, n-heptane was used to precipitate asphaltenes, and asphaltenes were found to be 7% of the weight of asphalt cement (Fig. 2).

The penetration data for the blending of asphaltenes is shown in Figure 3. It can be observed that for both the virgin(un-aged) and residual(aged) asphalt cements, the penetration values generally decrease with an increasing percentage of asphaltenes.

It can be interpreted from this behavior that an increase in asphaltenes content will increase the brittleness of asphalt cement and shrinkage cracking may occur in asphalt cement pavement at lower temperatures. This can also effect the binding characteristic of asphalt cement and ravelling may occur.

Note, that in the 200% virgin and residual samples, and the 150% residual sample, the penetration values are not according to trend. This is probably due to the incomplete dispersion of the asphaltenes during sample preparation.

The results presented in Figure 10 show a gradual increase in absolute viscosity with the addition of asphaltenes. However, there is a substantial increase in the absolute viscosity of the aged samples at higher percentage additions of asphaltenes. Therefore, asphalt cements are more susceptible to age hardening with an increase in the percentage of asphaltenes. This can also be inferred from the increase in the slope of the lines between virgin and residual samples respectively (Figure 4, 12 and 20). The age hardening of asphalt cement is due to oxidation of hydrocarbons and formation of oxidation product like ketones, Anhydride, Carboxylic acid and sulfoxide. Ketones and sulfoxide are the major oxidation products formed during oxidative aging; anhydrides and carboxylic acids are formed in smaller amounts. The major reaction pathway of hydrocarbon air oxidation is the formation of carbonyl compounds via the hydroperoxide intermediate. The most sensitive hydrocarbon moiety expected to be present in asphalt is that associated with the carbon atom adjacent to an aromatic ring system, commonly called a benzylic carbon. The hydrogen attached to the carbon in this position is relatively easy to displace, forming a free radical on the carbon. Branching in the attached hydrocarbon chains also increases the sensitivity of the asphalt cement to oxidation. The reaction is initiated by the abstraction of a hydrogen atom attached to a benzylic carbon of an asphalt cement molecule to form a free radical. The free radical reacts with atmospheric oxygen to form a peroxy radical. This in turn rapidly decomposes to form a ketone or, more likely, abstracts a hydrogen atom from the benzylic carbon of another asphalt cement molecule to form a hydroperoxide. The asphalt cement-free radical formed can react with atmospheric oxygen to repeat the process. The hydroperoxide is rather unstable and may decompose to form either a ketone or an alkoxy radical. The alkoxy radical may rapidly decompose to form a ketone. Smaller amount of anhydrides are formed through an alternate hydroperoxide decomposition route in certain asphalt molecules having stereospecific ring systems associated with the oxidizable alkyl moieties. Because the asphaltene fractions are known to contain the highest concentrations of aromatic ring systems, and thus benzylic carbons via the alkyl moieties attached. It has the highest content of hydrocarbon types sensitive to air oxidation, and that causes more hardening of asphalt cement. The substantial increase in absolute viscosity of the asphalt cements suggest that it may cause cracks in asphalt cement pavement and a reduction in fatigue life of pavement due to increased stiffness.

It is observed in Figure 19 that there is an increase in the kinematic viscosity of asphalt cement with an increasing percentage of asphaltenes. This may negatively effect the adherence of the asphalt cement to the aggregate particles in asphalt concrete.

It appears from Figure 26 that temperature susceptibility of the asphalt cement decreases with an increase in the percentage of asphaltenes. The decreasing trend of temperature susceptibility suggests that the asphalt cement with increased asphaltenes content can be used at the locations having high variability of temperatures between summer and winter.

The trends observed in the penetration, absolute viscosity and kinematic values, are due to the nature of asphaltenes. These compounds are the highest in molecular weight, polarity, and the most viscous hydrocarbon. Therefore, they have a very high tendency to interact and associate. They are mixtures of many compounds that have a strong tendency to associate in conglomerates. Asphaltenes play a major role as the viscosity building fraction of asphalt cements.

The trends shown in this study correspond closely to the findings of similar studies [28,35,37,39,40].

Saturates

The saturates are the first eluted(desorbed) by n-heptane from the chromatographic column. This fraction is not adsorbed by the alumina in the column because it lacks polar functional groups. The saturates fraction may contain saturated normal and branched-chain hydrocarbons (sometimes called napthenic hydrocarbons), and possibly a small amount of mono-ring aromatic hydrocarbons; however, those molecules containing ring systems are dominated by attached saturated hydrocarbon side chains. Sulfur is often found incorporated in molecules of the saturate fraction. Saturates are equivalent to paraffins in the Rostler analysis. Saturates were found to be 10% of the total weight of the asphalt cement.

The results presented in Figure 10 show that penetration increases with an increase in the percentage of saturates. Similar trend is noted for residual samples.

The absolute viscosity and kinematic viscosity results (Fig. 13,21) show that a decrease in viscosity is associated with an increased percentage of saturates. However, the absolute viscosity for the 200% residual sample is not according to the observed trends and may be the result of experimental error.

The increased (high) penetration values will reduce possibility of shrinkage cracking in asphalt cement pavement at lower temperature, but decreased (low) absolute viscosity may cause rutting or flushing during summer. This behavior indicates that the asphalt cement with more saturates content is suitable for the use in cold regions.

The trends observed in the penetration, absolute viscosity, and kinematic viscosity tests are according to the nature of saturates; saturates are liquid in physical state, and saturates contain non polar hydrocarbon having weak molecular interaction forces. Saturates with naphthene aromatics play an important role in producing fluidity to the asphalt cement structure. Thus, saturates have opposing characteristics to that of the asphaltenes.

It is observed in Figure 6 and 14, that there is a decrease in the slope of the lines between the virgin and residual readings respectively as the percentage of saturates increase. This behavior is attributed to the fact the saturates are relatively inert to reaction with oxygen. As previously described the oxidation product formed due to the presence of attached carbon with aromatic ring systems, considerable smaller amounts of ketones are formed as an increased percentage of saturates change the proportion of other fractions. The trend indicates that the age hardening potential of the asphalt cement decreases with the addition of saturates. This improves the durability of asphalt cement. In a previous study [44] it was concluded that there is no change in the quantity of saturates after age hardening.

Naphthene Aromatics

Napthene aromatics are the second fraction eluted from the chromarographic column with a more polar solvent, toluene. The molecular structure of naphthene aromatic is comprised of condensed non-aromatic and aromatic ring systems and may contain heteroatoms of oxygen, nitrogen and sulfur. Naphthene aromatics were found to comprise 46.5% by weight of asphalt cement.

The data presented in Figure 7. shows the relative change in penetration values with the addition of naphthene aromatics. It is observed that there is an increase in penetration with an increase in naphthene aromatics. This bahaviour indicates that naphthene aromatic imparts fluidity to asphalt cement. High penetration values at low temperatures prevent shrinkage cracking.

It is observed in Figure 15 and 22 that absolute viscosity and kinematic viscosity decrease with an increase in naphthene aromatics.

These trends are according to the nature of naphthene aromatics as naphthene aromatics are liquid in physical state and are considered a softening component in asphalt cement.

The increased(high) absolute viscosity is not desirable as it may results in rutting or flushing of asphalt cement pavement. The decreased(low) kinematic viscosity increases the adhesion of asphalt cement to aggregate in asphalt cement concrete, but very low viscosity results in tender mix problems during compaction.

It can be observed in Figure 8,16 and 23 that there is an increase in the slope of the lines between virgin and aged samples with an increase in the percentage of naphthene aromatics. It may be concluded from this behavior that asphalt cement is more susceptible to age hardening with an increase in naphthene aromatics. It is because naphthene aromatics degrade into asphaltenes during aging, thus, increasing the stiffness of the asphalt cement.

Temperature susceptibility results (Fig. 27) show that there is a decrease in temperature susceptibility with the addition of naphthene aromatics.

Polar Aromatics

Polar aromatics are the final fraction to emerge from the column when eluted with a highly polar mixture of methanol and toluene. Methanol aids in debonding this strongly adsorbed fraction. Its molecular structure comprises a higher percentage of condensed aromatic ring systems and functional groups containing heteroatoms than the other petrolene fractions. It is solid or semi-solid in physical state. Polar aromatics comprise 36.5% of the total weight of the asphalt cement (Fig. 2).

The results presented in Figure 8. show that penetration increases with an increase in the percentage of polar aromatics for virgin samples. However, penetration decreases with an increase in polar aromatics for residual samples. This trend can be attributed the fact that during aging the concentration of polar functional groups becomes sufficiently high to cause molecular immobilization through increased molecular interaction forces. That is, the asphalt molecules are not sufficiently mobile to flow past one another. This will result in fracturing or cracking of the asphalt cement pavement.

The absolute viscosity and kinematic viscosity of asphalt cement decrease with an increase in polar aromatics (Fig. 17,24).

Note, at the 200% addition there is a decrease in penetration and increase in absolute viscosity. This behavior indicates that at higher percentage of polar aromatics, stiffness in asphalt cement, increases due to the semi solid nature of naphthene aromatics.

It is observed in Figures 10,17 and 25 that there is an increase in slope of the lines between virgin and residual samples with an increase in the percentage of polar aromatics. It may be concluded, therefore, that asphalt cements with higher polar aromatic contents are more susceptible to age hardening. This is because the polar aromatics are highly reactive with oxygen due to the presence of carbon attached with aromatic ring systems. Possible reactions were explained previously already in detail.

Temperature susceptibility data presented in Figure 28 shows that temperature susceptibility decreases with an increasing percentage of polar aromatics. Thus making asphalt cement more suitable for use in the regions of varying temperature.

Conclusions

The conclusions presented below are based on the results of the penetration, absolute viscosity and kinematic viscosity tests. The data is somewhat limited, and the reader is advised that some of the trends may be altered by an extended data base.

1. A definite relationship exists between asphalt cement composition and its properties.
2. Asphaltenes act as a stiffener in asphalt cement, i.e., the stiffness of asphalt cement increases with an increase of asphaltene contents. These compounds are the highest in molecular weight, polarity, and contain the most viscous hydrocarbon.
3. Saturates and Naphthene aromatics act as a softening agent in asphalt cement. The stiffness of asphalt cement decreases with an increase in amount of saturates and naphthene aromatics. As they have weak molecular interaction and are liquid in physical state.
4. Asphalt cement becomes more susceptible to age hardening approximated by thin film oven test procedure with an increase in asphaltenes, naphthene aromatics and polar aromatics. As they contain hydrocarbon sensitive to oxidation.

5. Asphalt cement becomes less susceptible to age hardening approximated by thin film oven test procedure with an increase in saturate contents.

6. Temperature susceptibility of asphalt cement decreases with the addition of asphaltenes, naphthene aromatics and polar aromatics.

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APPENDIXES

APPENDIX A

TABLES AND FIGURES

TABLE 1

NOMENCLATURE OF PREPARED SAMPLES

Blend of reference percentage	Asphaltenes	Saturates	Naphthene aromatics	Polar aromatics
125	I	-	X	XIV
150	II	VII	XI	XV
175	III	VIII	XII	XVI
200	IV	IX	XIII	XVII
250	V	-	-	-
300	VI	-	-	-

- Samples I, II, III, IV, V, VI are asphaltene blends.
- Samples VII, VIII, IX are saturate blends.
- Samples X, XI, XII, XIII are naphthene aromatic blends.
- Samples XIV, XV, XVI, XVII are polar aromatic blends.

TABLE 2

COMPOSITIONAL ANALYSIS

Fractions	Mass (gms)	% of Total Mass
Asphaltenes	2.1	7.0
Saturates	3.0	10.0
Naphthene Aromatics	14.0	46.5
Polar Aromatics	11.0	36.5
Total	30.1	100.0

TABLE 3

PENETRATION TEST RESULTS (VIRGIN SAMPLES)

Sample No.	P.O.A.*	PENETRATION READINGS					Average
		I	II	III	IV	V	
-	100	63.5	64.5	65.0	-	-	64.33
I	125	58.5	58.0	59.0	-	-	58.5
II	150	57.0	58.0	57.0	-	-	57.33
III	175	50.5	48.5	52.0	52.0	50.0	50.6
IV	200	52.5	52.5	53.0	51.0	51.0	52.0
V	250	48.0	45.0	50.0	45.0	50.0	47.6
VI	300	43.5	46.0	44.5	-	-	44.67

*Percentage of Asphaltenes of base percentage

TABLE 4

PENETRATION TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.A.*	PENETRATION READINGS				Average
		I	II	III	IV	
-	100	42.0	42.0	40.0	-	41.33
I	125	30.0	32.0	28.0	-	30.0
II	150	20.0	19.0	22.0	24.0	21.25
III	175	27.0	31.0	28.0	-	28.67
IV	200	28.0	31.0	29.5	-	29.5
V	250	23.5	27.0	24.0	-	24.83
VI	300	18.5	21.0	21.0	-	20.17

*Percentage of Asphaltenes of base percentage

TABLE 5

PENETRATION TEST RESULTS (VIRGIN SAMPLES)

Sample No.	P.O.S.*	Penetration Readings			Average
		I	II	III	
-	100	63.5	64.5	65.0	64.33
VII	150	87.0	93.0	86.0	88.66
VIII	175	140.5	136.0	141.5	139.33
IX	200	189.0	193.5	184.5	189.0

* Percentage of Saturates of base percentage

TABLE 6

PENETRATION TEST RESULTS
(RESIDUAL SAMPLES)

Sample No.	P.O.S.*	Penetration Readings			Average
		I	II	III	
-	100	42.0	42.0	40.0	41.33
VII	150	46.5	52.0	48.5	49.0
VIII	175	86.5	86.0	82.5	85.0
IX	200	96.0	86.0	90.0	90.67

*Percentage of Saturates of base percentage

TABLE 7

PENETRATION TEST RESULTS
(VIRGIN SAMPLES)

Sample No.	P.O.N.*	Penetration Readings			Average
		I	II	III	
-	100	63.5	64.5	65.0	64.33
I	125	118.5	119.0	121.0	119.5
II	150	216.0	205.0	202.0	207.7
III	175	>300	>300	>300	>300
IV	200	>300	>300	>300	>300

*Percentage of Naphthene Aromatics of base percentage

TABLE 8

PENETRATION TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.N.*	Penetration Readings			Average
		I	II	III	
-	100	42.0	42.0	40.0	41.33
I	125	53.0	54.0	51.0	52.7
II	150	66.0	64.0	65.0	65.0
III	175	74.0	72.5	73.0	73.2
IV	200	90.0	95.0	88.0	91.0

*Percentage of Naphthene Aromatics of base percentage

TABLE 9

PENETRATION TEST RESULTS (VIRGIN SAMPLES)

Sample No.	P.O.P.*	Penetration Readings			Average
		I	II	III	
-	100	63.5	64.5	65.0	64.33
I	125	96.0	92.5	93.0	93.83
II	150	116.0	117.5	107.0	114.0
III	175	153.5	148.5	146.0	149.0
IV	200	130.0	129.0	131.0	130.0

*Percentage of Polar Aromatics of base percentage

TABLE 10

PENETRATION TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.P.*	Penetration Readings			Average
		I	II	III	
-	100	42.0	42.0	40.0	41.33
I	125	36.0	38.5	37.0	37.2
II	150	34.0	33.0	33.0	33.3
III	175	29.0	28.5	29.0	28.83
IV	200	25.0	25.0	26.0	25.33

*Percentage of Polar Aromatics of base percentage

TABLE 11

ABSOLUTE VISCOSITY TEST RESULTS (VIRGIN SAMPLES)

Sample No.	P.O.A.*	Absolute Viscosity Readings					Average
		I	II	III	IV	V	
-	100	2125	2092	2136	2073	2124	2110
I	125	2341	2336	2400	2327	2392	2359
II	150	2477	2467	2533	2486	2534	2499
III	175	2763	2764	2785	2723	2798	2767
IV	200	3044	2932	3072	3101	2932	3016
V	250	3198	3217	3078	3171	3478	3228
VI	300	3664	3824	3797	3580	3918	3757

* Percentage of Asphaltenes of base percentage

TABLE 12

ABSOLUTE VISCOSITY TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.A.*	Absolute Viscosity Readings			Average
		I	II	III	
-	100	5889	5942	5991	5940
I	125	9933	10410	10426	10256
II	150	12220	11715	11445	11793
III	175	12440	12576	12910	12642
IV	200	12974	12792	13033	12933
V	250	18988	19216	19139	19114
VI	300	23900	25270	24984	24718

*Percentage of Asphaltenes of base percentage

TABLE 13

ABSOLUTE VISCOSITY TEST RESULTS (VIRGIN SAMPLES)

Sample No.	P.O.S.*	Absolute Viscosity Readings					Average
		I	II	III	IV	V	
-	100	2125	2092	2136	2073	2124	2110
VII	150	1358	1362	1348	1343	1339	1350
VIII	175	709	718	703	696	715	708
IX	200	360	384	379	372	379	375

*Percentage of Saturates of base percentage

TABLE 14

ABSOLUTE VISCOSITY TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.S.*	Absolute Viscosity Readings					Average
		I	II	III	IV	V	
-	100	5889	5942	5991	-	-	5940
VII	150	4045	3847	4100	4026	4005	4005
VIII	175	1007	1118	1130	1101	1084	1088
IX	200	1470	1515	1498	1460	1548	1498

*Percentage of Saturates of base percentage

TABLE 15

ABSOLUTE VISCOSITY TEST RESULTS
(VIRGIN SAMPLES)

Sample No.	P.O.N.*	Absolute Viscosity Readings					Average
		I	II	III	IV	V	
-	100	2125	2092	2136	2073	2124	2110
I	125	977	989	958	973	957	971
II	150	520	503	513	501	491	506
III	175	300	300	300	290	296	297
IV	200	150	149	140	145	150	147

*Percentage of Naphthene Aromatics of base percentage

TABLE 16

ABSOLUTE VISCOSITY TEST RESULTS
(RESIDUAL SAMPLES)

Sample No.	P.O.N.*	Absolute Viscosity Readings					Average
		I	II	III	IV	V	
-	100	5889	5942	5991	-	-	5940
I	125	3333	3316	3351	3275	3344	3324
II	150	2217	2237	2273	2138	2296	2232
III	175	1540	1536	1583	1519	1541	1544
IV	200	1278	1257	1251	1215	1207	1242

*Percentage of Naphthene Aromatics of base percentage

TABLE 17

ABSOLUTE VISCOSITY TEST RESULTS (VIRGIN SAMPLES)

Sample No.	P.O.P.*	Absolute Viscosity Readings					Average
		I	II	III	IV	V	
-	100	2125	2092	2136	2073	2124	2110
I	125	1398	1307	1275	1508	1375	1373
II	150	977	976	978	983	969	977
III	175	876	823	839	821	822	836
IV	200	985	976	976	963	972	974

*Percentage of Polar Aromatics of base percentage

TABLE 18

ABSOLUTE VISCOSITY TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.P*	Absolute Viscosity Readings					Average
		I	II	III	IV	V	
-	100	5889	5942	5991	-	-	5940
I	125	5275	5247	5322	5022	5356	5244
II	150	6439	6678	6692	6641	6613	6613
III	175	7371	7527	7642	7361	7264	7433
IV	200	7932	8057	7811	-	-	7933

*Percentage of Polar Aromatics of base percentage

TABLE 19

KINEMATIC VISCOSITY TEST RESULTS (VIRGIN SAMPLES)

Sample No.	P.O.A.*	Viscosity Readings		Average
		I	II	
-	100	428	430	429
I	125	443	445	444
II	150	474	473	474
III	175	470	468	469
IV	200	511	496	504
V	250	526	517	522
VI	300	621	627	624

*Percentage of Asphaltenes of base percentage.

TABLE 20

KINEMATIC VISCOSITY TEST RESULTS
(RESIDUAL SAMPLES)

Sample No.	P.O.A.*	Viscosity Readings		Average
		I	II	
-	100	682	680	681
I	125	804	812	808
II	150	868	-	868
III	175	868	860	864
IV	200	1008	1000	1004
V	250	1012	1003	1008
VI	300	1239	1229	1234

*Percentage of Asphaltenes of base percentage.

TABLE 21

KINEMATIC VISCOSITY TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.S.*	Viscosity Readings		Average
		I	II	
-	100	682	680	681
VII	150	559	554	557
VIII	175	385	383	384
IX	200	341	343	342

*Percentage of Saturates of base percentage.

TABLE 22

KINEMATIC VISCOSITY TEST RESULTS (VIRGIN SAMPLES)

Sample No.	P.O.N.*	Viscosity Readings		Average
		I	II	
-	100	428	430	429
X	125	286	284	285
XI	150	211	211	211
XII	175	182	182	182
XIII	200	143	143	143

*Percentage of Naphthene Aromatics of base percentage.

TABLE 23

KINEMATIC VISCOSITY TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.N.*	Viscosity Readings		Average
		I	II	
-	100	682	680	681
X	125	505	506	506
XI	150	435	434	435
XII	175	381	374	378
XIII	200	371	365	368

*Percentage of Naphthene Aromatics of base percentage.

TABLE 24

KINEMATIC VISCOSITY TEST RESULTS
(VIRGIN SAMPLES)

Sample No.	P.O.P.*	Viscosity Readings		Average
		I	II	
-	100	428	430	429
XIV	125	342	342	342
XV	150	326	324	325
XVI	175	301	298	300
XV11	200	277	277	277

*Percentage of Polar Aromatics of base percentage.

TABLE 25

KINEMATIC VISCOSITY TEST RESULTS (RESIDUAL SAMPLES)

Sample No.	P.O.P.*	Viscosity Readings		Average
		I	II	
-	100	682	680	681
XIV	125	643	651	647
XV	150	664	675	670
XVI	175	-	-	-
XVII	200	779	784	782

*Percentage of Polar Aromatics of base percentage.

TABLE 26

TEMPERATURE SUSCEPTIBILITY

Sample No.	Percentage of Asphaltenes	Pen-Vis Number
-	100	-0.60
I	125	-0.65
II	150	-0.58
III	175	-0.72
IV	200	-0.59
V	250	-0.63
VI	300	-0.45

TABLE 27

TEMPERATURE SUSCEPTIBILITY

Sample No.	Percentage of Naphthene Aromatics	Pen-Vis Number
-	100	-0.60
X	125	-0.54
XI	150	-0.36
XII	175	-0.11
XIII	200	-0.57

TABLE 28

TEMPERATURE SUSCEPTIBILITY

Sample No.	Percentage of Polar Aromatics	Pen-Vis Number
-	100	-0.60
XIV	125	-0.54
XV	150	-0.39
XVI	175	-0.19
XVII	200	-0.49

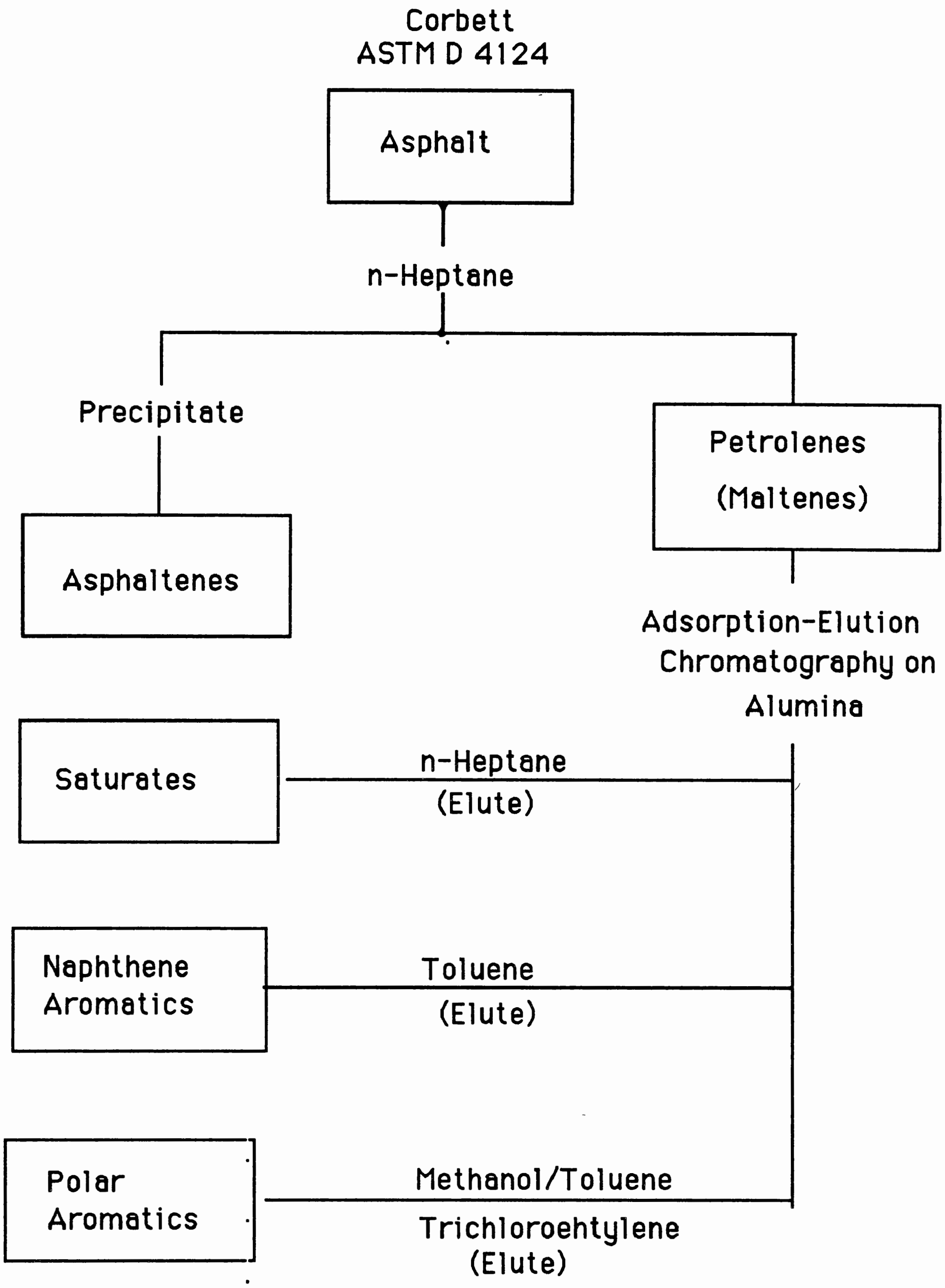


Figure 1. Adsorption/Desorption Chromatography [31]

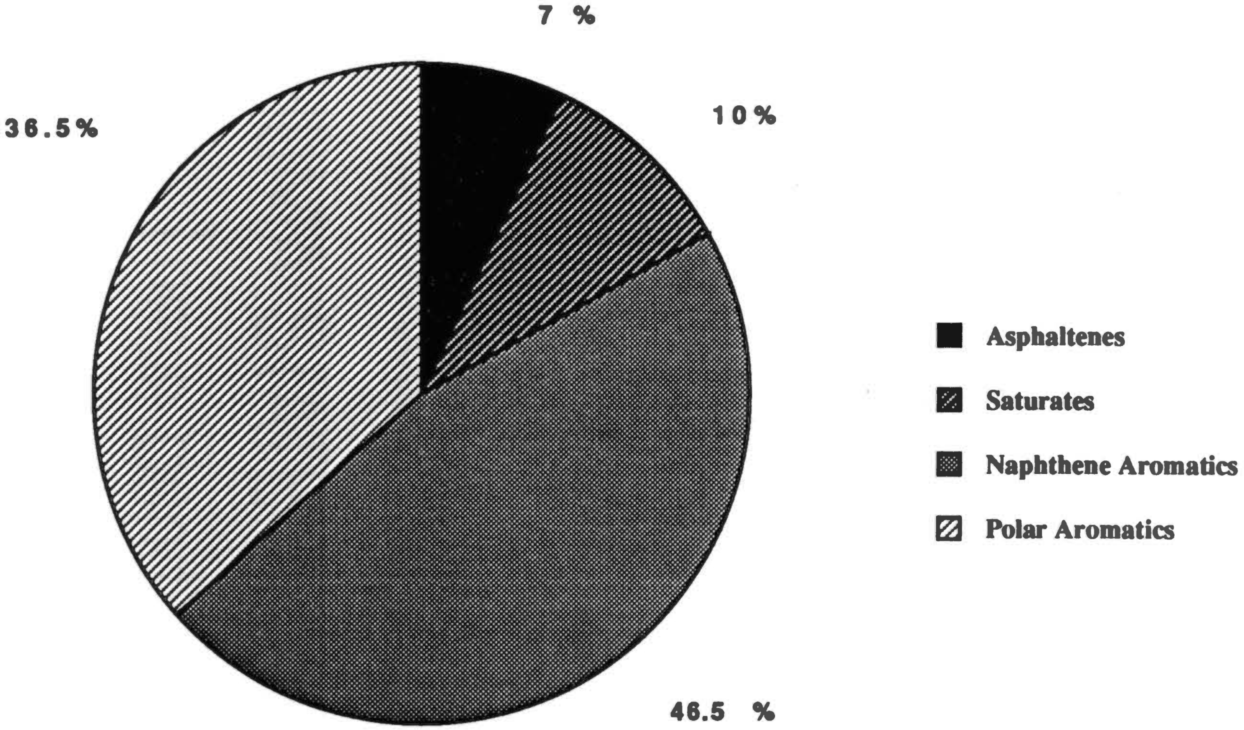


Figure 2. Percentage by Weight of Each Fraction

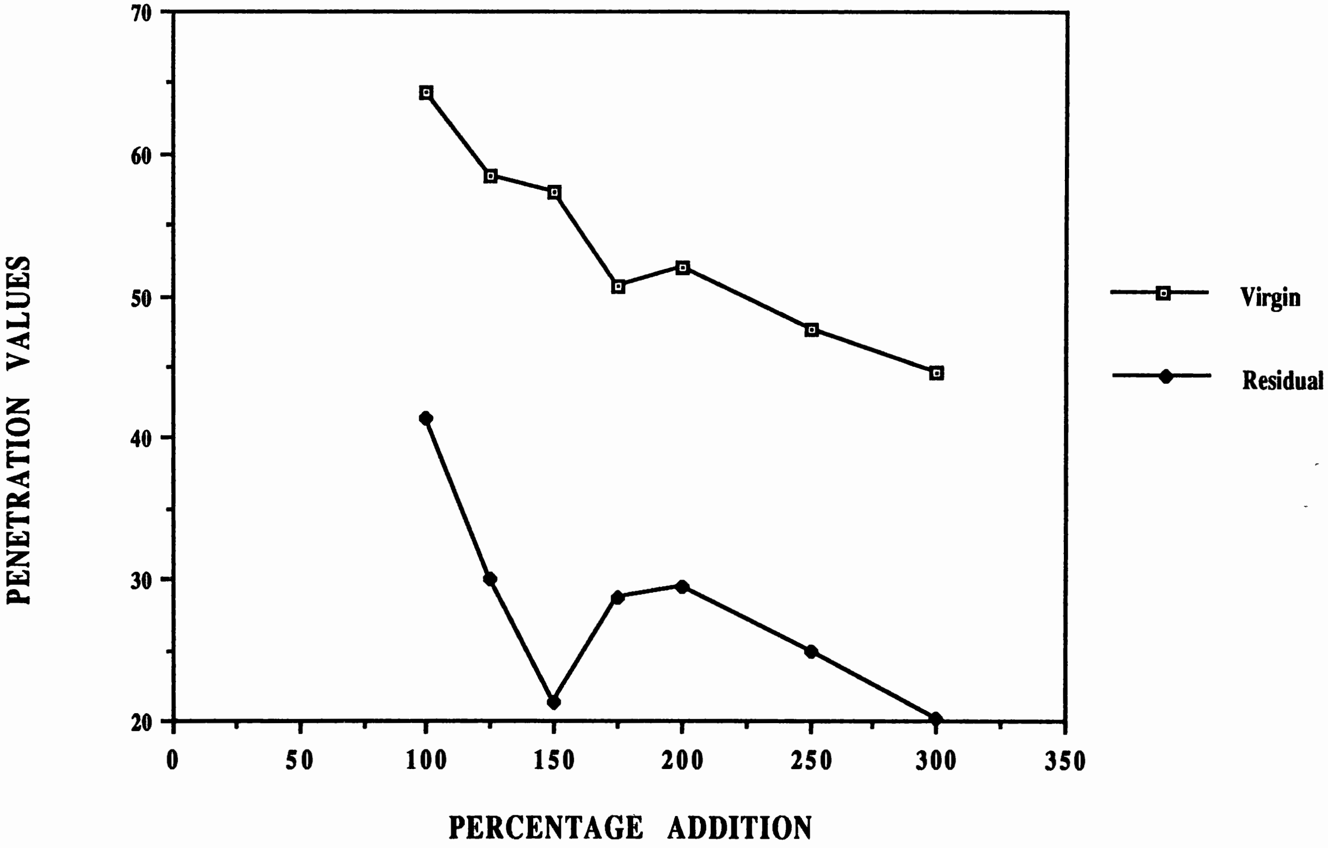


Figure 3. Asphaltenes Percent Addition vs. Penetration

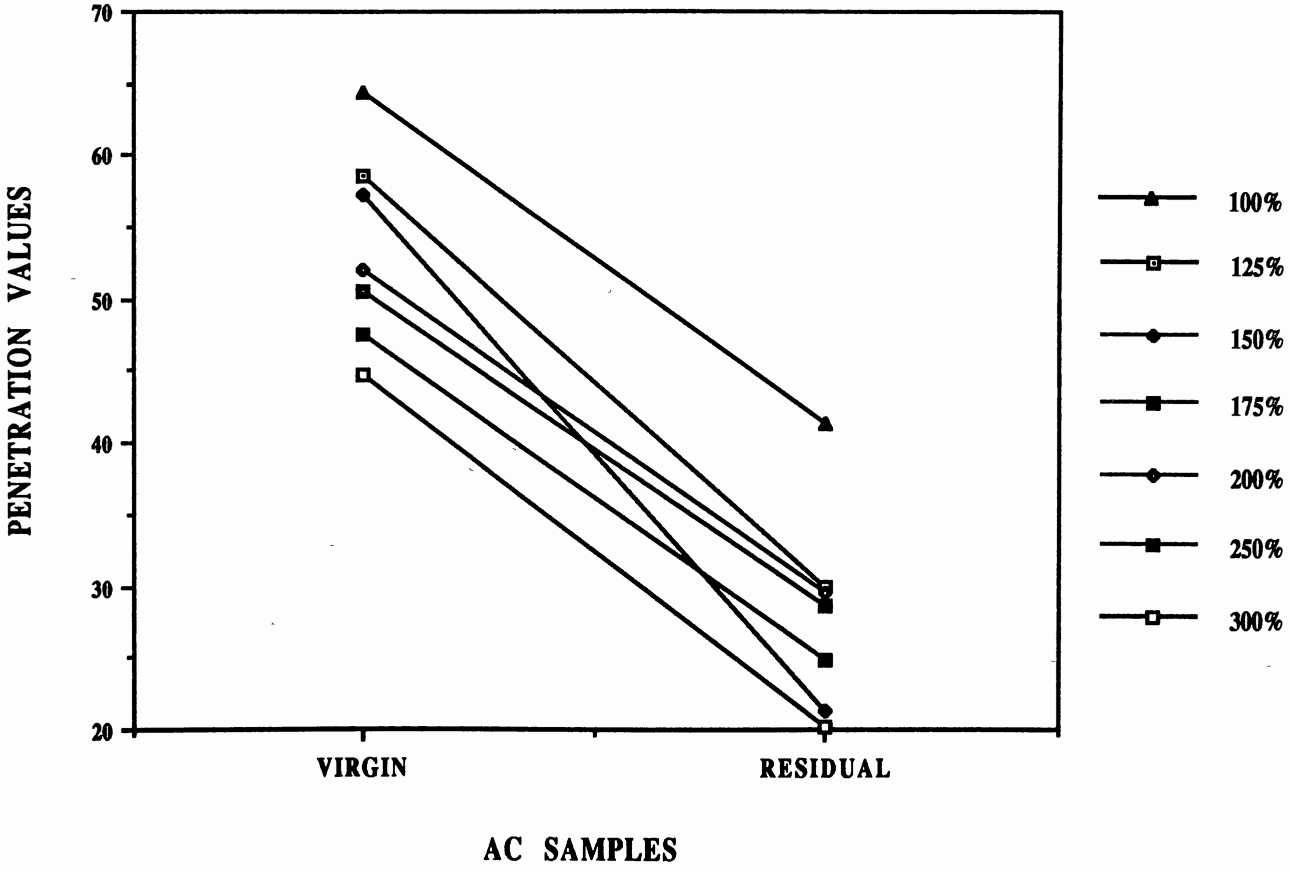


Figure 4. Penetration Values vs. Virgin and Residual-Asphaltenes

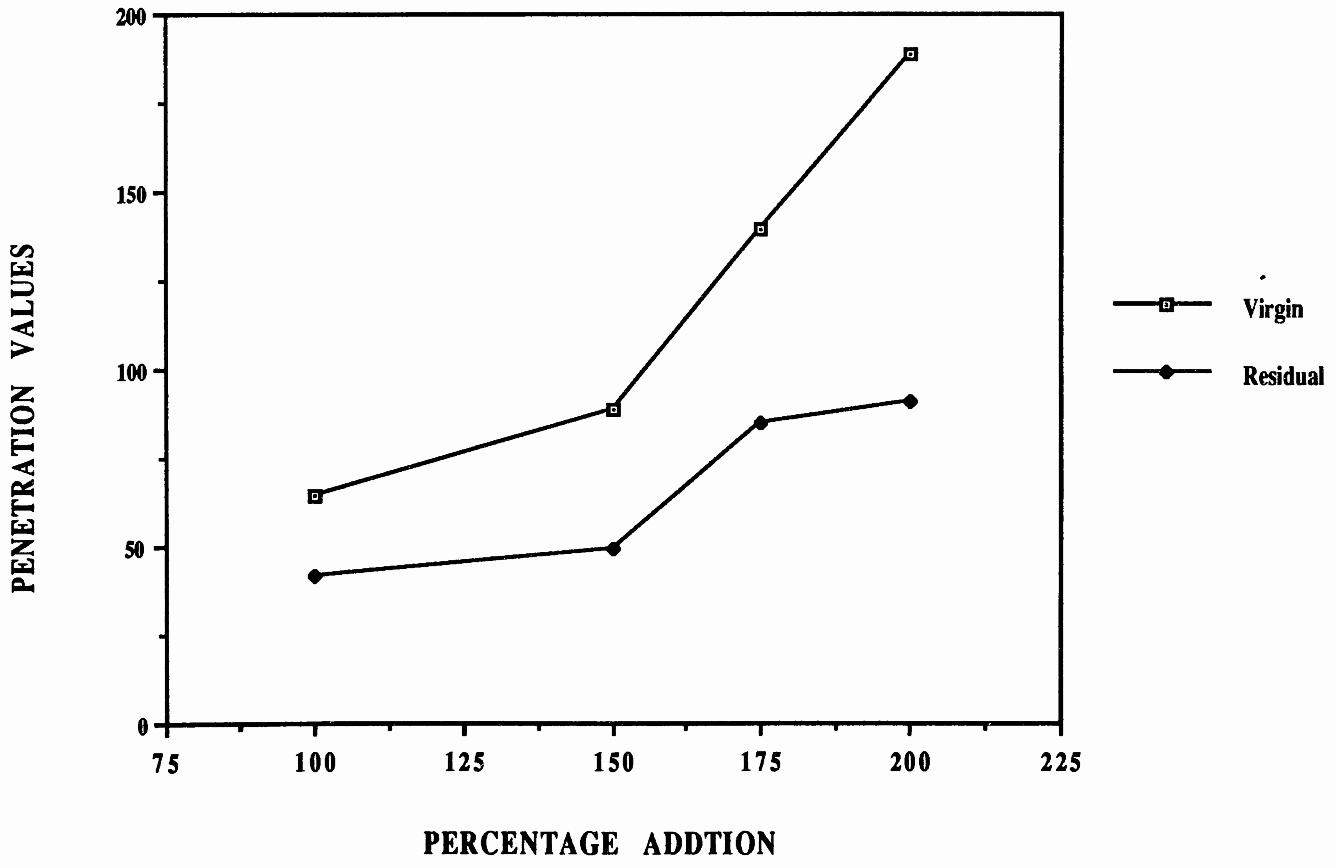


Figure 5. Saturates Percent Addition vs. Penetration

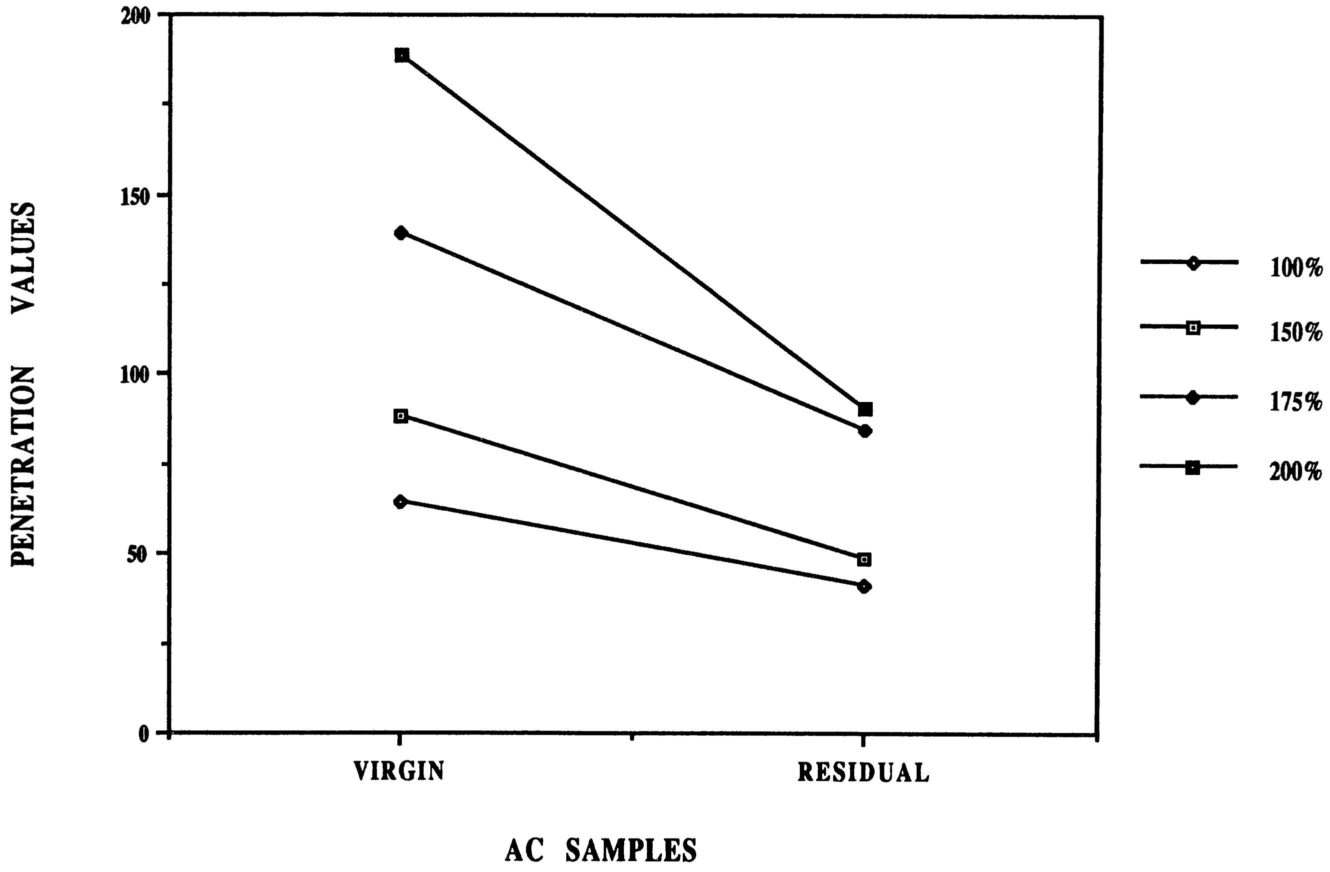


Figure 6. Penetration Values vs. Virgin and Residual-Saturates

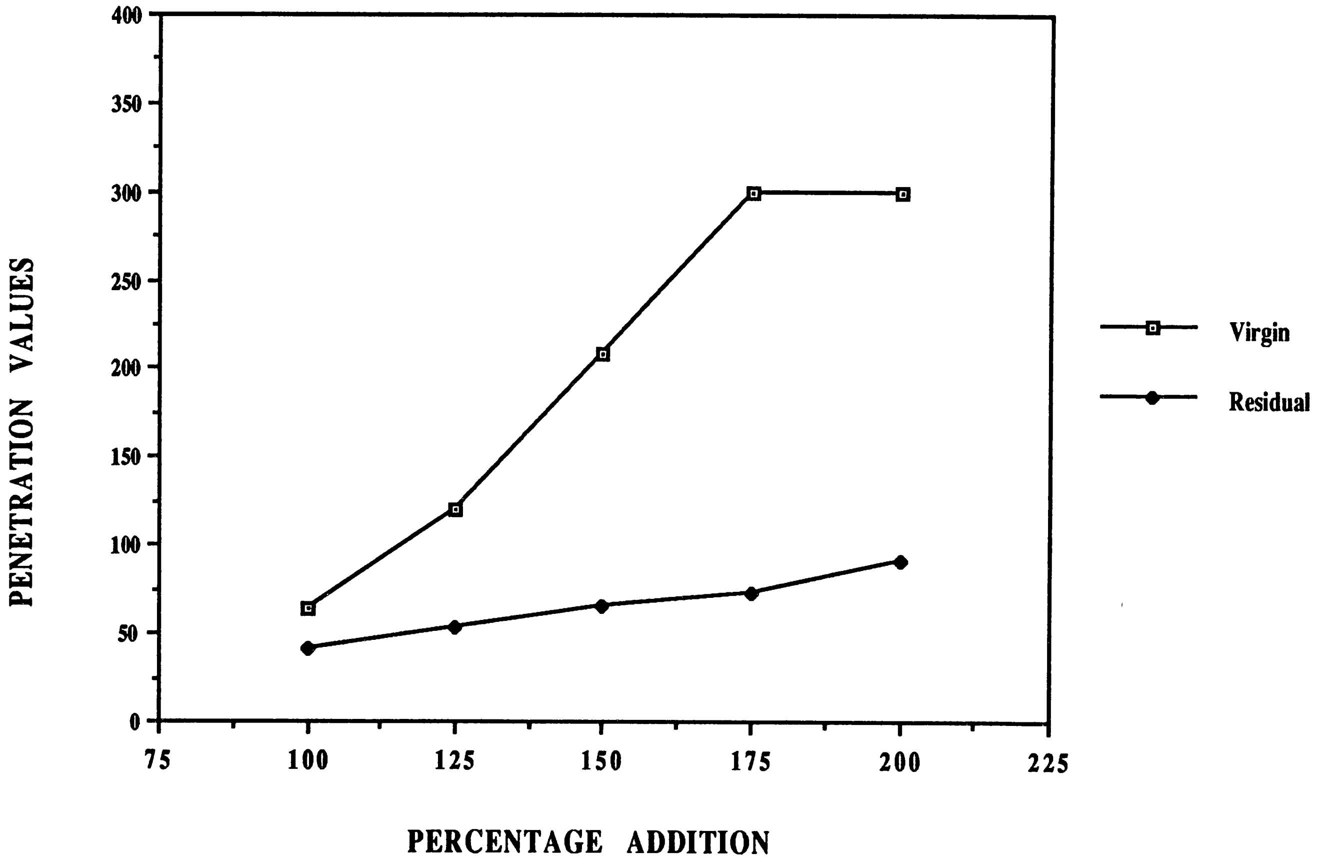


Figure 7. Naphthene Aromatics Percent Addition vs. Penetration

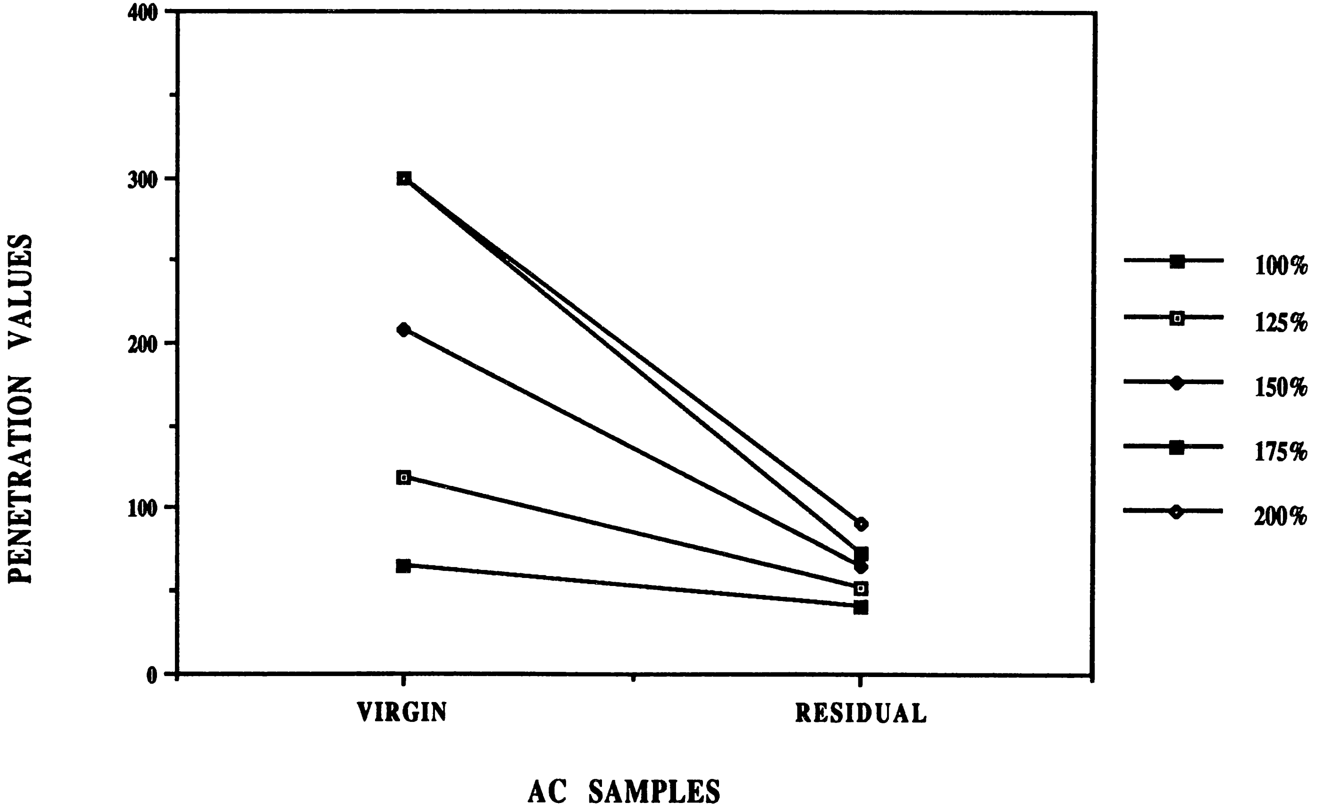


Figure 8. Penetration Values vs. Virgin and Residual-Naphthene Aromatics

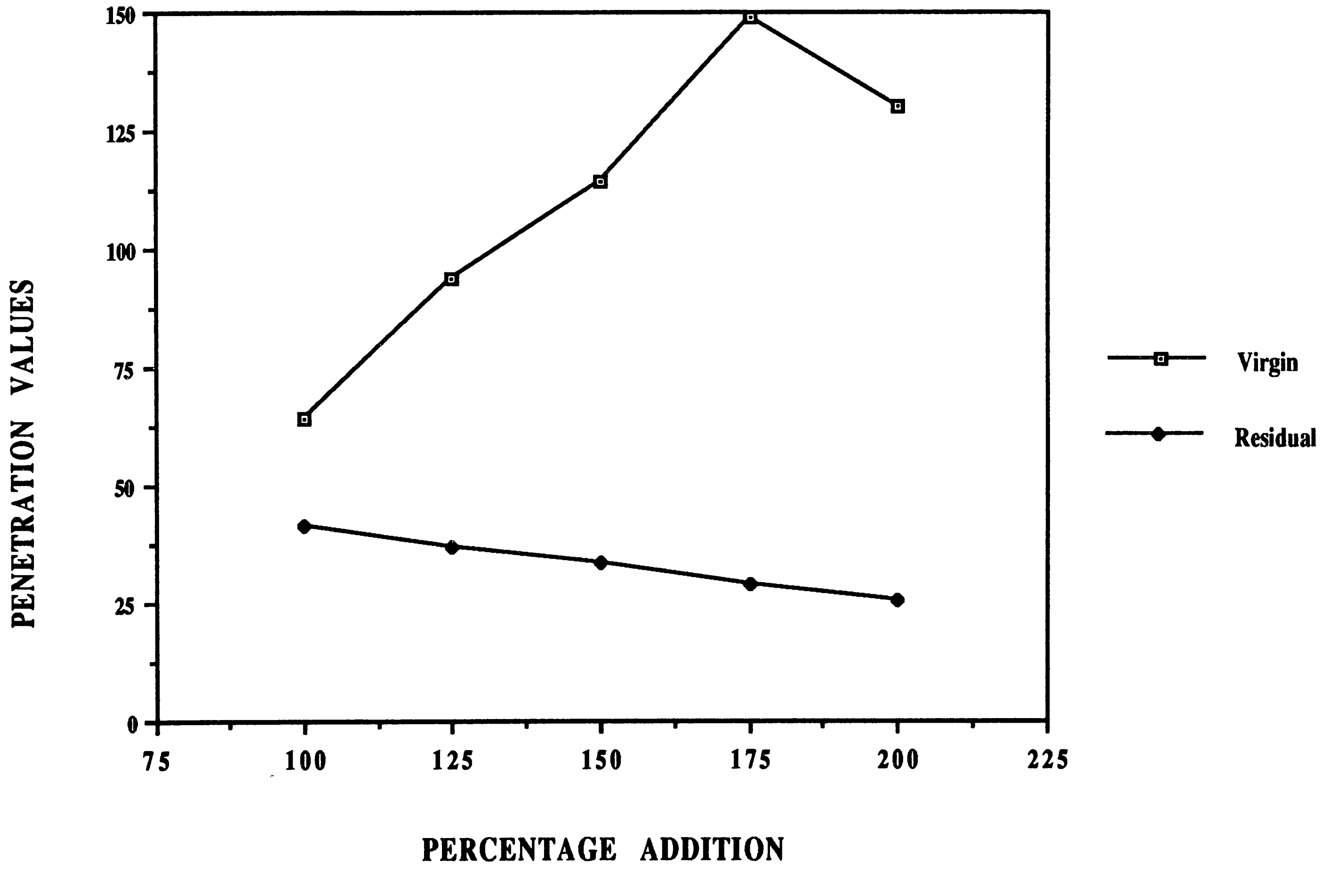


Figure 9. Polar Aromatics Percent Addition
vs. Penetration

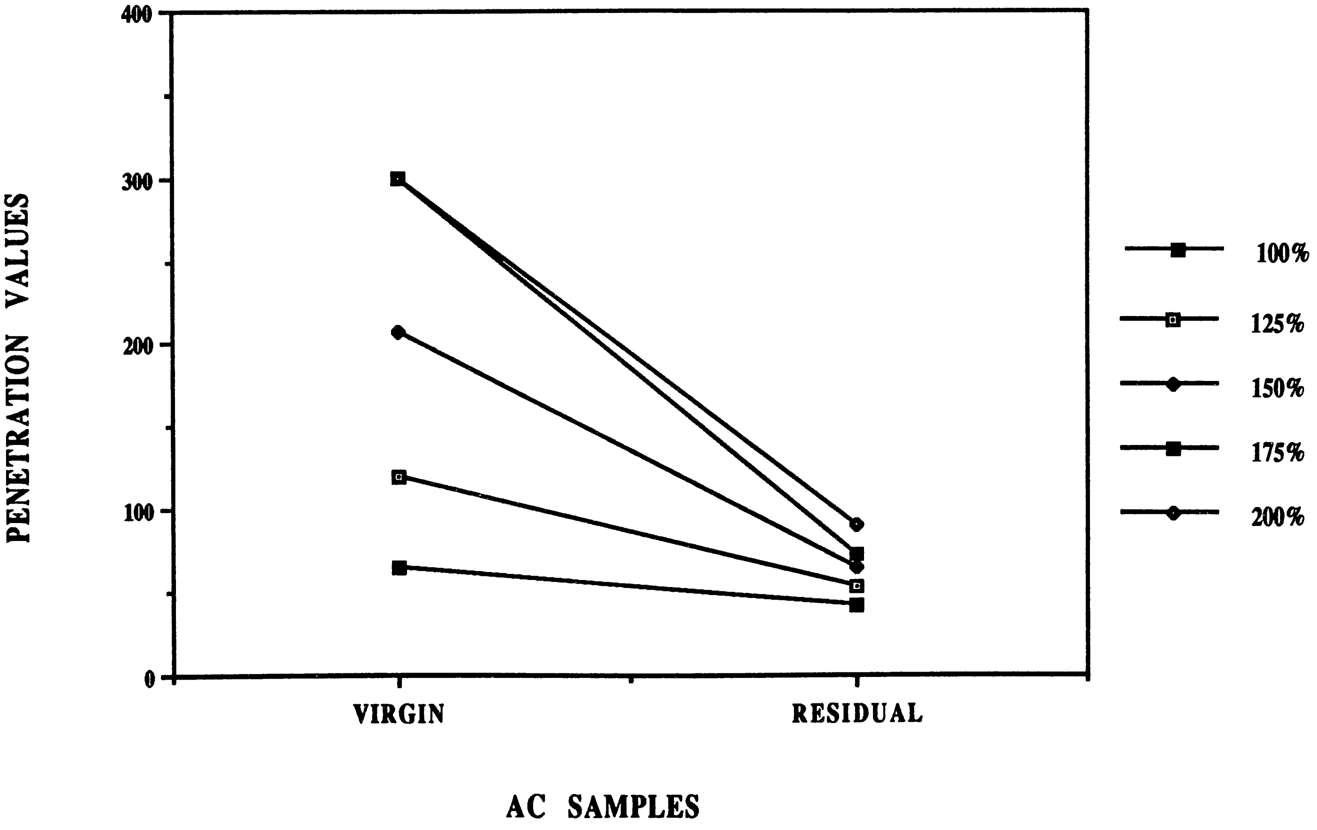


Figure 10. Penetration Values vs. Virgin and Residual-Polar Aromatics

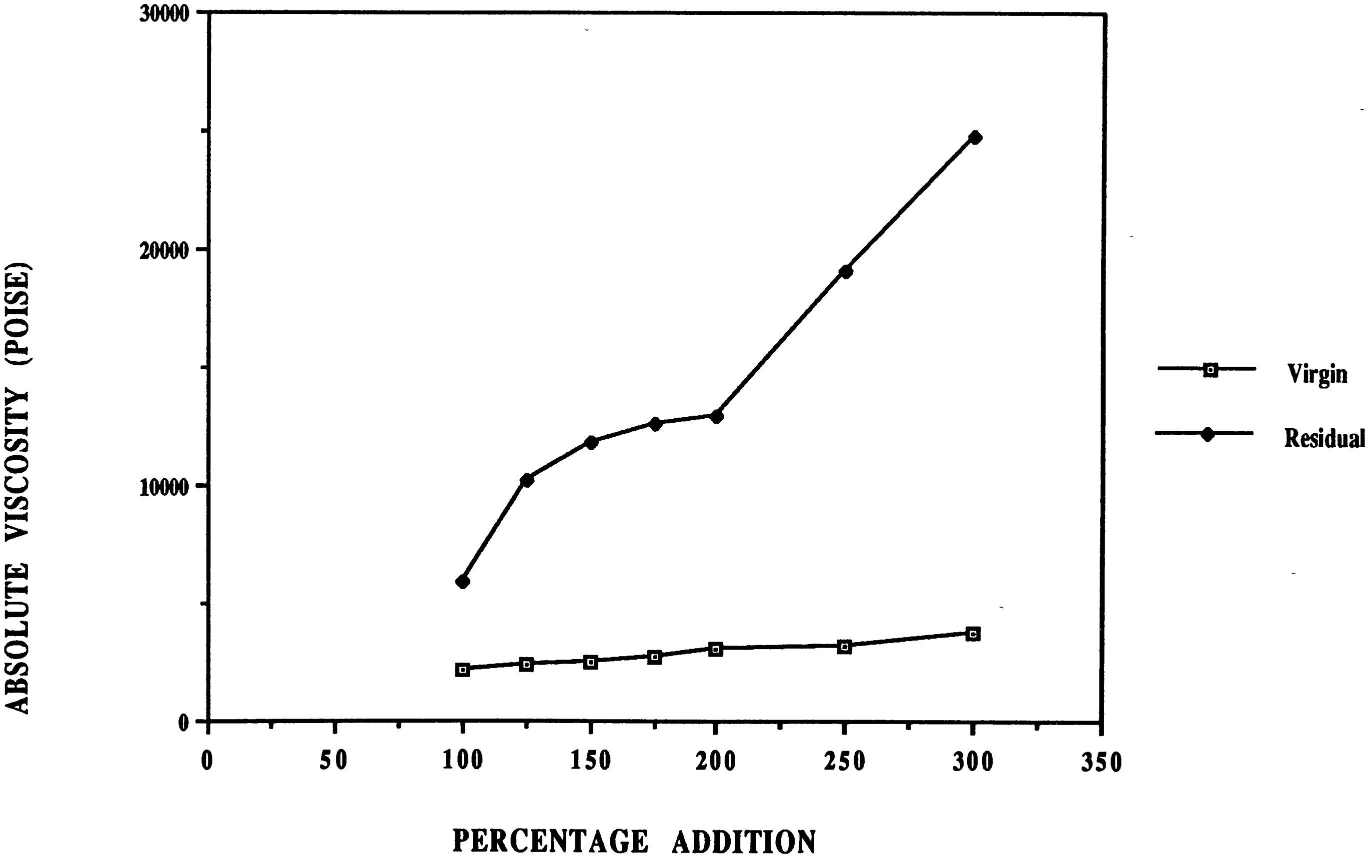


Figure 11. Asphaltenes Percent Addition vs. Absolute Viscosity

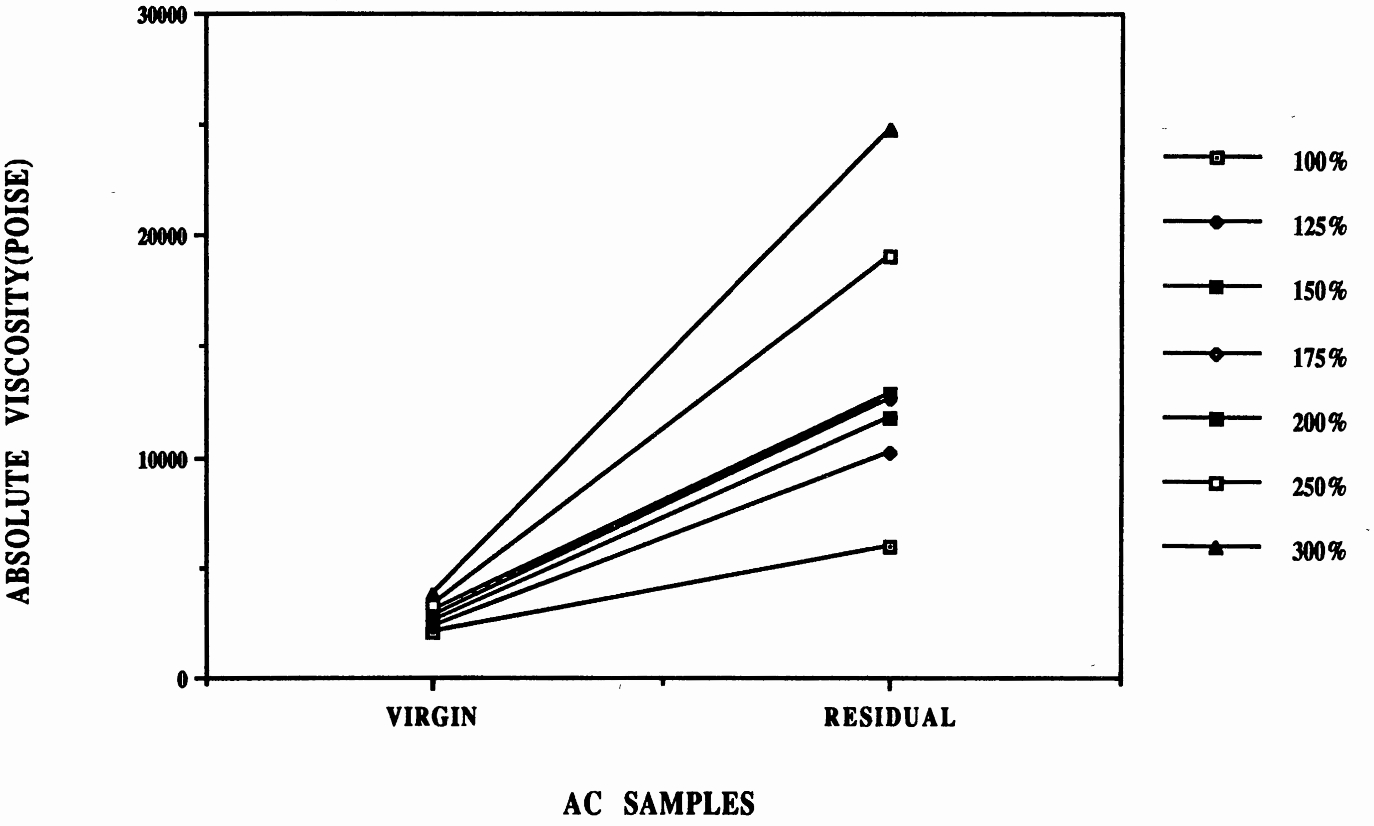


Figure 12. Absolute Viscosity vs. Virgin and Residual-Asphaltenes

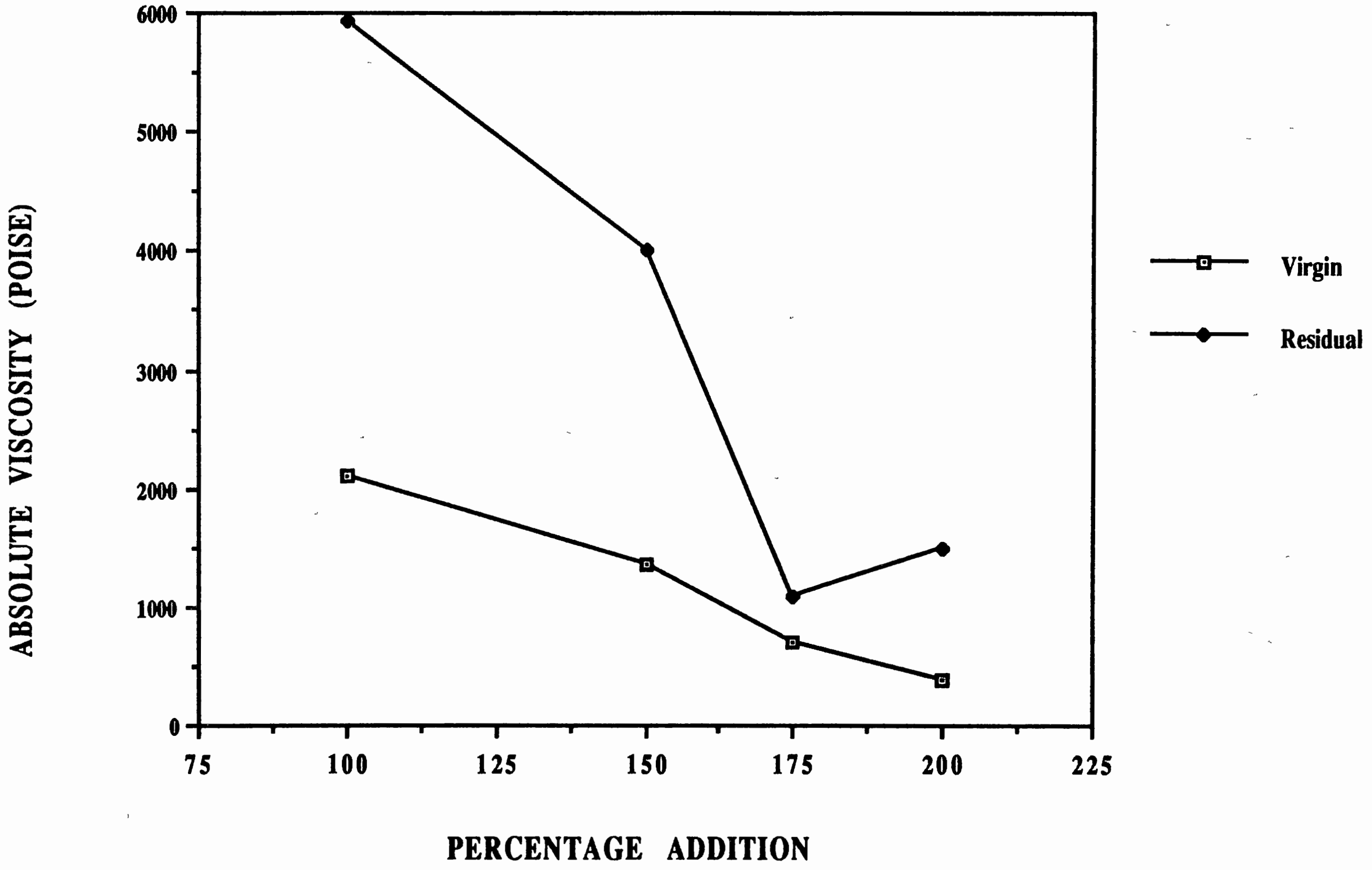


Figure 13. Saturates Percent Addition vs. Absolute Viscosity

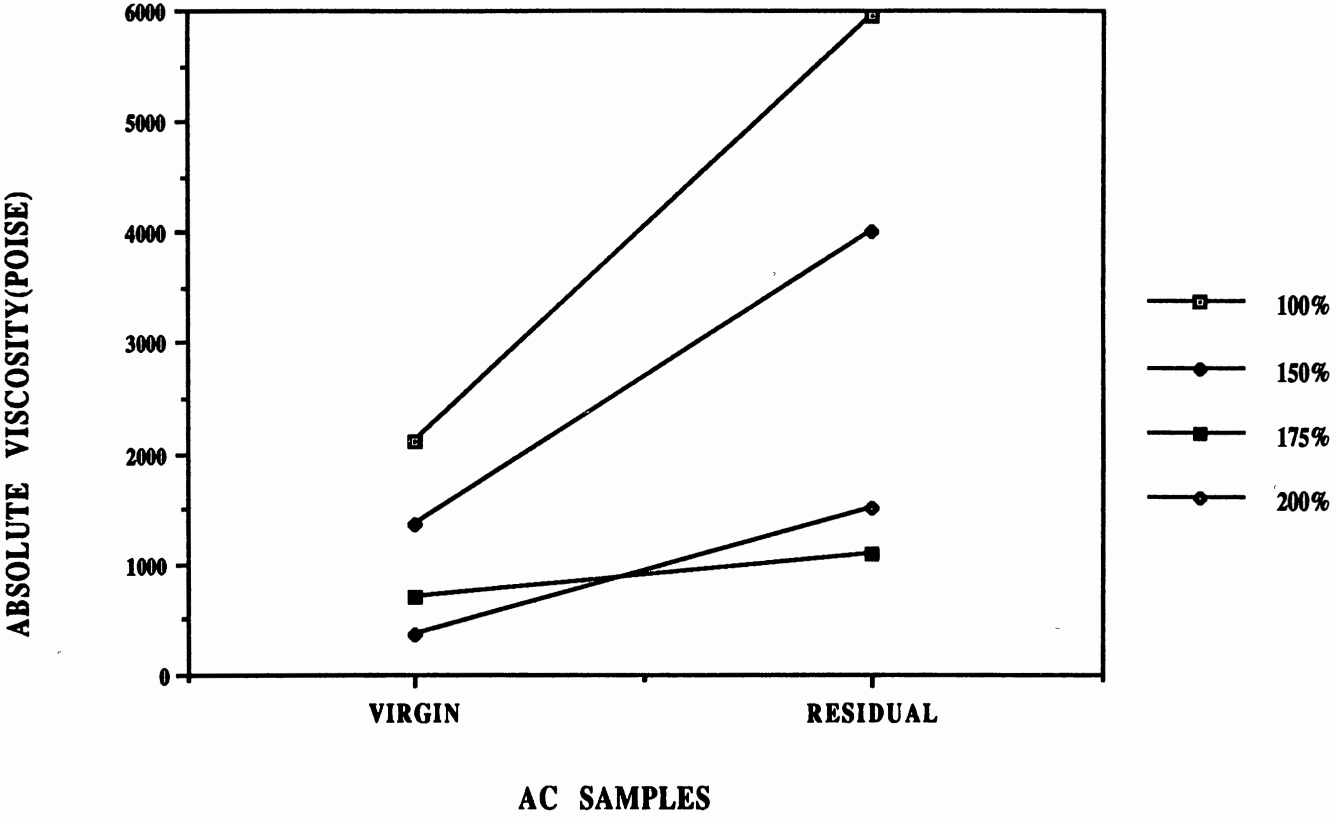


Figure 14. Absolute Viscosity vs. Virgin and Residual-Saturates

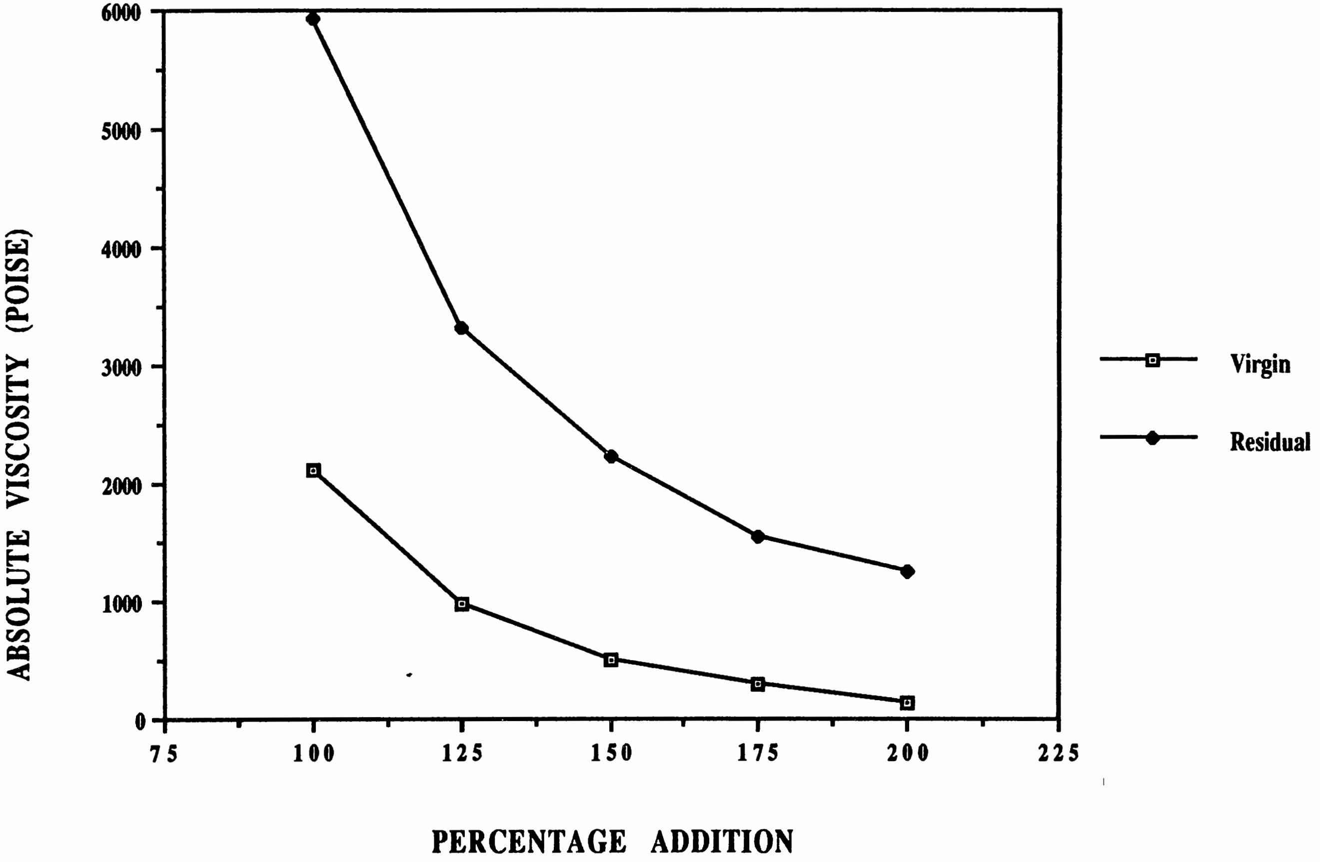


Figure 15. Naphthene Aromatics Percent Addition vs. Absolute Viscosity

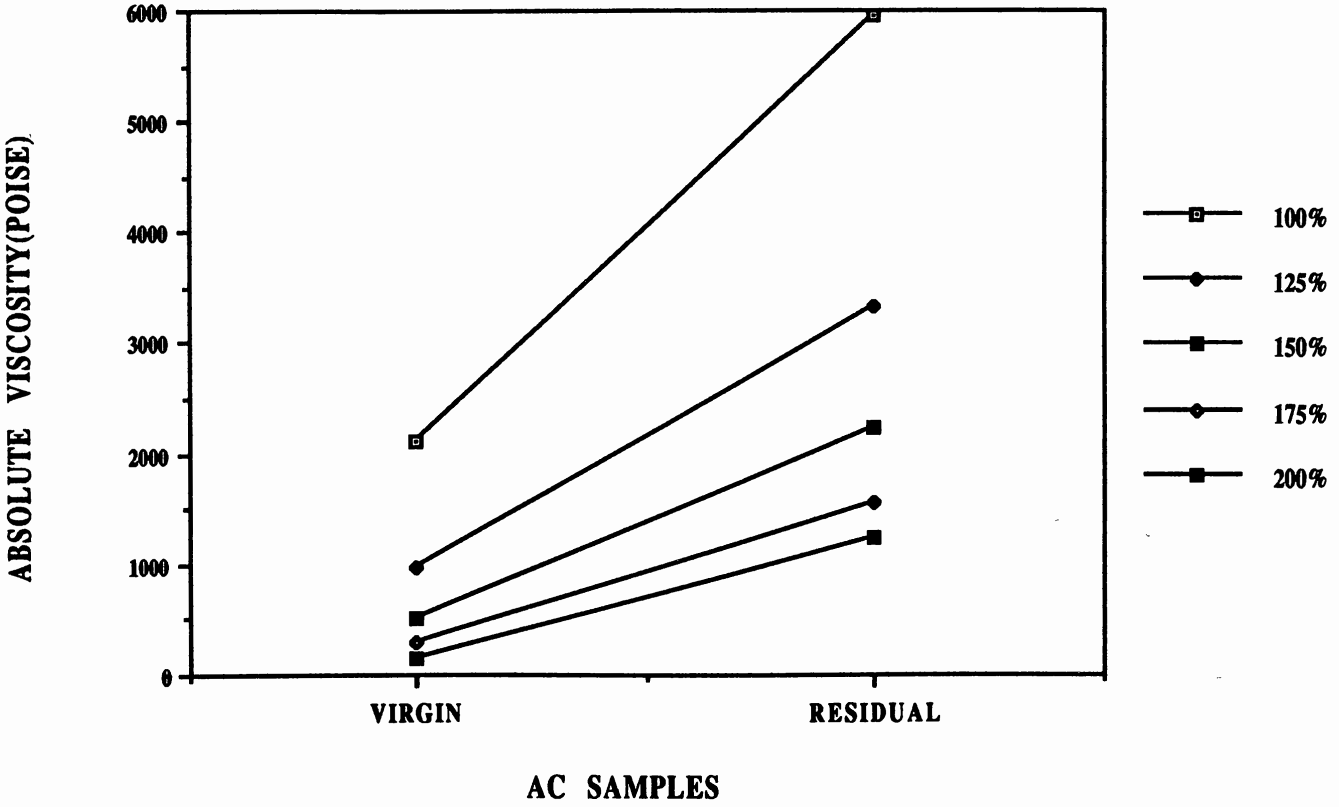


Figure 16. Absolute Viscosity vs. Virgin and Residual-Naphthene Aromatics

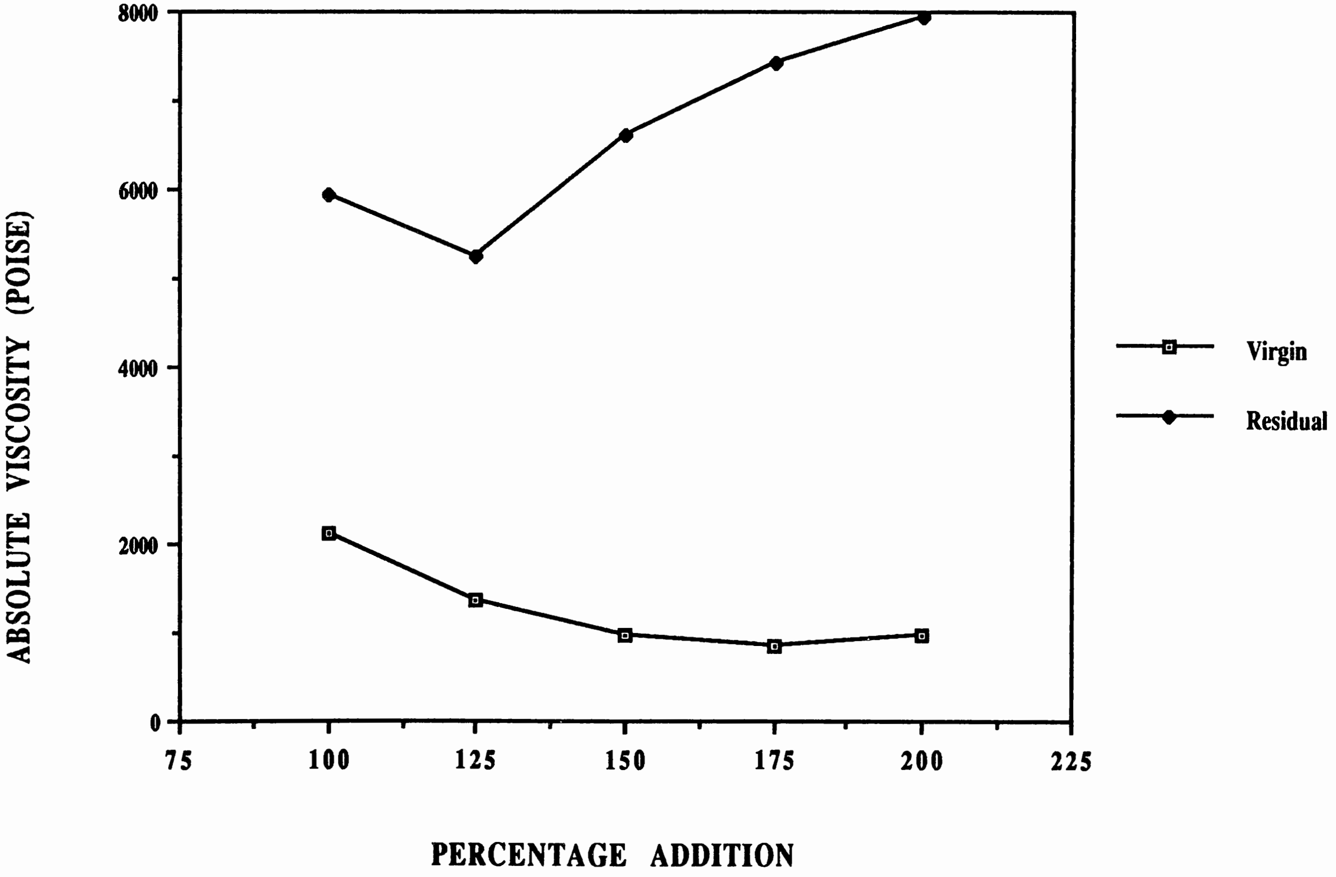


Figure 17. Polar Aromatics Percent Addition vs.
Absolute Viscosity

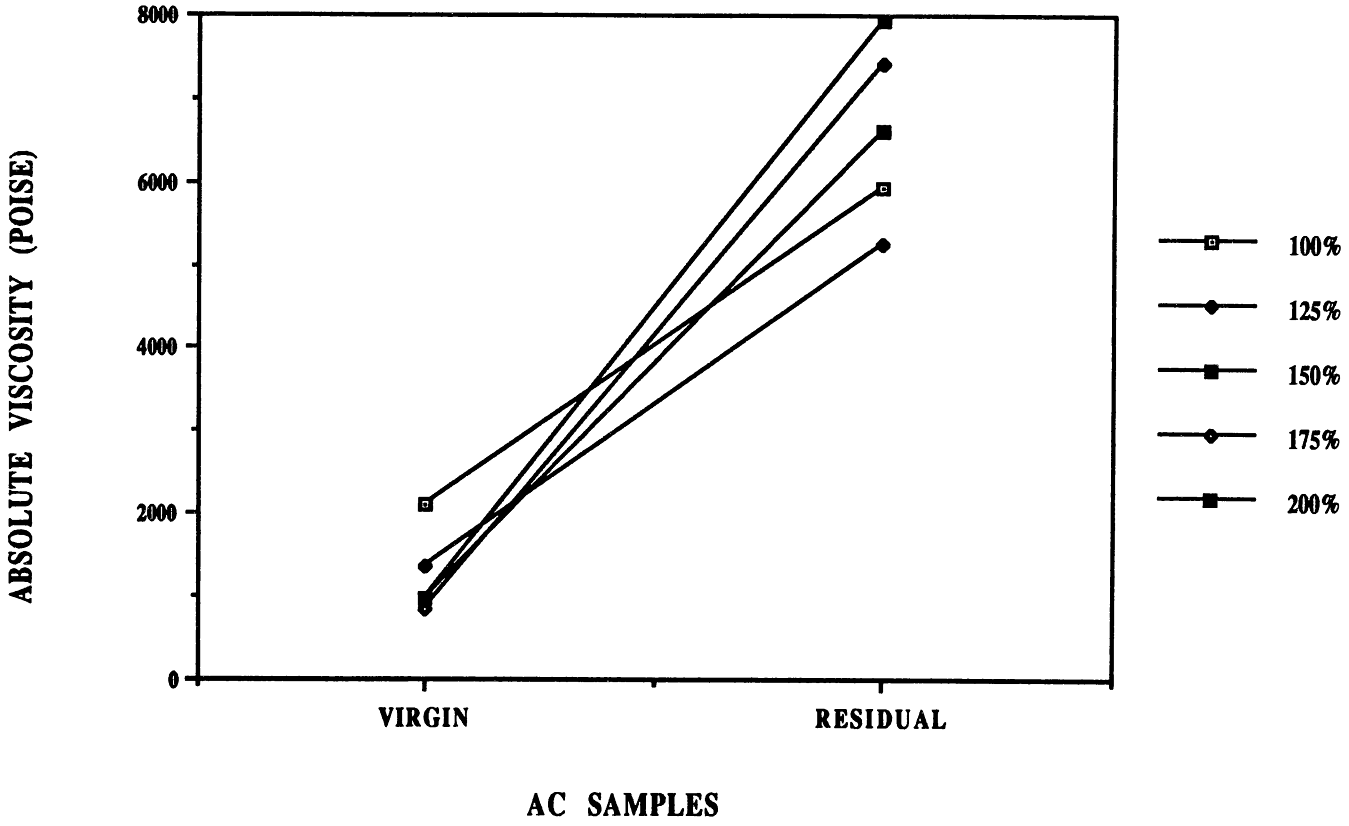


Figure 18. Absolute Viscosity vs. Virgin and Residual-Polar Aromatics

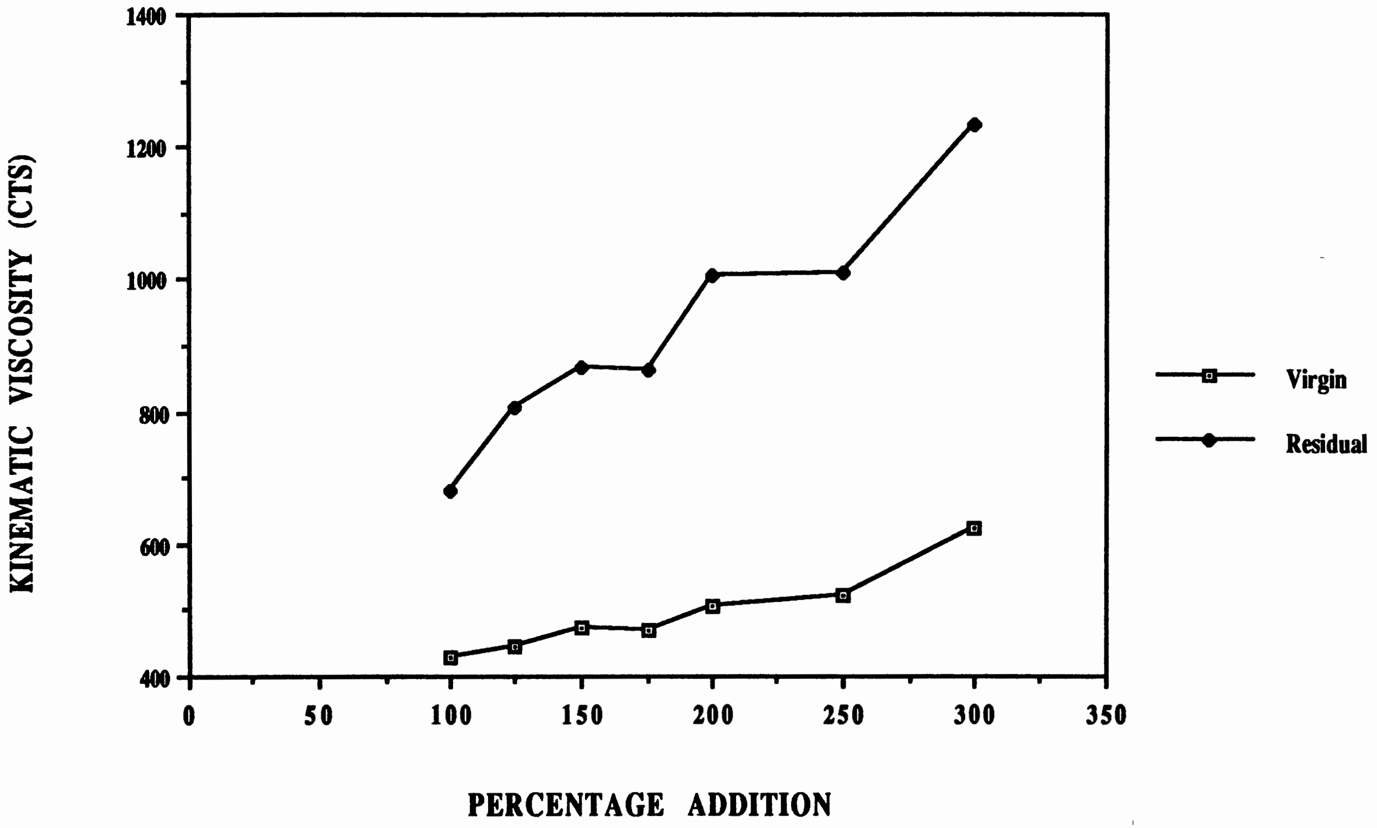


Figure 19. Asphaltenes Percent Addition vs.
Kinematic Viscosity

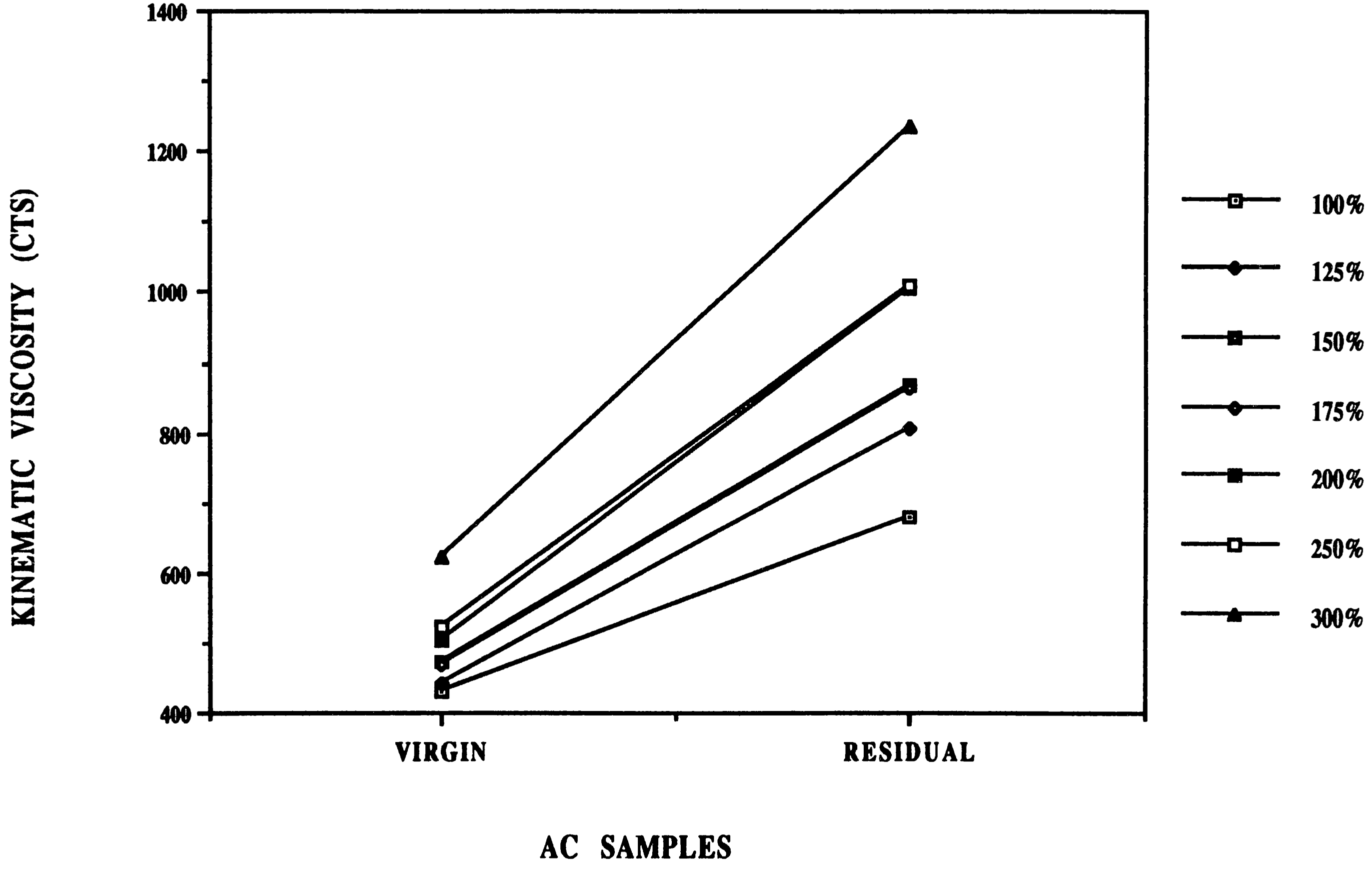


Figure 20. Kinematic Viscosity vs. Virgin and Residual-Asphaltenes

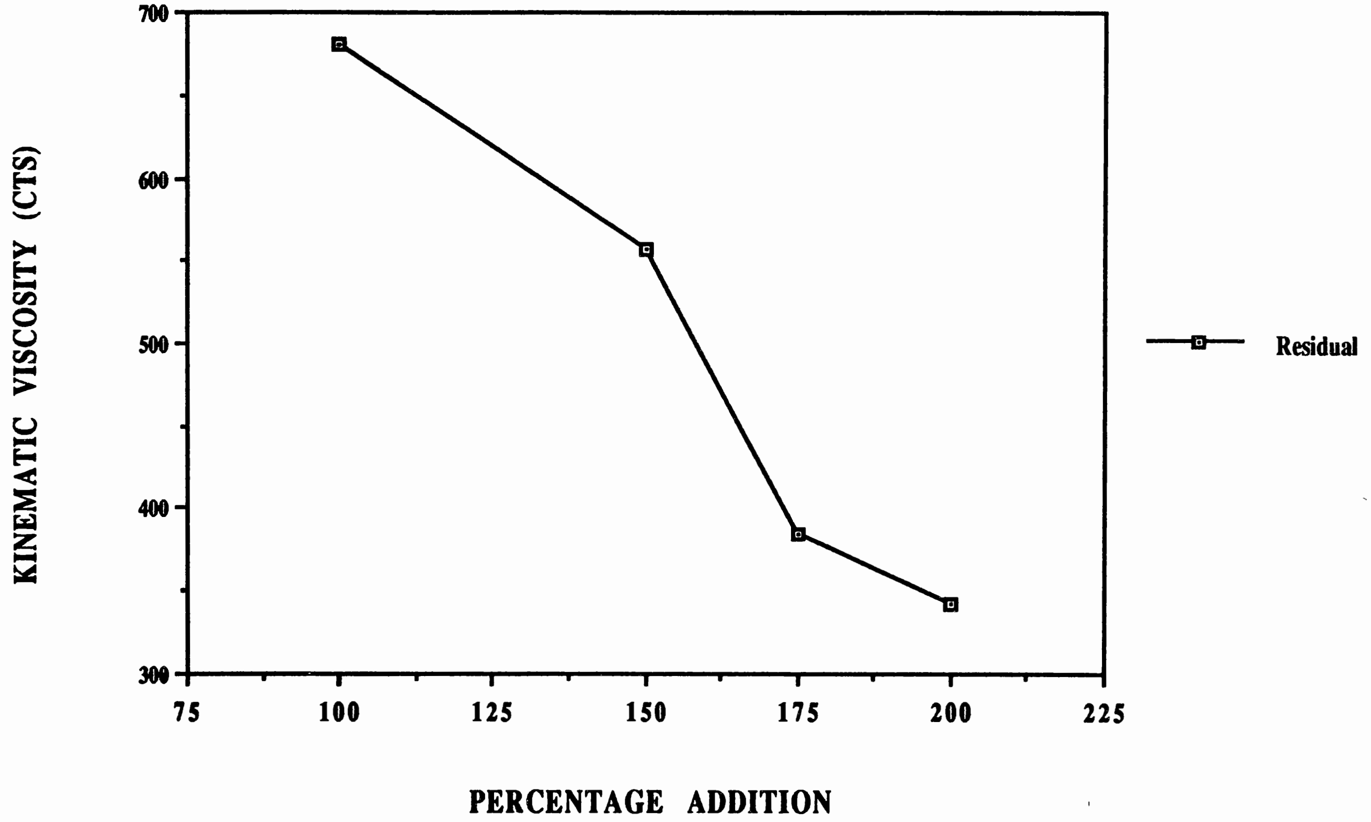


Figure 21. Saturates Percent Addition vs. Kinematic Viscosity

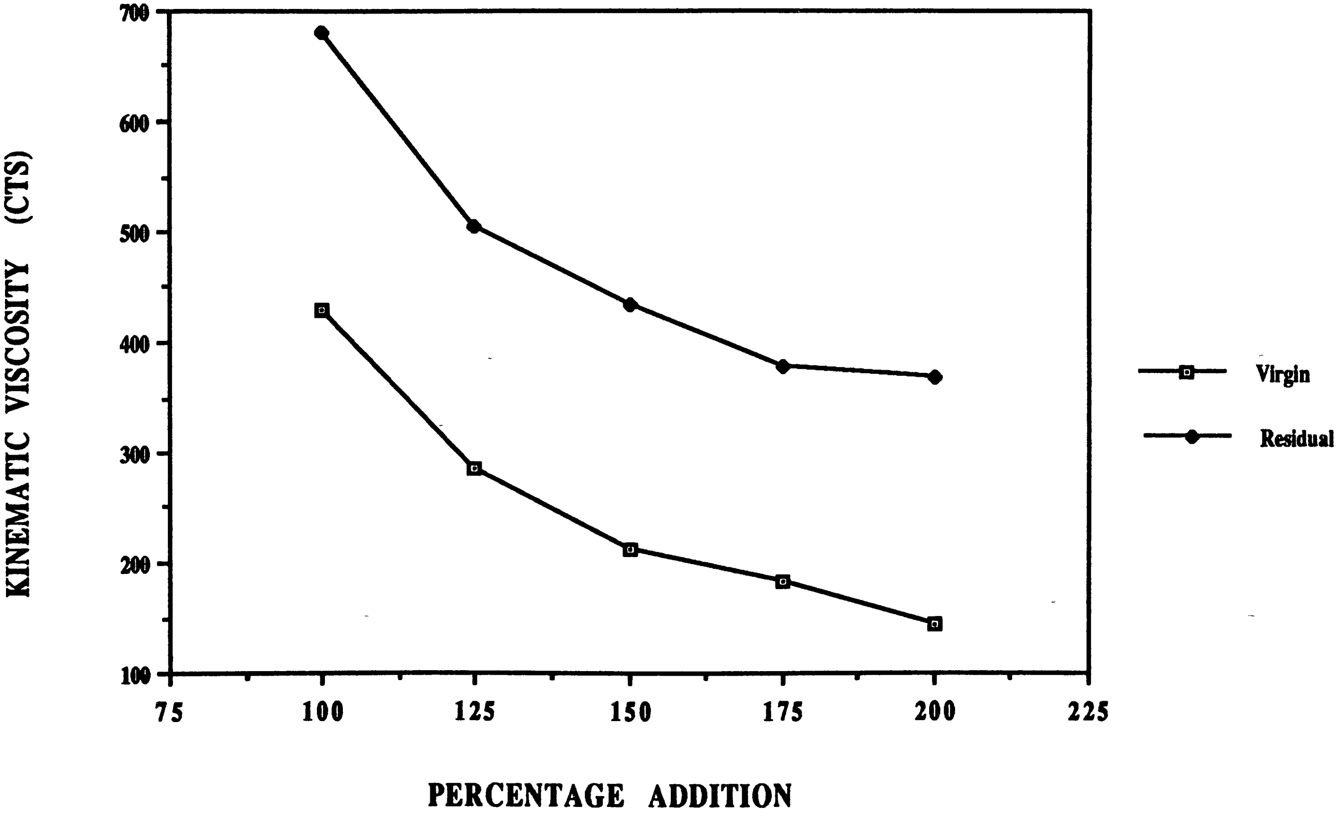


Figure 22. Naphthene Aromatics Percent Addition
vs. Kinematic Viscosity

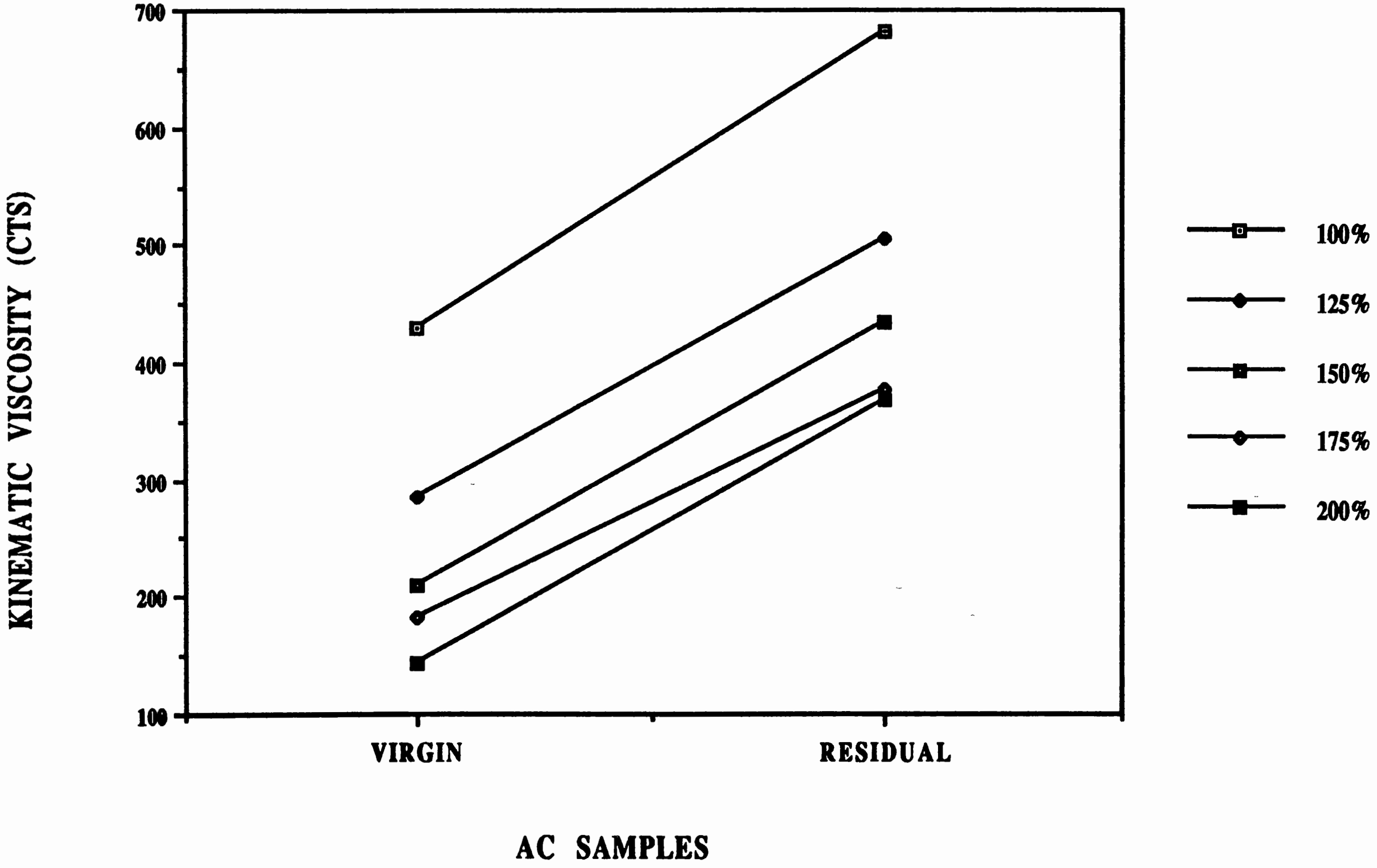


Figure 23. Kinematic Viscosity vs. Virgin and Residual- Naphthene Aromatics

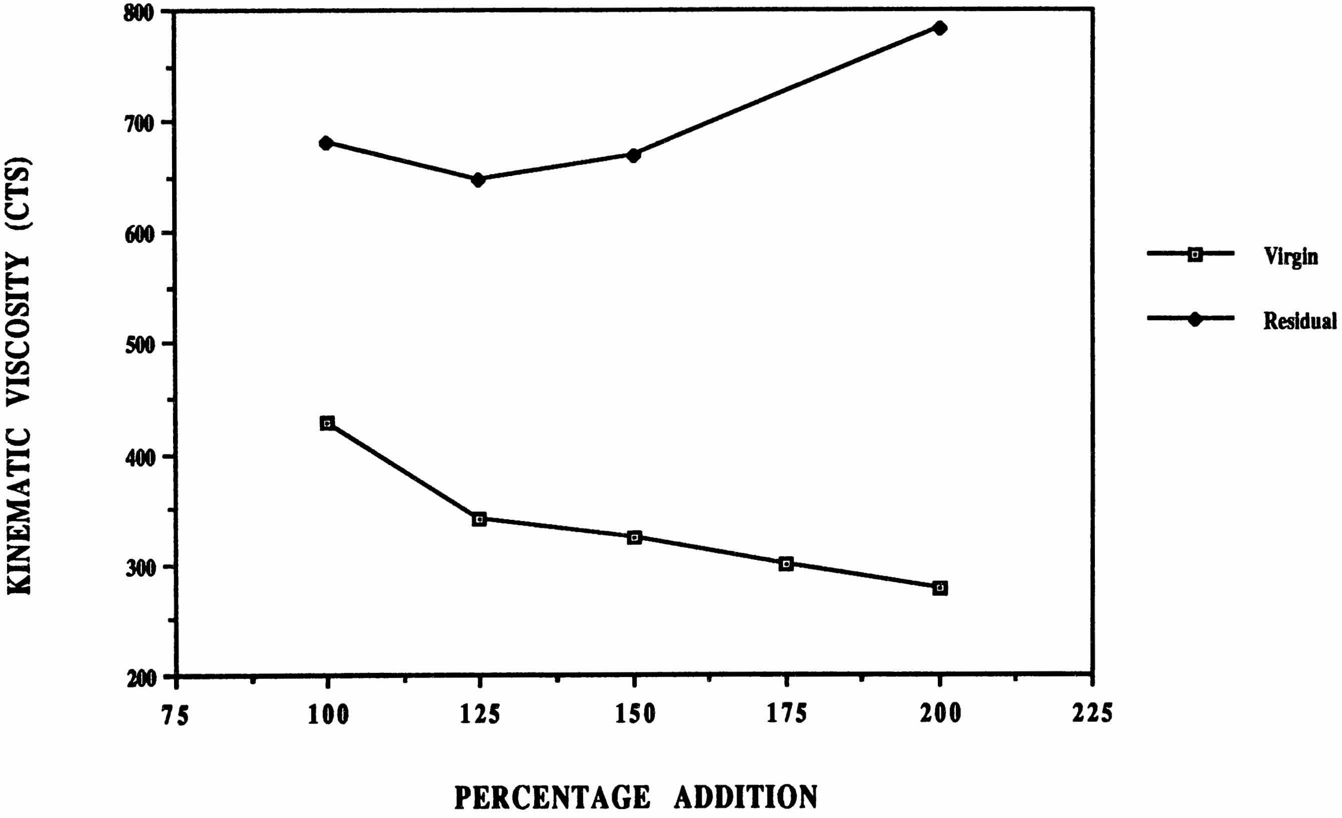


Figure 24. Polar Aromatics Percent Addition vs. Kinematic Viscosity

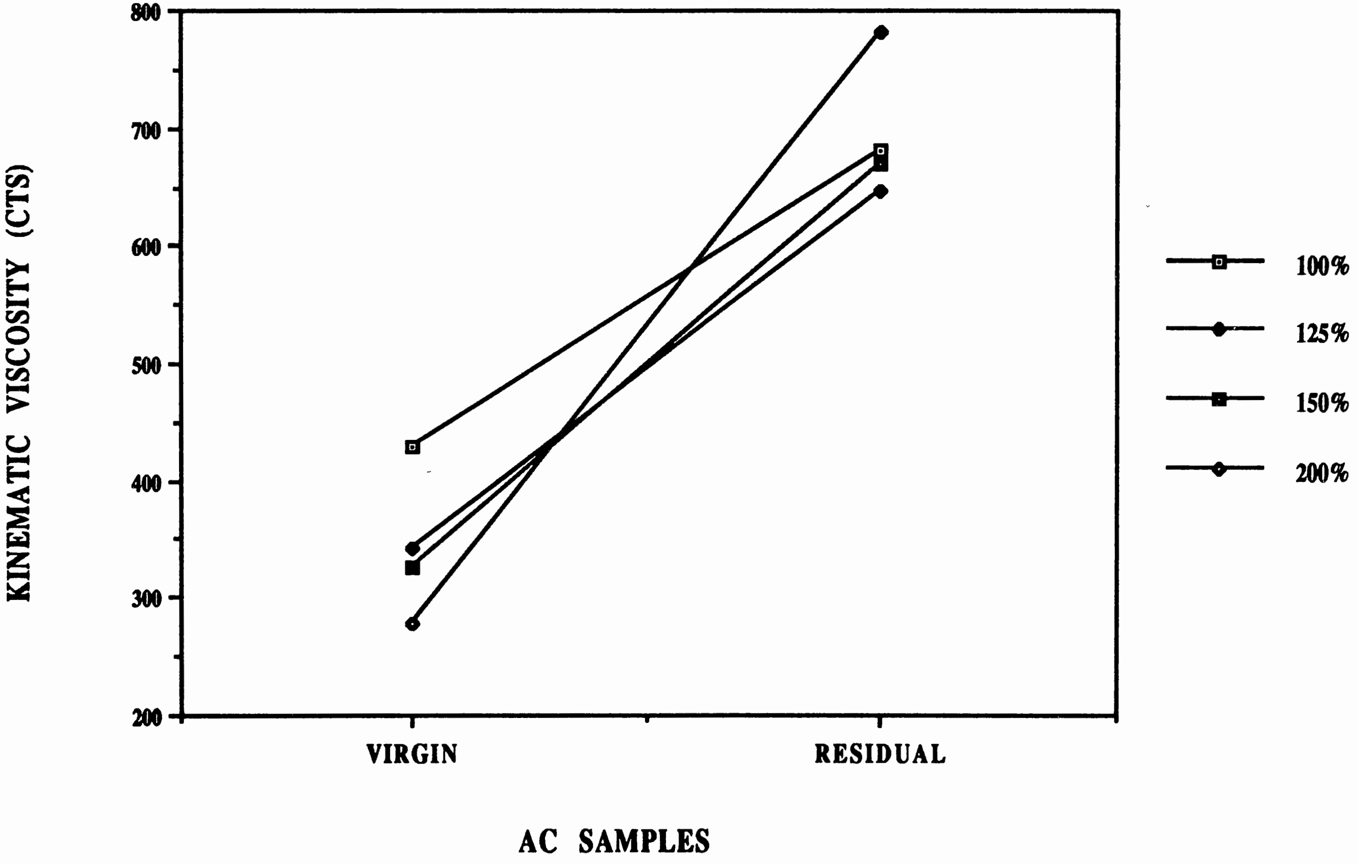


Figure 25. Kinematic Viscosity vs. Virgin and Residual-Polar Aromatics

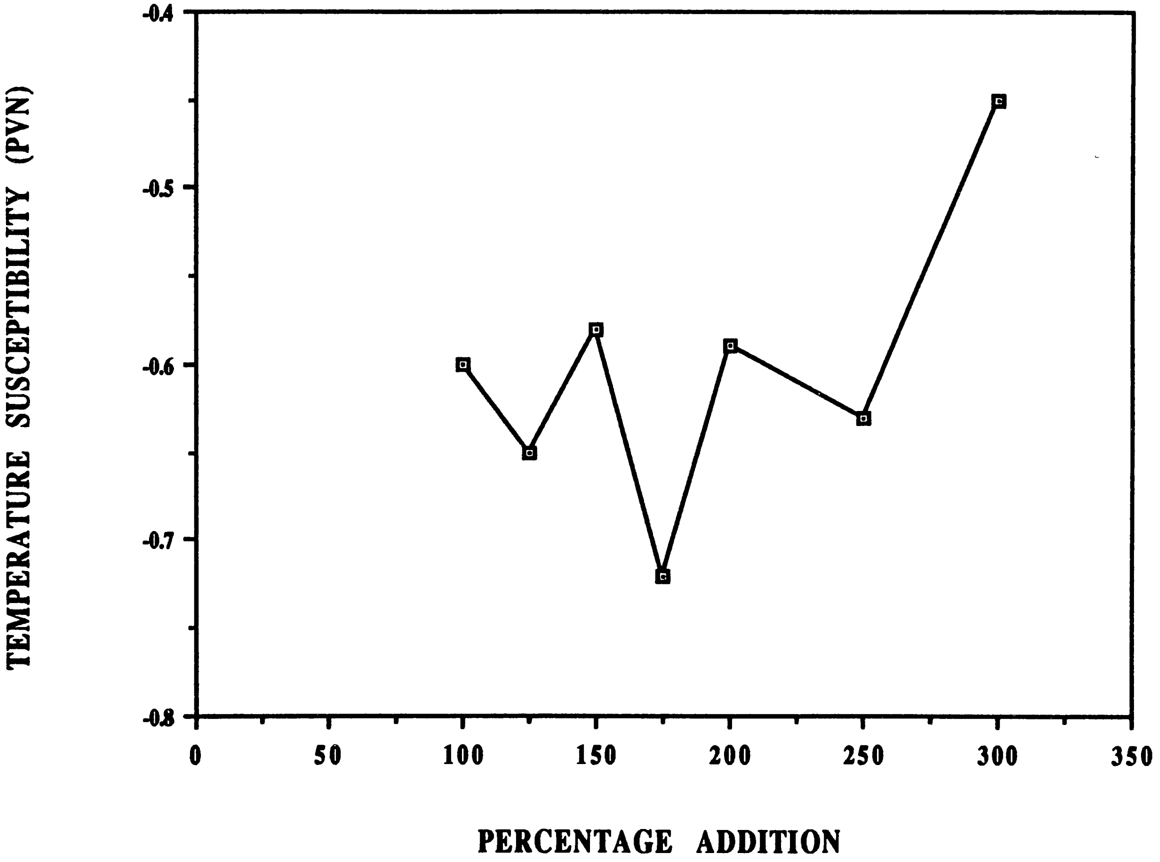


Figure 26. Temperature Susceptibility - Asphaltenes

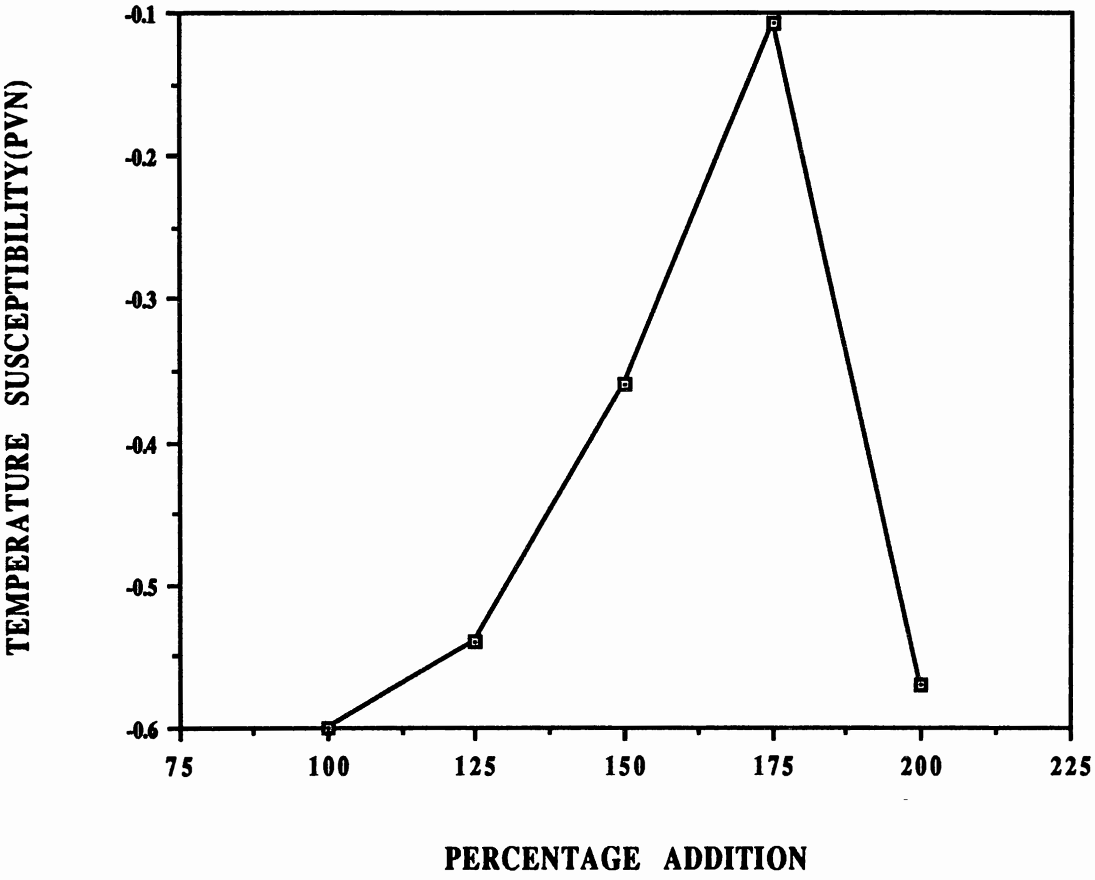


Figure 27. Temperature Susceptibility - Naphthene Aromatics

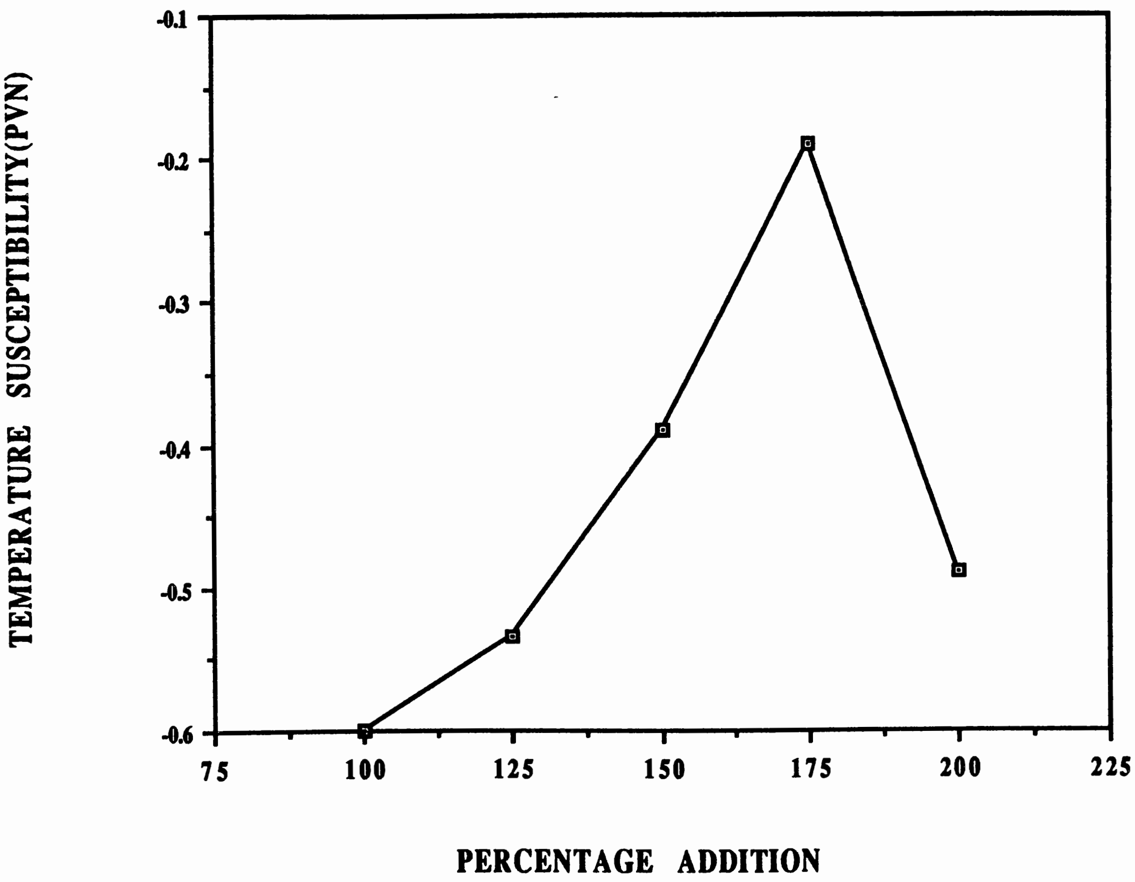


Figure 28. Temperature Susceptibility - Polar Aromatics

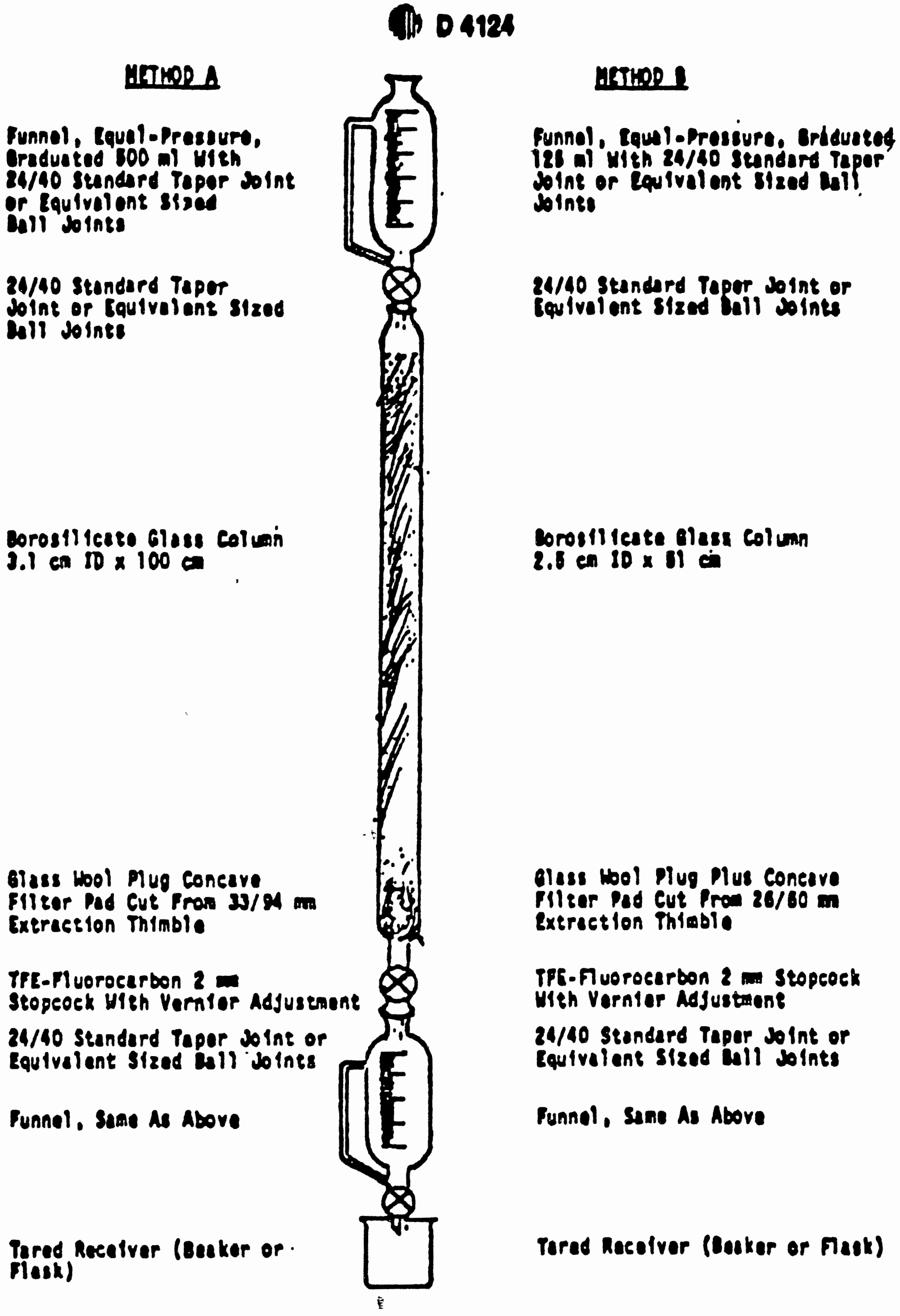


Figure 29. Chromatographic Column for Separation of Asphalt by Elution-Adsorption [45].

APPENDIX B

STANDARD TEST METHOD FOR SEPARATION OF ASPHALT INTO FOUR FRACTIONS

(ASTM D 4124-86)

Standard Test Method for Separation of Asphalt into Four Fraction

Significance and Use

This test method separates asphalts into four well defined fractions. Analysis of these fractions can be used to evaluate asphalt composition. For example, one can compare the ratios of the fractions with other asphalt systems to evaluate processing and aging parameters that relate to performance properties of the asphalt.

Apparatus and Materials

1. Glass Chromatographic Column, 1000mm long and 31mm in diameter with features as specified in Figure 29.
2. Steam bath, vacuum source, nitrogen source and drying oven.
3. Beakers, graduated; Erlenmeyer flasks, 400ml: Round - Bottom Flasks, 500-ml, if Rotavapor is used for solvent removal.
4. Funnels, two, pressure equalizing, 500 ml.
5. Funnel, Buchner, 12.5 cm.
6. Funnel, Separatory, 1-L, TFE-fluorocarbon stopcock preferred.
7. Flask, Suction, 2L.
8. Flask, Erlenmeyer, 2L, with foil covered rubber stopper.
9. Rinse Squeeze Bottle, 1-pt size, polyethylene or TFE-fluorocarbon.

10. Evaporating Dishes, porcelain, 16 and 28 cm.
11. Analytical Balance.
12. Filter Paper, slow to medium filter speed, qualitative grade, 12.5 cm diameter.
13. Extraction Thimble, 33/94 mm.
14. Stirrer, air powered.
15. Stirring Rod with suitable foil covered rubber stopper to fit 2-L Erlenmeyer flask.
16. Glass Wool, borosilicate.
17. Electric Heat Lamp or Hot Plate.

Reagents and Absorbent

1. Alumina, F-20 chromatographic grade, calcined at 775 degrees Fahrenheit for 16h and stored in an evacuated desiccator or airtight bottles.
2. n-Heptane, 99 minimum mol %. (Should be totally free of moisture).
3. Methanol, anhydrous, reagent grade.
4. Toluene, reagent grade.
5. Trichloroethylene, boiling point 86.5 to 87.5 degrees Centigrade.

Procedure

1. Weigh 10 to 15gms of asphalt and place into a 2-L Erlenmeyer flask. Warm the glass gently in a hot plate until the asphalt is in granular form. Disperse the asphalt over the bottom and lower sides of the flask before adding

n-heptane solvent in the ratio of 100ml of solvent per 1g of sample.

2. Install an air-powered stirrer assembly into the flask prior to placing flask and its contents on a steam bath. The stirring rod should rotate inside a foil covered rubber stopper that is used to seal the Erlenmeyer flask, to reduce the evaporation of n-heptane. Maintain the solvent temperature near its boiling point and stir the contents of the flask at a moderate rate until there is no visual evidence of undispersed asphalt adhering to the sides of the flask. Begin timing and continue stirring for an additional hour. After digestion, remove the flask and stirring assembly from the steam bath. Rinse the stirring assembly as it is removed from the flask with n-heptane from a squeeze bottle. Cover the flask with a foil covered rubber stopper and set aside overnight at ambient temperature, so the precipitated asphaltenes can settle to the bottom of the flask.

3. Set up a 12.5 cm diameter Buchner funnel fitted with a slow to medium filter speed, qualitative grade filter paper and a 2-L suction flask. The 1-L separatory funnel should be suspended about 25mm above the center of the filter paper.

4. Decant as much of the clear heptane petrolene solution as possible from the mixture prepared earlier. Place it directly in the separatory funnel.

5. Wet the filter paper in the Buchner funnel with n-heptane

from a squeeze bottle and apply sufficient suction to the flask to secure the filter paper firmly to the funnel surface before beginning the filteration step. Add petrolene solution from the separatory funnel at a closely controlled rate and in such a manner that all of the filtering takes place in the centre of the paper. The filter paper should be wetted periodically with n-heptane to ensure a tight seal with the funnel surface. After the filtering is completed, empty the suction flask before proceeding with the final phase of filtration process.

6. Using a filter paper, test the filtrate from the previous step for insolubles. Refilter if a ring appears.

7. Transfer the contents remaining in the Erlenmeyer flask directly to the Buchner funnel, using additional solvent from the squeeze bottle. Repeatedly wash the asphaltene cake until the filtrate becomes colorless. The insolubles should not creep over the edges of the filter paper into the filtrate. Next, transfer the filter paper and its content to a 500ml beaker and add 150ml of n-heptane. Heat the contents in the beaker for about 30 minutes with occasional stirring to remove n-heptane soluble materials entrained in the asphaltene cake. Filter the hot solution through the same Buchner funnel fitted with a tared, fresh piece of filter paper. Wash the asphaltenes cake until the filtrate is colorless. Test the filtrate for insolubles and repeat if ring appears.

8. Transfer the asphaltene cake on the filter papers to

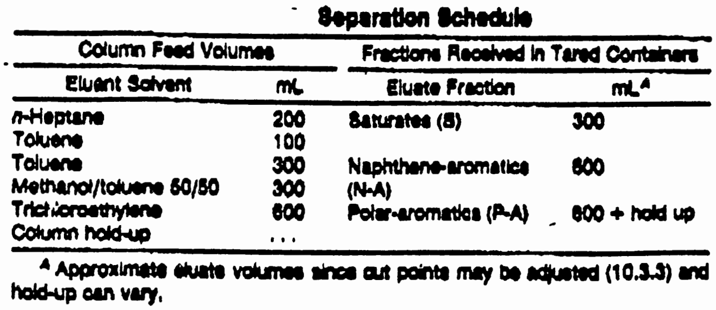
16 cm evaporating dish and dry in a 220 degree Fahrenheit oven until a constant mass is achieved. Record the net mass of asphaltenes recovered.

9.Remove heptane from the filtrate containing petrolenes. Concentrate the petrolene solution to about 50ml and then transfer the concentrate to a 150ml beaker. Sufficient fluidity should remain in the petrolene concentrate to permit easy transfer of concentrate to a chromatographic column for subsequent separation into three defined fractions.

10. Set up the chromatographic column as shown in Figure 29. Place a concave filter pad, cut from the bottom of a extraction thimble, on the bottom of the column. Make it tight by placing a glasswool plug. Add 450g of calcined alumina while gently tapping the column with a rubber coated object. Place a glass wool plug on top of the alumina bed, add 50ml of n-heptane to prewet the column.

11. Transfer the petrolene concentrate from nine to the column, using minimum amount of n-heptane. Start addition of eluants with 200ml of n-heptane from the equal pressure funnel at a drip rate of about 5ml/min. Collect the eluate simultaneously at the rate of 5ml/min. in the receiving funnel. Drain the eluate into tared containers in accordance with the schedule as shown on following page:

12. The liquid level in the column should not be allowed to drop below the top of the alumina bed until the hold-up is removed.



Separation Schedule

Column Feed Volumes		Fractions Received in Tared Containers	
Eluent Solvent	mL	Eluate Fraction	mL[A]
n-Heptane	200	Saturates (S)	300
Toluene	100		
Toluene	300	Naphthene-aromatics	600
Methanol/toluene 50/50	300	(N-A)	
Trichloroethylene	600	Polar-aromatics (P-A)	600 + hold up
Column hold-up	. . .		

[A] Approximate eluate volumes since cut points may be adjusted (10.3.3) and hold-up can vary.

13. Add the new eluant to the column before the final eluate cut from the previous eluant is taken. This procedure requires close attention, especially during the collection of the saturates and naphthene aromatic fractions. The cut point between the naphthene aromatic and polar aromatic fractions may be improved by either cutting short, or increasing the volume of this cut, as observed by the descent of the black polar aromatic ring. The elution volume varies with the composition of the feed. The cut point should be made as the black ring reaches the bottom of the alumina bed. The naphthene aromatic fraction produces a yellow to deep red color eluate whereas the polar aromatics eluate is almost black. Recover the three fraction by solvent removal and record the net mass of the fractions.

VITA

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Master of Science

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