DECLARATION

I, Salami Moses Gbenga, declare that this thesis is solely the result of my work and has not been submitted anywhere for any degree. All literature cited have been duly acknowledged in the references.

M.G. Salami

17/03/06

Date

CERTIFICATION

This thesis titled DEVELOPMENT AND CHARACTERIZATION OF LUBRICATING OIL FROM A NON-PETROLEUM BASE SOURCE (CASTOR OIL) by Salami Moses Gbenga meets the regulations governing the award of the degree of Master of Engineering (Chemical Engineering) of Federal University of Technology, Minna, and is approved for its contribution to knowledge and literary presentation.

Dr M.O. Edoga
(Supervisor)

21-03-06
Date

Dr F. Aberuagba
(Head of Department)

20-04-06
Date

External Examiner

Date

Prof. J. O. Odigure
(Dean, SEET)

22/04/2006
Date

7/6/06
Prof. J.A. Abalaka
(Dean, Postgraduate School.)

Date

DEVELOPMENT AND CHARACTERIZATION OF LUBRICATING OIL FROM A NON-PETROLEUM BASE SOURCE (CASTOR OIL)

A THESIS

Presented to

The Postgraduate School
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By

Salami, Moses Gbenga
(M.ENG/SEET/2001/727)

IN PARTIAL FULFILMENT OF THE
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DEDICATION

This piece of work is dedicated to my father, Pastor Ezekiel Salami, and my mother Mrs. Julianah Salami for their love and contributions towards my education.

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First of all, I acknowledge the Almighty God for his love and grace over my entire life.

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ABSTRACT

The suitability of castor oil based lubricant as a potential substitute for that of petroleum based lubricant was investigated by subjecting the former to various characterization and analyses. Castor oil was extracted from castor beans by indirect leaching (Soxhlet apparatus) and subsequently was characterized. The castor oil was further blended with viscosity improver and other additives namely; antioxidant and corrosion inhibitor. The various samples of lubricating oil thus formulated were characterized and compared with other lubricating oils of Nigerian Industrial Standard (NIS) and Society of Automotive Engineers (SAE) standards. The characteristics of lubricating oil which included viscosity (determined at 40 and 100^{0}C respectively), flash point, pour point, base number, metal content and appearance, were determined for the formulated lubricating oil samples in accordance with American Society for Testing and Materials (ASTM) and Institute of Petroleum (IP) standards. The oil samples were also subjected to different process conditions, namely temperature (40–100^{0}C), pressure (1–2 bars) and time (4– 6 hours).

The results of the characterization and analyses were obtained as follows: Sample A was found to be consistent with SAE 30W, Sample B was consistent with SAE 40, and Sample E was consistent with SAE 20W/50. The oils appearance was found to be bright and clear, which implied that they passed the appearance test which is often difficult to be satisfied by most of lubricating oils. All the oil samples compared favorably with Society of Automotive Engineers (SAE) specifications. It was found that almost all the lubricating oil samples maintained their physiocochemical properties under test, except Sample J which was a pure blend. Out pf a;; the models, Model E emerged as the best model and is given as:

$$V = 236.5029 - 2.1610P_1 - 0.2040P_2 - 0.2713P_3 + 0.0009P_1P_2 + 0.0014P_1P_3 + 0.0025P_2P_3.$$

where V is the viscosity (cSt), P_1 is the temperature (^{0}C), P_2 is the pressure (bar) and P_3 is time (h).

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ABBREVIATIONS

ANOVA	Analysis of Variance
API	American Petroleum Institute
ASTM	American Society for Testing and Materials.
B&C	Bright and Clear
B.P	Boiling Point
COC	Cleveland Open Cup
CP	Centipoise
cst	Centistokes
DCO	Dehydrated Castor Oil
d f	Degree of Freedom
F.F.A	Free Fatty Acid
I.P	Institute of Petroleum
M.S	Mean Square
NIS	Nigerian Industrial Standard
SAE	Society of Automotive Engineers
SS	Sum of Squares
S.V.	Saponification Value
T.B.N.	Total base number
V	Viscosity
V.I	Viscosity Index
E.P	Extreme Pressure

NOTATIONS

^0C	Degree Celsius
Cp	Specific heat
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
P_1	Temperature
P_2	Pressure
P_3	Time
W_0	Weight of empty specific gravity bottle
W_1	Weight of castor oil + weight of specific gravity bottle
W_2	Weight of water + weight of specific gravity bottle
H	Kinematic viscosity (cSt.) at 40^0C of a petroleum product of viscosity index 100 having the same kinematic viscosity (cSt) at 100^0C as the petroleum product whose viscosity index is to be determined
L	Kinematic viscosity, (cSt.) at 40^0C of petroleum product of viscosity index 0 having the same kinematic viscosity at 100^0C as the petroleum product whose viscosity index is to be determined
U	kinematic viscosity, (cSt) at 40^0C of the petroleum product whose viscosity index is to be determined.
V	Viscosity of the lubricating oil

GREEK SYMBOLS

ρ	Density (kg/m^3)
η_K	Kinematic viscosity (m^2/s)

CHAPTER

1.0 INTRODUCTION

1.1 Background

Lubricants are usually liquids or semi- liquids, but may be solids or gases or a combination of solids, liquids and gases which reduce friction between surfaces by providing something between the surfaces concerned which prevents them from rubbing together and injuring one another. It is believed that friction is caused by the interlocking action of two surfaces and also by the attraction of one material to another. A reduction in the energy loss to friction and longer component life can be achieved if the surface can be separated; this consequently, can be achieved by the lubrication of the systems. Lubrication is simply the use of a material, otherwise known as lubricant to improve the smoothness of surfaces of the moving parts.

Lubricant, whether synthetic or natural could be a liquid oil used for lubrication. Presently lubricants are majorly sourced from petroleum because, a very wide range of suitable liquids, varying in molecular weights and viscosity can be produced by the various refining processes. Uninterestingly, petroleum itself is a finite product and it is a highly competitive source of many petrochemicals, and subject to the vagaries of market forces. As a consequence, an alternative source becomes imperatively unavoidable, hence the present study.

However, one of the most interesting recent development is a growing awareness that vegetable oils are useful alternatives to petroleum-sourced lubricating oils. About 50 years ago, Weiss in Tanzania used a locally pressed castor oil as a gear box and engine oil to keep his Land Rover on the road during one of the post-war oil shortages. The results of many tests carried out on its uses, and also its acceptance as a jet engine lubricant (Weiss, 1983) is an indication of its prospects. A study of "oilier" oils pointed out the secrets of these plant-based lubricants. It had been established in the 1920s that fatty oils act as lubricants because they contain active molecules which adhere to the metal surface by strong physical or weak chemical forces (adsorption) thus forming one or more persistent layers (William, 1967). They stick to the metal under the conditions which would destroy the fluid film of conventional oil. It has been observed that no pure vegetable oil or mineral oil possesses all the properties required of lubricants by modern technology; hence a mixture of some extent is necessary. Such mixtures are often very specific in their components, but in general, the lubricants most commonly used are very similar, typical of ordinary motor cars or farm tractors lubricants. It is in view of the above reasoning that substitution by vegetable oils becomes possible and practical, the main limiting factor being their availability and price. Price may not be the most critical issue in developing countries like Nigeria with home grown supplies of castor seeds. With the rising price of petroleum products, and the increasing difficulty of paying for them, the price differential of oil seeds becomes insignificant.

Castor oil is one of the few naturally occurring oils that is almost a pure compound, consisting mainly of hydroxyl and glycerides. Research into the uses of castor oil as a lubricant probably exceeds that of any other vegetable oil (Macfarlane, 1975), and for many years, it has been an additive in special blends. The London Transport Executives also tested a castor-based oil as general and engine lubricants and found it as effective as mineral oils.

1.2 Aims and Objective

The overall objective of this work was to formulate lubricating oil from a non-petroleum based oil such as castor oil using statistical design typical of "simplex lattice". Specifically, the aim was to extract and formulate castor- oil based lubricant using simplex lattice design typical of 2^3-factorial, that can substitute the conventional petroleum based lubricants. More so, the formulated castor-oil based lubricants would be characterized and analyzed so as to establish it's suitability as a potential substitute for the conventional lubricant.

1.3 Approach

To achieve the above stated objectives, the following procedure would be adopted:

(1) The extraction of castor oil from castor seeds using indirect leaching method (Soxh-let apparatus). Indirect leaching method was adopted because of its simplicity, availability, relatively low cost and selectivity in extraction.

(2) Characterization and analysis of extracted castor oil. This would involve characterization and analysis in accordance with standard international specifications.

(3) Formulation of the lubricating oils using simplex lattice design typical of 2^3- factorial. This will involve the blending of castor oil with viscosity improver and other additives.

(4) Characterization of the formulated lubricating oils. The oil samples thus formulated would be subjected to analyses to verify their conformity with international standard specifications.

(5) Finally the application of the lubricating oil samples would be conducted so as to ascertain their efficiencies and performance.

CHARPTER

2.0 LITERATURE REVIEW

2.1 Historical Background

The castor plant, *Ricinus communis L* is a member of the *euphorbiaceae* or spunge family, which contains a number of plants mostly native to the tropics. Although generally known as the castor bean plant and the seeds as castor beans, it is not a legume. It is a plant whose contemporary distribution in the warmier regions is world-wide. Its origin is obscured by its wide dissemination in ancient times; and the ease and rapidity with which it becomes established as a native plant. It certainly appears indigenous to East Africa, especially in the Ethiopian area, but elsewhere there is invariably considerable evidence indicating its introduction. A close examination of literature shows that castor plant originated from Ethiopia in East Africa.

Castor seed was an important item of commerce in ancient Egypt, and have been found in tombs dating from B.C. 4000. Hollow castor stems were used to store "Kohl", a cosmetic in the eighteenth dynasty, B.C 1567-320 (Hayes, 1953). Ancient historians such as Herodotus mentioned the use of castor oil as lighting oil in ancient Egypt as well as describing the method of extraction some of which are relevant in recent times. Strabo (Weiss, 1983) noted that the oil was used by people to anoint their bodies, despite the unpleasant odour. Both the plant and the oil were known also to the Hebrews under the name "qiqayon", which indicates it was probably the plant referred to in the book of Jonah, as that which the Lord caused to grow and provide shelter for Jonah as he sat outside the city of Nineveh. Israel now has a major plant breeding organization which is a leading producer of commercial quantities of its hybrid seeds.

In India (Weiss, 1983), the growing of castor and the use of its oil are well established that its origin is lost in time. The plant was described as indigenous and the oil used in lamps. The oil was and is still used extensively in local medicines mainly as laxatives, but also to alleviate rough and dry skin conditions.

Castor is a fairly recent introduction to the new world, probably transferred by slaves from Africa, but is now to be found growing in a neutralized state over almost the whole of America wherever favourable conditions occur. Its distribution has been fastened by large scale commercial planting and horticulturists, and since the plants freely produce viable seeds, a large indigenous population was quickly established. The oil has found wide application in modern technology, and there are many hundreds of industrial uses of castor oil and its derivatives. It is interesting, to say the least, to speculate on the methods by which the ancients found that castor oil was a purge, but the whole bean a fatal poison. Aulus Celsus AD14-37, has this to say "in this way, medicine arose from the experience of the recovery of some and the death of other; differentiating the harmful from the salutary things" Even today, strict safeguards are necessary to ensure that the expressed oil for medical use is not contaminated by toxic elements. The attractive seeds have caused frequent fatalities, and records of such tragedies are numerous and continuing.

2.2 Castor Seed

The capsule usually contains three seeds, flattened oval shaped, with a shining brittle testa enclosing a white, highly oleaginous kernel. Seeds may be coloured red, brown, buff or black, but usually several colours occur as a very attractive mottling on the testa. In many countries, they were used to make necklaces and belts, in some as ornaments around domestic utensils. Seeds range in size, from a few millimeters to nearly 25mm long in giant types; and in breadth from 5 to 16mm. The 100 seeds weight may vary from 10 to 100g, but most of the dwarf internodes varieties average some 30g. In general, the weight of the individual seed increases as the number of seeds produced by each plant decreases. However, there appears to be a correlation between the seed's size and the oil content, for when the range of seed's size is large, kernel percentage is more closely correlated with oil content than other factors. The testa is thin and often brittle, the degree of brittleness also depending to some extent on the age and oil content of the seeds.

2.3 Cultivation of Castor Seeds

A large proportion of castor seeds which find their way into the international markets from many less developed regions have been obtained from wild or semi- cultivated plants, and systematic cultivation of pure stands of castor by peasant farmers is the exception. More often, castor is interplanted on areas unsuitable for other crops or merely protected when found growing. When castor is deliberately sown as a cash crop, the standard of cultivation varies as widely as the regions in which it is grown.

Since castor is often grown in agricultural marginal areas, relationship between rainfall, time of planting, and plant population are very important in achieving optimum yields. Production cost will probably be higher than for a similar crop grown in more fertile or productive regions, and thus the necessity of ensuring maximum returns per hectare is more important.

2.4 Constituents of Castor Seed

The most important constituents of castor seed is the oil, usually between 40-60 per cent in commercial varieties. The expressed oil is rich in triglycerides, principally ricinolein, the fatty acid component being ricinoleic acid; $C_{17}H_{32}OHCOOH$, whose three hydroxyl groups confer on castor oil the unique property of solubility in alcohol. This property is taken advantage of in this piece of work. Analyses of castor seeds from number of countries and with a specific emphasy on Nigerian castor is shown in tables 2.1 and 2.2.

Table 2.1 Analyses of Castor Seeds (Weiss, 1971).

Characteristic (%)	India	Brazil	Mexico	Italy	Ethiopia
Kernel	66.8-74.4	-	-	-	66.0
Hull	25.6-33.2	-	-	-	-
Oil	45.6-51.8	48.6	46.0	52.6	47.0
Moisture	3.1-5.8	5.5	7.1	8.0	6.5
Protein	12.0-16.0	17.9	-	20.5	22.1
Carbohydrates	3.1-7.0	13.0	20.0	19.9	-
Crude fibre	23.1-27.2	12.5	20.0	15.9	-
Ash	2.0-2.2	2.5	1.9	2.9	2.9

Table 2.2: Partial Analyses of African Castor Seed (Weiss, 1971).

Characteristic (%)	Kenya		Nigeria	
	Aden local	Kitui local	Benue local	Kabba local
Moisture content (loss at 105^0)	4.9	5.2	5.2	5.0
Oil content % (MFB)	49.3	49.0	49.0	52.3
Acid value (KOH/g)	1.9	1.3	1.8	1.6
100 seeds weight (g)	48.9	59.2	61.3	65.2

2.5 Castor Oil Production

Castor oil produced majorly in commercial mills. However, medically consumed castor oil can not be produced in the common mills. This is because of the high level of quality required. The oils required for medical purposes are produced by specialized operations. Seeds are decorticated, cold pressed or pressed at 32^0C depending on the technique. These operations yield oil of a pale straw colour, which can be bleached by ultraviolet light, and which after filtering provides oil of medical quality.

Castor oil can be produced by double or single pressing the seed. Those factories that single press castor first clean and dry the whole seeds to a moisture content of 4-5 percent at a temperature of approximately 93^0C, after which the seed is "conditioned" by spraying with live steam to increase the moisture content to 5-6 percent. The conditioned seeds are then fed directly into a mechanical screw press, the resulting cake containing 6.5 to 8 percent moisture. Oil from the single press operation is No. 1 quality, and after addition of a clarifier may be readily filtered at 38^0C to 48^0C.

For double pressing, seeds after cleaning are warmed to approximately 65^0C and immediately passed to a mechanical screw press. Oil thus obtained is of No.1 quality, and if warmed to 50^0C and pretreated with small amount of clarifier, can be readily filtered. Storage of castor oil presents few problems other than those of selecting the most economical method. For long term storage, method of heating, or in the tropics, cooling may be necessary. Refined castor oil can be stored for up to 6 months to one year with little change in colour or acidity. Both crude and refined castor oil can be stored for one or two years without accumulation of peroxides, insignificant amounts or increasing the oxidative rancidity (Salunkhe, 1986).

2.6 Castor Oil

Crude castor oil is a pale straw colour, but the refined bleached type is almost colourless, sometimes with a faint yellow tinge. The crude castor oil has a distinctive odour usually considered offensive by many people, but can easily be deodourized. Castor oil can be stored and does not easily become rancid. It is mixable with absolute ethanol, methanol, ether, chloroform and glacial acetic acid. Castor oil does not dissolve to any extent in mineral oil unless mixed with another vegetable oil. Castor oil is seldom used for conventional soap making, neither is it used as edible oil. The fully hydrogenated castor oil has an unusually high melting point of 86^0C to 88^0C.

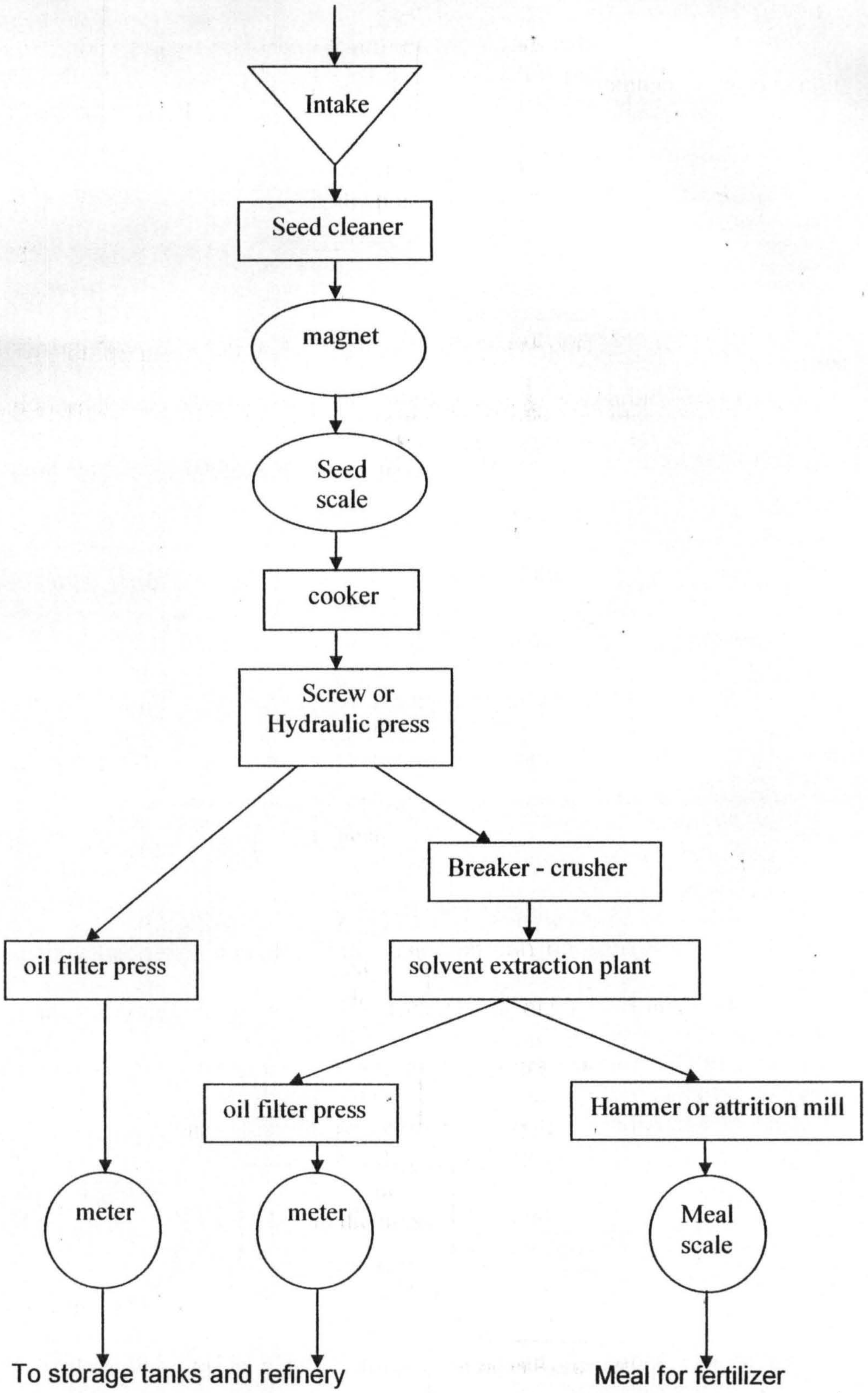


Figure 2.1: The Flowsheet for Castor Seed Oil Extraction with Pressing and Solvent Extraction.

2.7 Castor Oil Purification Methods

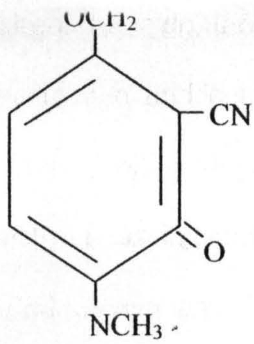
Once the oil has been expressed from the seeds, it is necessary to remove any impurity from the oil; that makes it such an important commodity. The oil is essentially a pure triglyceride, and contains almost 90% of glyceryl tri-ricinoleate. It is the ricinoleic triglyceride that is needed in order to produce high quality castor oil that will be used for chemical reactions. Characterizing properties of castor oil include a higher density, viscosity, and reactivity than common triglycerides found in other vegetable oils. These properties are exploited when refining the oil from the impurities. The steps to refining the crude oil include settling and degumming of the oil, bleaching, neutralization, and deodourization of the oil (Nawar, 1996). The settling and degumming of the crude oil is done to remove the acqueous phase from the lipid and to remove phospholipids from the oil. Bleaching of the oil results in the removal of colouring materials and the removal of colouring phospholipids and oxidation products, the adsorption of the impurities by neutral clay: care must be taken because a highly acid activated clay can react with the oil and cause an undesirable dehydration reaction. Neutralization can be done in one of two ways: by alkali (chemical) or steam stripping (physical means). The neutralization step is necessary to remove free fatty acids from the oil. Caustic soda (alkali) is mixed in the proper amounts and the aqueous solution (called soap-stock) is removed, leaving the neutral oil behind. Unfortunately, the use of alkali to neutralize the oil results in poor soap stock separation and high neutral oil losses. This is why steam stripping is preferable. Steam stripping is done under vacuum to remove moisture, free fatty acids, odorous matters, and other impurities from the oil. Because it is performed under vacuum conditions, the oil can be kept at a low temperature, preserving its chemical structure and not subjecting it to temperature in which undesirable dehydration reaction can occur.

2.8 Oil Packaging and Shelf Life

Due to the fact that castor oil contains double bonds in its lipid structure, it is prone to an undesirable reaction called lipid oxidation. Lipid oxidation occurs when the double bonds in the fatty acid react with oxygen to form peroxides and change the chemical nature of the oil. There are many factors which influence the rate of oxidation in foods: fatty acid composition, free fatty acids versus the corresponding arylglycerols, oxygen concentration, temperature, pro-oxidants, radiant energy (visible and ultraviolet light), and the presence of anti oxidants. In general, one wants to store the oil in a controlled environment. Castor oil is not as prone to oxidation as much as other oils unless exposed to hight temperatures. (Weiss, 1971).

2.9 Composition of Castor Oil

Castor oil is made up of almost entirely triglycerides, principally ricinolein, having its fatty acid component as ricinoleic acid. Castor oil has the unique property of solubility in alcohol due to the presence of hydroxyl group in ricinolein. Ricin was first isolated by Dixon (Aust. Gaz; 4, 137, -155, 18867 – 87). The structure of Ricin is shown below.



Ricin is one of a small group of phytotoxins which also include abrin, circin, and robin. They are all extremely toxic, antigenic, thermolabile, and aglutinate red cells. The specification and composition for castor oil are shown in tables 2.3 and 2.4. In the United Kingdom, industrial castor oil is usually of two grades, the best conforming to the requirements of British standards specification No. 654 known as "English firsts". The second grade is "English seconds" or "Indian commercials" for which the standards are less stringent. It is generally darker in colour, and the only specific requirement is that it should not contain more than 5 per cent of free fatty acid as oleic acid.

Table 2.3;Specification for Raw Cold-Pressed Castor Oil.

ASTM D 960-521952 (1967)

Physico-chemical properties	Values
Viscosity, cSt.	6.30 – 9.00
Acid Value	0.40 – 4.00
Iodine Value	84.00 – 88.00
Hydroxyl Value	160.00 – 168.00
Acetyl Value	145.00 – 154.00
Specific gravity at 25/25^{0}C	0.957 – 0.961
Saponification Value	176.00 – 184.00
Unsaponification Value	0.70
Refractive Index at 25^{0}C	1.477 – 1.478
Flash point (Tag closed cup), ^{0}C.	230.00
Flash Point (Daveland open cup), ^{0}C.	285.00 – 290.00
Anti Ignition Temperature, ^{0}C.	449.00
Pour point	33.00
Colour (Gardener), max.	3.00
Clarity	Clear
Solubility in alcohol	Complete
Fine Point, ^{0}C	322.00
Coefficient of Expansion, Per ^{0}C.	0.00066

Table 2.4: Fatty Acid Composition of Castor Oil (Weiss, 1971).

Acid	% Composition
Ricinoleic	89.50
Linoleic	4.20
Oleic	3.00
Stearic	1.00
Palmitic	1.00
Dihydroxystrearic	0.7
Eicosanoic	0.30
Linolenic	0.30

2.10 Uses of Castor Oil

Castor oil is among the world's most versatile natural products (Wiess, 1971). It is a major raw material for the production of many products and chemicals such as sebacic acid, a basic ingredient in the production of synthetic resins and fibres. Castor oil is used as a constituent of embalming fluids, in soap manufacture, as Turkey red for dying and finishing of textiles, as hydrogenated castor oil (opal wax) in polishes, for electrical condenser impregnation, carbon paper, ointments, cosmetics and hair dressings; as dehydrated castor oil in protective coatings, as blown oil (oxidized oil) for plasticizing oil cloth, artificial leather, coated fabrics and lacquers; in brake fluid where a degree of compressibility is important, and in printing inks.

Castor oil is traditionally associated with medical purposes, but this is now a negligible proportion of total consumption amounting to about 1 percent in the US and in the UK.

2.10.1 Castor wax

This is a hard brittle, high melting point product that is practically odourless (faint characteristic fatty or waxy odour only) and tasteless. It is usually supplied as uniform free flowing white flakes. The colour of the solid wax is cream to pearl by reflected light, and bluish white by transmitted light. When molten, it is clear, transparent, very fluid and colourless to slightly straw coloured. The solid wax has an amorphous structure, dull to waxy luster and white streaks. Its uses are many, including acting as solid lubricant, and as a pressure-mould release agent in the manufacture of formed plastics and rubber goods.

2.10.2 Oxidized oil

Blown or oxidized oil is prepared by mixing it intimately with air or oxygen at temperature between 80–130^{0}C. This oxidation is accompanied by some polymerization and colour change in addition to decomposition. Blown castor oil is available in a wide range of varying viscosity, acidities and colours. In general, the higher the viscosity, the higher the specific gravity, the acid and saponification values; and the lower the iodine and hydroxyl values. Oxidized castor oils are employed widely to provide plasticizers, adhesives, bases for lubricants and hydraulics. Its advantages over raw castor oil lies in the fact that high viscosity oil shows less tendency to oxidize from film when subjected to heat.

2.10.3 Hydrogenated oil

Since ricinoleic acid is an unsaturated acid, hydrogen can be added to the double bond to yield a saturated acid of higher melting point. Hydrogenation produces hydroxyl-stearic acid, which can be used in the alkoxylation and may be incorporated as metallic scaps in a wide range of glasses.

2.10.4 Sulphated oil

In 1874, Turkey Red Oil (sulfated castor oil) was made by the action of concentrated sulphuric acid (95%) on castor oil at 20 – 30^{0}C (Edgar, 1985). Sulfation yields a range of intermediates used in textile and leather goods as wetting and dying agents.

2.10.5 Plastics and rubber

Large varieties of plastics and rubber having engineering applications are produced from soft rubber and plastics by impregnating them with castor oil containing urethane. Divers plastic applications include pottery compounds, mallet heads, coupling agents, processing oils, plasticizers and polyols.

2.10.6 Paints, inks and adhesives

Excellently clear and pigmented urethane coating can be prepared from castor oil and oxygen. The castor oil may be used directly or alcoholized with propylene glycol and polyethers. Blown castor oil is also reported as producing clear finishes for wools (Thorpe and Whitaley, 1958). Excellent adhesive properties are obtained when castor oil is reacted with ethylene and such products have been used in cements and other patching materials. Other areas where castor oil is useful include: polyols, glycerin, dimmer acids, polyamides, alkylresins, ricinoleic acid, thixothopic agents, castor oil – all grades, wetting and dispersing additives and dehydrated castor oil (DCO).

2.11 Recovery of Fats and Oils from their Sources

Oils and fats occur in oil seeds (18 – 70%), fruit pulp (30-58%), animal tissues (60 – 90%), and fish (10 – 22%). The method for removing the oil is largely dependent upon the source. Oil seeds tend to contain a much larger proportion of solid materials associated with the oil, requiring careful reduction in size and usually some heat treatment before being pressed or solvent extracted to recover the oil. Oil seeds are normally dried to 7 – 13 per cent. The aim for oil mills is to operate them year round, often necessitating rather prolonged storage in the plant or prolonged travel time in the case of imports. Oil seeds as received at the mill are normally admixed with materials accumulated during harvesting and transportation. They must be cleaned of trash metals, sticks or stones. Also as in the case of soya beans and castor seeds for example, there is an outside seed coat (hull) which is high in fibre. If this is not removed before the oil is extracted, the resulting oil may be affected. Discussed below are the methods of oil recovery from oil seeds.

2.11.1 Mechanical methods

The oldest method of oil extraction was the application of pressure to batches of oil bearing material confined in bags, clothes, cages, etc. Levers, wedges, screws etc were used as a means of applying the pressure. Gradually, the hydraulic ram system was adopted, using pressure from 500 – 6000 psi or more. The first stage of extraction is pre – pressing using a high pressure continuous screw – press expeller. The expeller usually consists of a barrel containing stainless steel helical screw. The pitch of the screw flights gradually decreases towards the discharge end, to increase the pressure on the pulp as it is carried through the barrel. Extracted oil is filtered, and collected in a settling tank. The material removed from the oil, called 'foot', is fed back into the stream of fresh material. The material discharge from the press, called the 'cake', contains 8 to 10 percent oil. It is crushed into coarse meal and subjected to solvent extraction with hexane or heptane. The screw press diagram is shown in Figure 2.2.

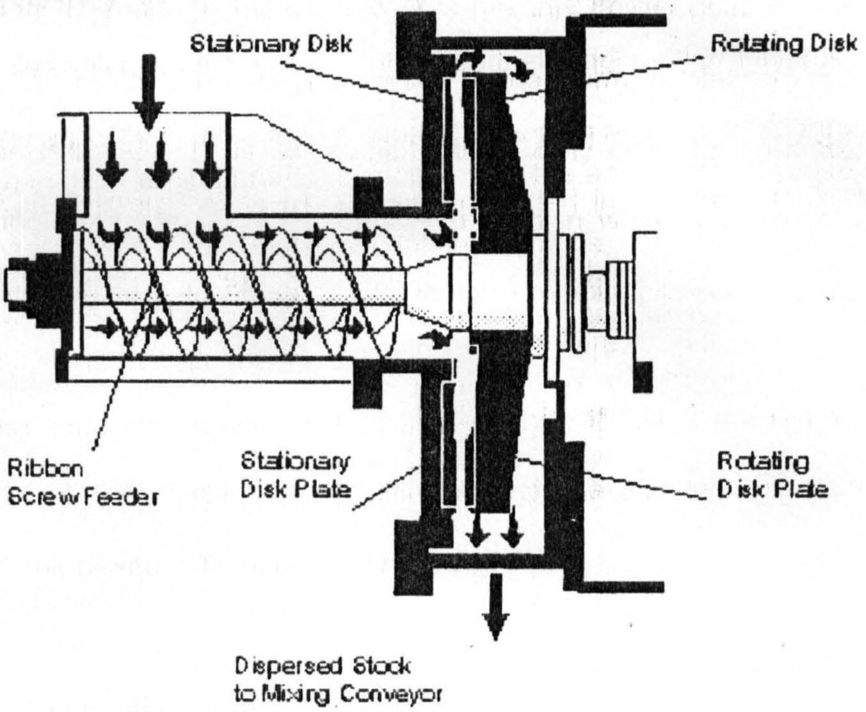


Figure 2.2: Screw Press Diagram

2.11.2 Solvent extraction

Analytical determination of oil content is done by extracting from a finely ground dry sample with a boiling fat solvent; such as petroleum ether and normal hexane. Only little difference is encountered in commercial extraction. The most common solvent is hexane, boiling point 63 – 69^{0}C (146 – 156^{0}F). Where condenser water is too warm, heptane (b.p, 90 – 99^{0}C or 194 – 210^{0}F) is sometimes used. Many other fat solvents are either too flammable or not selective enough in what they extract. For example, the use of trichloroethylene is now prohibited in Europe because it causes the corrosion of the equipment.

Extractor design is determined by the rate at which equilibrium is reached between a lean miscella (oil – solvent mixture) outside the seed particles and the oil within the particles. As the oil content is reduced, to commercially acceptable level, usually 1% or below, equilibrium is obtained slowly, in part due to relative insolubility of the last remaining oil. The rate at which equilibrium is approached is affected by the intrinsic capacity for diffusion of solvent and oil, the size and shape of seed particles, their internal structures, and finally the solubility of the remaining oil. It is generally agreed that hot solvent is better than cold solvent.

2.12 Refining of Crude Castor Oil

Crude oils contain variable amounts of non-glyceride impurities. Some, such as sterols, are relatively inert; others, like tecopherols, are generally desirable; some like free fatty acids, phosphatids, and certain pigments, are objectionable. They tend to make the oil dark coloured, susceptible to foaming and smoking on heating, and liable to precipitation of solid material when the oil is heated under operations. The objective of refining is to remove the objectionable impurities with minimum damage to the neutral oil (glycerides) and tocophorols and ensure minimum loss of oil. In Europe, it is called "neutralization", and "refining", the term used to include all processing through deodorization.

2.12.1 Alkali refining method

Alkali refining method is the most common refining method. It involves mixing the crude or degummed oil with a known quantity and concentration of sodium hydroxide at a known temperature, processing time and with prescribed agitation conditions. The insoluble soap stock is separated and the oil washed with hot water to remove residual soap. After that, the oil is dried to a moisture and volatile (M & V) content of about 0.10 percent. The alkali treatment is designed to remove the undesirable crude oil impurities without saponifying any neutral oil which would increase refining loss.

Laboratory refining may serve as a guide, but plant experience normally dictates the best operating conditions. The minimum amount of alkali required for neutralization can be calculated from free fatty acid (FFA) of the oil to be refined, using the formula.

%NaOH = %FFA x 0.142, where the FFA is expressed in terms of oleic acid (M.W. = 282).

For any desired excess of NaOH, the calculation is:

%NaOH = %FFA x 0.142 + % excess NaOH.

Alkali concentration is usually expressed in terms of the Baume scale. Table 2.5 shows the alkali concentration.

Table 2.5: Alkali Concentration in %NaOH and in Degree Baume (Frank, 1983).

Degrees Baume at 15^0C	% NaOH
10	6.57
12	8.00
14	9.50
16	11.06
18	12.68
20	14.36
22	16.09
24	17.87
26	19.70
28	21.58
30	23.50

2.13 Mechanism of Lubrication

The basic purpose of lubrication is to maintain, between the surfaces one is concerned with, something which will keep them from rubbing together and injuring one another. Friction is a common element in daily life; one can walk up a steep ramp without slipping back because of high friction between shoe soles and ramp surface; but friction in well designed machines is very much lower. One can express the amount of frictional resistance to motion in terms of the coefficient of friction, which is the ratio of frictional force opposing motion to the load at right angle to the surface, i.e.

$$\frac{\text{Frictional force opposing the motion}}{\text{Load at right angle to the surface.}}$$

This ratio is very roughly constant for any pair of surfaces. For un-lubricated metal of ordinary smoothness and cleanness, exposed to the atmosphere, it may have a value of about one. For well designed and well lubricated systems, the coefficient may be as low as 0.005; and under very special conditions, values as low as 0.000, 005 have been attained.

These variations show that there are differences in kind as well as in amount of lubrication. If the surfaces are very smooth and a layer of fluid is kept between them, they do not touch and, for this condition, they play no vital part in the lubrication.

2.14 Lubricating Oils and their Functions

An engine lubricating oil has many functions to perform if it is to give satisfactory service:

1. It must minimize friction and wear.
2. It must keep the engine parts clean, especially piston rings and ring groves, oil ways, and filters.
3. It must possess properties enabling it to prevent deposition of carbon, soot, and lacquer; to absorb and carry away harmful substances resulting from incomplete combustion.

4. It must act as a cooling medium, transferring heat to the water jackets, crankcase, and sump walls from the piston and bearings.
5. It must provide a sealing medium between cylinder walls and piston rings to prevent "blow-by" of the gases through the high spots and valley of the mating parts.
6. It must protect against corrosion and other harmful reactions.

A study of the "oilier" oils pointed out the path to these efficient lubricants. It has been established that fatty oils act as they do in lubrication, because they contain active molecules which adhere to the metal surface by strong physical or weak chemical forces (adsorption), thus forming one or more persistent layers. These stick to the metal under normal conditions which would destroy the fluid film of conventional oil.

2.15 Properties of Lubricating Oil

A lubricating oil that will perform the afore mentioned functions must possess the under listed properties;

1. It must remain a pumpable liquid of suitable viscosity and flow properties at the operating conditions.
2. It must be able to stay in the engine or on the lubricated parts until lost by either leakage or discarding.
3. Remain unchanged as feasible, both physically and chemically.

4. It must resist leakage, dripping, or undesirable throw off from the lubricated surface.
5. Good lubricating oil must be able to withstand relatively high temperatures, sustaining a workable viscosity.
6. It must not be poisonous or reactive producing harmful material or gas.

2.16 Physiochemical Properties of Lubricating Oil

The suitability of lubricants for the work they must do is governed to a varying but considerable extent by the ease with which they flow under the condition of service. This is particularly true of lubricating oil, although the matter becomes more important for aviation gas turbine fuels at high altitude. Ease of flow is expressed by viscosity and by extent to which consistency suffers change with change in temperature. Both properties are influenced by pressure, and to varying extents by the degree of agitation.

2.16.1 Viscosity

The viscosity of a fluid can be described as its internal friction, the resistance it offers to motion, either of foreign body through it or of it against a foreign body. It can be measured by timing the flow of a given volume of the fluid through a properly calibrated tube of a capillary size. The result is kinematic viscosity measured in centistokes. The change of oil viscosity with change of temperature is considerable, so that measurement must be done at a standard temperature. Lubricating oil is classified as to the extent of the viscosity change with temperature by the viscosity index scale, D567 – 53. The number for ordinary oils on this scale is between 0 and 100, the '0' value referring to large and '100' to small change.

2.16.2 Viscosity index

The numerical method of indicating the extent to which an oil changes in viscosity, with changing temperature. The higher the viscosity index, the more stable oil viscosity, as the temperature increases. For instance, oil of viscosity index VI 100 will thin out slowly than an oil of viscosity index VI 50 under the same temperature.

2.16.3 Cloud point

Of significant importance is the temperature at which a cloud of turbidity – other than the separation of dissolved water becomes visible. The cloud is ordinarily caused by wax in a micro – crystalline form. The cloud point is the temperature at which a solid material, usually paraffinic waxes and similar compounds in the case of petroleum liquids, begins to separate when the sample is cooled under carefully controlled conditions.

2.16.4 Pour point

Pour point denotes the lowest temperature at which oil will just flow, when it is cooled under prescribed test conditions. The apparatus and procedure for pour point (included in D 97) are the same as for cloud point; but the sample must be pre-warmed in specified way to wipe out effects of differences in thermal history; the second main difference is that the sample's jar is withdrawn from the cooling bath at each 5^0F interval instead of 2^0F, and the third is that the jar is tilted at each withdrawal to see if the sample can still flow. The first time no motion can be observed, the jar is held horizontally for seconds. If there is still no flow (observable motion), the pour point is taken to be the temperature at the previous checking point.

2.16.5 Flash point

The flash point is the temperature at which a liquid or oil vapourizes in sufficient quality to ignite momentarily a flash from a source of ignition. A high flash point is desirable in lubricating oil because it indicate good resistance to combustion and a low degree of evaporation at normal or working temperature. The flash point of oil varies with the viscosity and quality of the oil. The minimum allowable flash point is generally placed above the prevailing ambient temperature to avoid explosion.

2.16.6 Base number

Base number expressed in milligrams of KOH per grams of sample, is the quantity of acid that is required to titrate a sample to a specified end point. To determine the base number of lubricating oil, the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water, and the resulting single phase solution is titrated at room temperature with standard acid alcoholic solution to the end point indicated by the colour change of the added methyl indicator. (green – yellow).

New and used petroleum products can contain basic constituents that are present as additives. The relative amount of these materials can be determined by means of titration method. The base number is a measure of the amount of basic substances in the oil, always under the conditions of the test.

2.16.7 Metallic content

Some oils are formulated with metals containing additives that act as detergents, antioxidants, antiwear agents etc. Some of these additives contain one or more of these metals: barium, calcium, zinc, and magnesium. Each metallic test method provides a means of determining the concentrations of the metal, which gives an indication of the additive content in the oil.

2.16.8 Appearance

It has long been the practice to include in fuel and lubricant specification a requirement that they must be clear, bright and free from particulate matter. The test as specified in ASTM specification (ASTM D4176) involves visual examination for colour and clarity. Other aids such as photographs and charts are used to ensure that a standard is maintained.

The table below shows the standard physiochemical properties specification as obtained in Nigerian indigenous lube oils.

Table 2.6: NIS Requirements for Engine Lubricating Oil

	Specifications		
	Single	Grades	Multigrades
Characteristics	SAE30	SAE40	SAE20W50
Appearance	B & C	B & C	B & C
Colour	Report	Report	Report
Specific Gravity@15^{0}C	0.870-0.898	0.899-0.910	0.893-0.889
Kinematic Viscosity@40^0 C	88.0-110.0	135.0-155.0	135.5-180.0
Kinematic Viscosity@100^0 C	10.2-12.9	13.5-16.8	17.1-22.0
Viscosity Index (min)	95	95.0-110.0	125
TBN, mgKOH/g, (min)	5.0	5.0	5.0
Sulphated Ash, wt%, (max)	Report	Report	Report
Water Content, % vol. (max)	0.025	0.025	0.025
Flash Point, Col, ^{0}C (min)	204.0	204.0	204.0
Pour Point, ^{0}C, (max)	- 18.0	- 9.0	- 23.0

Table 2.7: SAE Specifications for SAE 50

Properties	Values
API Service Designation	GL – 5
SAE Grade	50
API Gravity	20
Viscosity:	
cSt@ 40^0C (100^0F):	138
cSt@ 100^0C (210^0F):	18
cP@ 0^0C (32^0F):	1,250
cP@ - 26^0C (- 15^0F):	24,250
cP@ -30^0C (- 22^0F):	45,250
cP@ - 40^0C (- 40^0F):	270,000
Viscosity Index:	154
Flash Point, ^{0}C (^{0}F)	235 (455)
Pour Point, ^{0}C (^{0}F)	- 40 (- 40)

Table 2.8: SAE Classification for Crankcase Oils (Eugene, 1997)

SAE Viscosity Number	Specific gravity at 15^0C	API gravity	Viscosity range at 98.9^0C (cSt).
SAE 20	0.904-0.898	25-27	5.73 – 9.62
SAE 30	0.92 – 0.89	22 – 28	9.62 – 12. 94
SAE 40	- 0.92	22	12.94 – 16.77
SAE 50	-	-	10.77-22.68

Table 2.9: Range of Physical Properties of Lubricating Oil (Oyekunle, 1986).

Type of oil	^{0}API gravity	Viscosity (cSt) at 37.8^{0}C	54.4^{0}C	98.9^{0}C	Viscosity Index
Motor, light	24-30	-	18-40	4.3-8.9	70 – 100
Motor, medium	22-28	86-141	40-63	10.7-18	50 – 100
Motor, heavy	20-27	-	-	15.5-33	40 – 100
Aircraft, light	24-36	-	-	10.2-16.7	90 – 100
Aircraft, heavy	23-25	-	-	20.5-31	90 – 100
Diesel engine, lightest	23-25	-	25.3-40	-	40 – 70
Diesel engine, heaviest	22-25		-	14.3-18	40 – 70
Engine & machine spindle	25-27	20.5-26.5	-	-	-

2.17 Influence of Temperature and Pressure on the Viscosity of Lubricating Oils.

It is known that the viscosity of most liquids changes a good deal with change in temperature. Oils of different chemical nature change viscosity to different extents when warmed through the same temperature ranges, but oil of approximately the same chemical nature but of different molecular weight (boiling point), will show different viscosity changes over the same range. In general, oils of more aromatic character decrease in viscosity faster for a given rise in temperature than do the paraffinic oils and oils of higher molecular weight similarly show greater change in viscosity per degree temperature rise than do the lighter, less viscous oil of lower molecular weight.

viscosity per degree temperature rise than do the lighter, less viscous oil of lower molecular weight.

There has not been a strong theoretical basis for relating temperature and viscosity. Most of the charts available such as ASTM viscosity temperature charts (D341) and others are based on Walther equation(Lansdown).

$\log. \log(\eta + C) = A + B \log T$. Where η is kinematic viscosity, T is temperature, C is invariable constant and A and B are characteristics of a particular oil.

These charts have log and log.log coordinates corresponding respectively to temperature and kinematic viscosity. The viscosity of oil plotted at several temperatures on such a chart will give a straight line, and the data at two points are of course adequate to supply its slope. The intercept and the slope of the line correspond to A and B of the equation. It is important to note that these charts, like the equation upon which they are based, are intended for used in petroleum oils in the temperature ranges where the rate of shear and the time at which shearing occurred are not significant.

It will be evident that lubricating oil can provide better lubrication under operating conditions if its viscosity stays high when the oil is hot; likewise it can afford easier winter starting if the viscosity stays low when the oil is cold. As a result, high viscosity index, which signifies a relatively flat viscosity – temperature curve, has become one mark of quality associated with the image of premium grade oil.

The effect of pressure on viscosity of lubricating oils is appreciable, although so far, it does not seem to have been applied very seriously by engineers. However, since the imposition of higher pressure causes increase of viscosity, this influence has been invoked as an explanation for another phenomenon. It is known that the working of an ordinary cylindrical journal in a sleeve bearing develops a high pressure zone in the oil film which does the lubricating. It has been suggested that the increase in viscosity is responsible for effects now included under the mysterious name "oiliness". This rise in viscosity is attributed to increase in pressure. There seems to be little doubt that the marked increase of load carrying capacity of an oil film, as the film itself is made thinner, can safely be attributed to the effect of pressure on viscosity. The greater oiliness shown by lard oil and other vegetable oils over a comparable mineral oil is due to smaller increase of viscosity with pressure. The increase of viscosity with higher pressure is accompanied by an increase in the extent to which viscosity is affected by temperature; likewise, rise of temperature decreases the effect of pressure. In both cases, it can be said that moderate changes of viscosity are approximately proportional to changes of density, whether these latter are caused by changes in temperature or of pressure. Oils also acquire a non-Newtonian character when high pressure is applied. It has been possible to construct an equation relating pressure as well as temperature to viscosity. The magnitude of the viscosity changes with pressure is appreciable; an increase of, say 1,000 psi is reported to raise the viscosity of a convectional lubricating oil 25to30 percent. The change of viscosity with pressure change is influenced appreciably by the chemical structures of the compound or mixture of compounds under study. There are systematic changes of viscosity-pressure coefficients as molecular weight or boiling point is changed, but these vary as the chemical structure changes. Table 2.10 shows the thermal properties of lubricating oil at various temperatures.

Table 2.10: Typical Thermal Properties of Engine Oil (Eugene, 1997).

Temperature (^0C)	Mass density ρ (Kg/m^3)	Specific heat C_P(kg/kg^{0}C)	Kinematic Viscosity η_K (m^2/s)
0	899	1.796	0.00428
20	888	1.880	0.00090
40	876	1.964	0.00024
60	864	2.047	0.839×10^{-4}
80	852	2.131	0.375
100	840	2.219	0.203
120	828	2.307	0.124
140	816	2.395	0.080
160	805	2.483	0.056

2.18 Oil Consumption

Oil loss from an engine occurs mostly by leakage, foaming, vapourization and by burning in the engine. Foaming tendency can be determined by ASTM D892 and may be overcome by small addition of silicon. Volatility is best determined by vacuum distillation D1160; although flash point 'D92' can give preliminary and qualitative indication. There are other tests that can indicate the evaporation of lubricating oil. Oil flow into the engine is controlled by viscosity at pump and cylinder wall temperatures. Viscosity index is also significant for oil consumption; that conferred by certain additives may not be completely effective under operating shear. Oil change recommendations vary from 2,000 to 6,000 miles between drains, depending on car and oil. Main reasons for oil change are to drain out accumulated dirt and to replace oil in which additives has become depleted.

2.19 Oil Performance Evaluation

The principal functions performed by additives in lubricating oil formulation are; (1) acid neutralization, (2) oxidation inhibition, (3) rust prevention and (4) viscosity improvement. These functions provide engine cleanliness and extend trouble free operations. Dispersals supplement these functions and, in addition provide protection against low temperature sludge deposits.

Lubricating oil formulations may contain several different natural and synthetic sulphonates comprising neutral/or over-based detergents. Phenates may also be included with the sulphonates to fine-tune the final oil formulation to maximize performance. Since the introduction of chemical additives to lubricating oils, various organizations world-wide have established systems to define or classify engine oils by performance levels. Most of times, accelerated laboratory engine tests, are designed to provide correlations with a specific service that the vehicle would encounter.

2.20 Additives for Lubricating Oils

Despite the fact that petroleum oil has displaced vegetable and animal oils as all purpose lubricants, the fact still remains that, fatty oil still possess some advantages for special problems. One of such is the lubrication of the planetary transmission of the model 'T' Ford automobile; which require greater oilness than afforded by unmixed petroleum oils. The development of modern engine and transmission technologies would be impossible without advanced lubricant additives. Vehicle design advances are translated into new performance requirements for lubricants and additives. The primary purpose of high quality lubricant design is to maintain engines and transmissions in design conditions as long as possible whilst enhancing vehicle operational characteristics.

Lubricant additives can be divided broadly into two categories; those which protect metallic surfaces and those which enhance the performance of the base fluid. Figure 2.3 is the pie chart that shows engine oil formulations. Also Table 2.11 shows the structure of some additives.

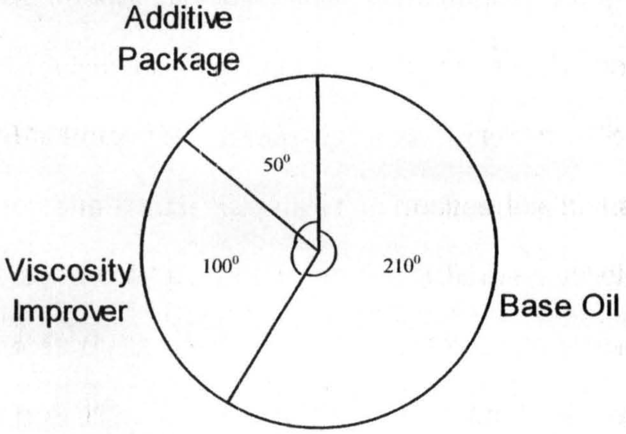


Figure 2.3: Pie Chart Showing Engine Oil Formulation

2.20.1 Viscosity – Index improvers

The fall in viscosity with increase in temperature of oil of a given grade, or viscosity level, can be made less steep by thickening higher oils with polymeric substance such as polybutenes and copolymers of polymethacrylates. The polymer may increase in solubility as the temperature increases, and correspondingly, the molecules uncoil and thicken the base oil more at high than at low temperatures and thus counteract, to some extent the natural decrease in viscosity the base oil would undergo.

2.20.2 Pour – Point depressants

The dewaxing process removes the higher melting hydrocarbons, but some component remain which may solidify and gel the oil. This reduces the fluidity at low temperature. Small amount of chemicals such as metallic soaps, condensation products of chlorinated wax and alkylnaphthalenes or phenols, polymethacrylates and a host of others increase fluidity at low temperatures. The mechanism of their actions is still uncertain, but it probably involves adsorption of additive molecules on the surface of growing wax crystals. The adsorbed layer either reduces intercrystal forces or modifies crystal growth.

2.20.3 Anti Oxidants

Lubricants are exposed to oxidation by atmospheric oxygen in practically all of their applications. This results in the formation of acids and sludge which interferes with the primary function of the lubricant. Substantial increases in the service life can be obtained by using small amounts (0.1–1.0%) of antioxidants.

Antioxidants are chemical compounds or substances which inhibits and slow down the rate oxidation of oil in the engine. We have few chemicals which fall under this categories ranging from phenols, amines, many compounds of sulphur, phosphorous, and certain metallo-organic compounds which act in more than one capacity; for example antioxidant and dispersant or detergent and oilness agents. There are varieties of actions among inhibitors; phenolic compounds tends to hold off oxidation almost completely for a definite time characteristic of the system; after which the reaction will process pretty much as it would have done in the absence of any inhibitor. Another class known as retardants will allow slow oxidation over a long time period without any sudden break – through, but with an ultimate slow loss in effectiveness. Many sulphur compounds seem to belong to this class.

2.20.4 Antiwear and friction-reducing additives

If sliding surfaces can be completely separated by an oil film, friction and wear will be at a minimum. There are many systems, however, in which the combination of component geometry and operating conditions is such that a continuous oil film can not be maintained. If no separating film of any kind were interposed, however, complete seizure would result. If the pressures and temperatures between such contacting surfaces are moderate, the provision of a boundary lubricating film will suffice, whereas if, as in some gears, conditions of both temperature and pressure are severe, some form of extreme pressure lubrication may be necessary.

In internal combustion engines operating at low cylinder temperatures, for instance, condensation of acids from the gaseous combustion products on the cylinder and ring surfaces results in corrosive wear. In such cases, the addition of alkaline – earth phenates to the lubricating oil to neutralize the acids has succeeded in reducing wear rates.

2.20.5 Extreme pressure additives

Certain types of gears, particularly the typoids used in automotive rear-axle transmission, operate under such severe conditions of load and sliding speed. This result in high temperature and pressure, that ordinary lubricant can not provide complete protection against metal contact. Welding, transfer of surface metal, and ultimate destruction of gear results, in certain machining operations, it is necessary to prevent the chip from welding to the cutting tool. For such applications, lubricants containing sulphur and chlorine compounds are used. As temperatures developed in the contact, these react chemically with the metal surfaces; the resulting sulphide ad chloride film provides penetration-resistant, low-shear-strength film which prevents damage to the surfaces.

2.20.6 Dispersants

In internal-combustion engines, some of the products of combustion, which include carbonaceous particles, particularly fuel, sulphur acids, and water, enter the oil film on the cylinder walls. These materials may react to form lacquers and sludge which are deposited on the working part of the engine. The lubricant is called upon to keep engine parts (oil screens, ring grooves) cleans, and this is accomplished by the use of so called detergent oils. The most commonly used dispersants are alkaline earth salts. Of these, the most successful have been the salts of petroleum sulphonic acids, phenates, salicylates, thiophosphates and oxidized olefinphosphorous pentasulphide reaction products. These materials owe their effectiveness partly to their surface activity, which ensures that foreign particles are kept in suspension in the lubricating oil; and partly to their alkalinity which enables them to neutralize combustion acids that would otherwise catalyze the formation of lacquers.

Table 2.11: Additives and Solvents (Eterigho, 2001).

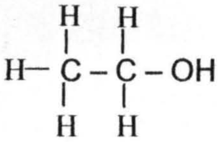
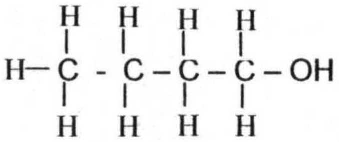
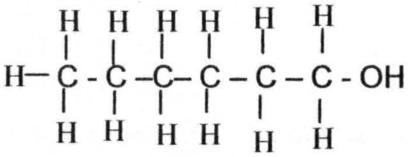
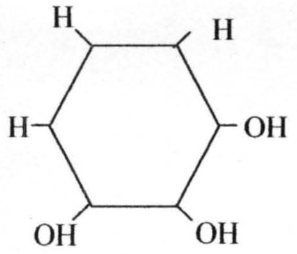
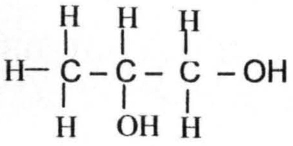
NAME	STRUCTURE	COMMENT
Ethanol (CH_3CH_2OH)	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$	B.P=78^{0}C; melting point=117^{0}C Density at 20^{0}C = 0.789 g/cm^3 It undergoes the reactions; oxidation, substitution, elimination and acid base reactions Viscosity=1.05 cp
Butan – 1 – ol ($CH_3(CH_2)CH_2OH$)	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$	B.P = 118^{0}C Solubility=7.7 g/100g H_2O at 20^{0}C; Density = 0.810 kg/m^3 at 20^{0}C; Viscosity = 3 cp The reactivity is almost the same as ethanol.
Hexan – 1 – ol ($CH_3CH_2CH_2OH$)	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$	Boiling point = 156^{0}C Solubility = 0.58 g/100g H_2O at 20^{0}C. The reactivity is almost the same as ethanol
Cyclohexanol		Boiling point = 161^{0}C, Solubility = 3.6g/100g H_2O at 20^{0}C. Density at 20^{0}C = 0.949 g/cm^3, Viscosity = 60 cp

Table 2.11 Continues: Additives and Solvents (Eterigho, 2001).

NAME	STRUCTURE	COMMENT
Pyrogallol or (1,2,3, trihydroxybenzene) $C_6H_3(OH)_3$		Molecular weight = 126.11 g Specific gravity = 1.453 Melting point = 133 – 134^{0}C Boiling point = 309^{0}C Very soluble in alcohol and ether.
Propylene Glycol (1,2-propanediol)	 $\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{OH}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}OH}$	This is the product formed by the oxidation of propylene by permanganate. It is a solvent in soft drinks, syrups, flavours and colours. Ingredient in cleaning creams; and sun – tan lotion. Viscosity = 2.7 cp
Tributylphosphate $[CH_3(CH_2)_3]_3PO_4$		Molecular weight = 266.32 g A liquid with specific gravity of 0.925 g/cm^3. B.P= 122 – 123^{0}C. Insoluble in water
Triethylene Glycol $HO(CH_2)O(CH_2)_2O(CH_2)OH$		B.P= 276^{0}C, It is a high boiling solvent
Zinc Oxide (ZnO)		It has a wurtzite structure when heated in absence of oxygen, it turns yellow and becomes semi – conductor owing to loss of oxygen.

2.21 Health Aspect of Lubricants

On the whole, lubricants are rather stable, inert materials, and the health problems which arise from their use tend to be long-term rather than immediate. Some of the longer-term health problems include cancer and dermatitis, but there is strong evidence that these occur only when the victim has been careless and has allowed his skin to be in contact with oil or oil-soaked clothing for very long periods. Nevertheless, the lubricant manufacturers have made great effort to identify and remove the dangerous components.

Additives are more or less reactive chemicals, whereas base oils are generally chemically inert. Additives therefore tend to be more irritant and toxic than base oils. Because additives are usually used in small concentrations, any risk is very much reduced, except in lubricants which contain high concentrations of additives, as found in lubricating oils. Nevertheless, all additives are now carefully screened for toxicity; and those with higher toxicity, such as chlorinated naphthalenes and or the phosphates, have been replaced.

Phosphates are used as EP and antiwear additives, and occur in three forms: ortho, meta and para – phosphates. The ortho form has been detected to be highly toxic, causing damage to the nervous system, resulting in blindness or paralysis.

Lead naphthenate soaps have been used for many years as EP additives in industrial gear oils. It was found that slight increase in lead concentrations occurred in some steel industry workers who handled large quantities of those types of gear oil. In general, additives are likely to be of hazard in lubricants. It should be emphasized that the health risks associated with lubricants can be avoided by care in avoiding prolonged contact with skin.

2.22 Formulation of Lubricating Oil

Many products are formed by mixing together two or more ingredients. A good example is the formulation of lubricating oil using the base stock and the various additives. The formulation of lubricating oil is an important approach in the development of the modern lubricating oil, finished lubricants are manufactured from one or more base stocks blend with one or more additives. They are made to meet performance specifications for use in automotives, marine, aviation, and myriads of industrial uses. Often a formulation is specific to a particular marque of equipment. The question is of course, can the research and the service investment in the product be recovered in the end price.

The blending of lubricating oil may involve a chemical reaction taking place between the base oils and additives and hence the use of base oils of known chemical quality is central to the lubricating oil blending.

2.22.1 The simplistic unifactor approach

The simplistic unifactor approach of blending or mixture involves the variation of one factor at a time, hence the name unifactor. Under this approach, the lubricant is formulated under the variation of a factor while others are kept constant. The lubricants resulting from such formulation are not optimal in their performances.

2.22.2 The simplex – lattice design

While the simplistic unifactor approach to lubricating oil formulation allows the variation of a factor at a time, the statistical design permits the variation of more than one factor at a time. The statistical design or formulation gives an optimal performance because both the factors and the system variables are considered in the formulation. The mixture components which are the additives and the base stock are to satisfy the constraints $x_i \geq 0$, $x_1 + x_2 + \ldots x_q = 1.0$. Each component can take values from zero to unity; and all blends among the ingredients are possible. A mathematical equation can be obtained to represent the model. By modeling, we mean a model or an equation is postulated to represent the response surface.

Simplex lattice designs were introduced by Scheffe in the years (1958 – 1965) of the period in which research on mixture experiments was been developed. An ordered arrangement consisting of uniformely spaced distribution of points on a simplex is known as lattice. The name lattice is used here simply to make reference to an array of points. A lattice may have a special correspondence to a special polynomial equation. The number of points in (q,m) simplex lattice is

$$\begin{pmatrix} q+m-1 \\ m \end{pmatrix} = \frac{(q+m-1)!}{m!(q-1)!}$$ where m! is "m factorial"

m! = $m(m-1)(m-2)......2(1)$

The symbol (a^b) is the combinatorial symbol for the number of ways 'a' things can be taken 'b' at a time. For example, a!/b! (a-b)!. Hence in (3,3) simplex lattice, we have

$$\begin{pmatrix} 5 \\ 2 \end{pmatrix} = 10 \text{ points}$$

CHAPTER

3.0 INSTRUMENTATION AND EQUIPMENT

The table below shows the list of equipment used; their makers as well as their function in this piece of work

TABLE: 3.1: List of Equipment

Equipment	Source	Comment
Atomic Absorption Spectrometer	Perkin Elmer (USA)	Zinc and Calcium content Analysis
Hydrometer	-	Specific gravity
Bar chart	-	Appearance
Viscometers	-	Kinematic viscosity
Potentiograph	Metrolim Herisau (Switzerland)	Acid Number/ Base Number
Cleveland semi-automatic	-	Flash point
Specific gravity bottle	-	Relative density
Seta-Lec cloud and pour point refrigerator	Stantiope –Seta	Pour point

3.1 List of Chemicals

Listed below are the chemicals used in the course of this research work;

Table 3.1 List of Chemicals and there sources

Chemicals	Source
Castor Oil	Extracted
Normal Hexane	Chemical Engineering Lab, Minna
Citric Acid	Oando Lub Blending Plant, Kaduna
Potassium cyclohexanebutyrate	Oando Lub Blending Plant, Kaduna
2-ethylhexanoic acid	Oando Lub Blending Plant, Kaduna
Xylene	Oando Lub Blending Plant, Kaduna
Phosphorous pentoxide	Oando Lub Blending Plant, Kaduna
Motor spirit	Oando Lub Blending Plant, Kaduna
paratone (viscosity improver)	Oando Lub Blending Plant, Kaduna
Additive package	Oando Lub Blending Plant, Kaduna
Potassium hydroxide	Oando Lub Blending Plant, Kaduna
Toluene	Oando Lub Blending Plant, Kaduna
Isopropyl alcohol	Oando Lub Blending Plant, Kaduna
Methyl indicator	Oando Lub Blending Plant, Kaduna
Chlorobenzene	Oando Lub Blending Plant, Kaduna
Glacial acetic acid	Oando Lub Blending Plant, Kaduna
Perchloric Acid	Oando Lub Blending Plant, Kaduna

3.2 Specifications and Standards of Equipment

This section is meant to define and state the specifications of equipment used for various experiments and analysis. The specifications of equipment for each test are discussed below.

3.2.1 Density apparatus

The sample to be tested is brought to prescribed temperature and a test portion transferred to a hydrometer cylinder at approximately the same temperature

i. Hydrometer cylinder:- the cylinder is made from clear glass, has a diameter of 30mm and a height of 30cm so as to allow the hydrometer float in the sample with at least 25mm clearance between the bottom of the hydrometer and the bottom of the cylinder.

ii. The hydrometer made from glass is graduated in units of density and conformed with ASTM specification as given in the table below.

Table 3.2: Hydrometer Specification

Specification	unit	Range	Each Unit	Scale Interval	Maximum Scale error	Meniscus Correction
LSOSP	Kg/m^3 at 15^{0}C	600-1100	50	0.5	+0.3	+ 0.7

iii. Thermometer

Density thermometer of specification I P39C was used. The thermometer is scaled in ^{0}Cand graduated with an interval of ± 0.1.

3.2.2 Kinematic viscosity

The apparatus used for this experiment were Marjory viscometer (U-Tube) and thermometer.

i. **U-Tube Viscometer**

The viscometers used were U-tube miniature type having the range of 0.2 to 3,000cSt. The Table 3.3 shows the specifications of the thermometer used.

Table 3.3: Viscometer Specification

S/No	Viscometer Numbers	Viscometer Constants
1.	150/775	0.035972
2.	300/1724	0.24195
3.	350/1068	0.53477
4.	150/778	0.54215
5.	350/1067	0.54215
6.	150/1330	0.042632
7.	350/1381	0.47487
8.	150/766	0.03807

3.2.3 Acid and Base number

i. **Potentiograph**

The equipment used for the above two analyses was potentiograph; a potentiometer titrimeter (automatic type). The equipment makes use of general-purpose electrode with pH of 0 to 11. The reference electrode is sleeve type (saturated calomel electrode).

ii. **Stirrer:** The Stirrer is a magnetic stirrer with variable and controllable speed.

iii. **Titration beaker:** A 250ml beaker made from boro-silcate glass was used.

3.2.4 Flash point

i. Cleveland semi automatic open cup apparatus: this consist of the test cup, heating plate, test flame applicator, heater and supports.

ii. Thermometer: The thermometer having the specification below was used.

Temperature Range	Thermometer Number	
	ASTM	IP
-6 to + 400^{0}C	11C	28C

3.2.5 Calcium and zinc content

Internal standards are used to compensate for inter element effects of x-ray excitation and fluorescence. The apparatus for this analysis is Atomic Absorption Spectrometer.

i. Spectrometer: The equipment is equipped for soft x-ray detection of radiation in the range of 0.1 to 1.0 nanometers. For optimum sensitivity, the spectrometer is equipped with the following;

1. X-ray generating tube, with chromium, rhodium, or scandium target.
2. Helium purqeable optical path
3. Interchangeable crystals – Germanium (Ge), liF_{200}, graphite, and / or pentaerythritst (PE). Other crystals can be used.
4. Pulse height analyzer other means of energy discrimination

5. Shaker or ultrasonic bath; capable of handling from 30ml to 1litre bottles.
6. X-ray sample cells: Of metal or plastic construction fitted with a suitable film window. Suitable films include mylar, polypropylene, or Kapton with film thickness between 6μm and 9μm.

3.2.6 Miscellaneous specifications and considerations

Other specifications and considerations such as apparatus preparation, sample, preparation and safety precautions can be obtained from ASTM and IP Handbooks.

CHAPTER

4.0 EXPERIMENTAL PROCEDURES

The experimental procedures involved the following:

4.1 Treatment and Screening of Castor Seeds

The seeds obtained from castor seed capsules were screened to remove dirt and inclusions. The seeds were subsequently decorticated and sun-dried. The seeds were dried in an oven at 180^0C for 1hour. After the drying, the seeds were allowed to cool for fifteen minutes and were reweighed. These procedures were repeated 12 times, until a constant weight was obtained which ensured that they were moisture free.

4.2 Extraction

The treated seeds were manually crushed with the aid of pestle and mortar. Five grams of the seeds' flakes was put into the thimble in the extraction chamber of Soxhlet apparatus. 100ml normal hexane was charged into the round bottom (Soxhlet apparatus) flask and the set up was heated at 100^0C using a heating mantle. (Plate I). The evaporating extraction solvent was condensed into the thimble by the condenser, where it leached the oil out of the seeds' flakes. The oil rich solvent, after reaching a level was siphoned back into the round bottom flask for subsequent round of extraction. The thimble was discarded of its raffinate, while the solvent was evaporated leaving behind pure castor oil.

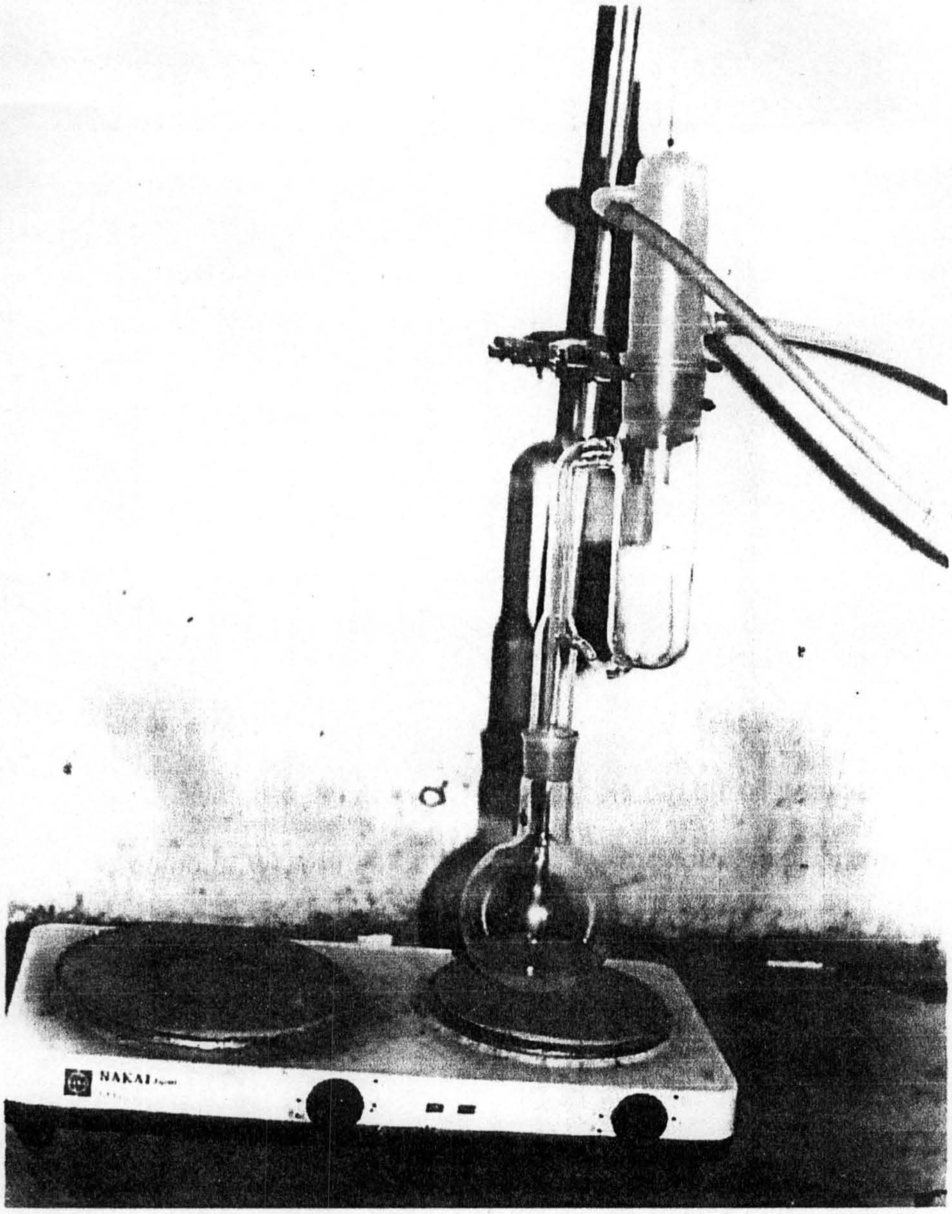


Plate I: Soxhlet Apparatus Set Up

4.3: Characterization of Castor Oil

The castor oil was characterized and analyzed by determining the following properties:

4.3.1 Specific gravity

A 25ml specific gravity bottle was weighed empty and the weight was recorded as (Wo)g. The same bottle was filled with castor oil and the weight determined again as (W_1)g. Another 25ml – specific gravity bottle was filled with water at 4^0C and its weight recorded as (W_2)g. The difference in weights of the castor-oil and water filled specific gravity bottles, and the empty bottle gave the weights of the castor oil and water respectively. The specific gravity of the castor-oil was determined by taking the ratio of the density of castor oil-to the density of water.

4.3.2 Kinematic viscosity

The apparatus for the determination of viscosity include U-tube viscometer, medium liquid (motor spirit) and the stop-watch.

With the aid of suction pump, the castor oil was introduced into the viscometer which has been cleaned with motor spirit and dried in air. The viscometer (with its content) set up was immersed in the motor spirit bath maintained at 40^0C for 15 minutes. Castor oil was sucked into viscometer bulb using a suction pump and was left to fall freely. The time of falling and the viscometer constant were noted. This procedure was repeated using 100^0C medium bath.

4.3.3 Acid value

The acid number was determined dissolving 20g of castor oil in a mixture of toluene and isopropyl alcohol that contained 10 percent water by volume. The resulting single-phase solution was titrated at room temperature with standard alcoholic base solution until the colour changed from yellow to green using methyl indicator.

100ml of titration solvent and 0.5 ml of indicator solution was added to 20g of castor oil in a 250ml Erlenmeyer flask. The mixture was vigorously mixed until a yellow-orange homogenous solution was obtained. Immediately, 0.1M potassium hydroxide (KOH) solution was titrated with the oil mixture until a greenish solution was obtained. A blank titration was made by titrating the base with titration solvent (mixture of toluene and isopropyl alcohol). The volume of the KOH used in each case was read directly from the potentiograph.

4.3.4 Saponfication value

2.5ml of butan-2-one was added to the 3.0g of castor oil in Erlenmeyer flask, followed by 25ml of alcoholic KOH. The condenser was connected to the flask and the flask was heated for 30 minutes. About 5ml of naphtha was added to the mixture in the flask. The solution was titratrated with 0.5M Hydrochloric acid (HCl) while hot .Phenolpthalein indicator was used. The blank titration was also performed.

4.4 Degumming of Castor Oil

To degumme the castor oil, 5ml of citric acid was added to the oil and was heated at a temperature of 180^{0}C for 20 minutes. The container was made airtight. The oil was filtered after cooling.

4.5 Formulation of Lubricating Oil

The formulation of various grades of lubricating oil was done by incorporating base oil, viscosity improver and other additives. For each sample, various proportions of base oil (castor oil), viscosity improver (paratone), and other additives were added into a dry beaker. The mixture were heated to a temperature of 60^0C and thoroughly mixed using electric stirrer until a homogenous mixture was obtained.

Table 4.1: Proportions of Constituents of Grades of Lubricating

Grades	Base oil (Castor oil)(g)	Viscosity Improver (g)	Additive Packages (g)	Total (g)
A	74.60	3.00	22.40	100.00
B	79.00	4.00	17.00	100.00
C	70.60	7.00	22.40	100.00
D	72.00	7.60	20.40	100.00
E	71.40	8.60	20.00	100.00
F	75.20	5.00	19.80	100.00
G	73.80	6.00	20.20	100.00
H	75.20	3.50	21.30	100.00
I	78.80	3.20	18.00	100.00
J	100.00	0.00	0.00	100.00

4.6 Characterization of Lubricating Oil Samples

The characterization of the castor oil samples was based on standard specification of the Society of Automotive Engineers (SAE J300 DEC 95), American Society for Testing and Materials (ASTM D92 – ASTM D417611) and Institute of Petroleum (IP). The tests and analyses carried out included the flash point, pour point, base number, appearance, and viscosity at 40 and 100^0C.

4.6.1 Viscosity at 40 and 100^0C

This was performed as recorded in Section 4.32.

4.6.2 Appearance

The major specification in this test involved visual assessment and comparison with set standard (D417611). It has been the practice to include it in fuel and lubricant tests.

The sample was put into a clean cylinder and checked visually for evidence of water or particulate contamination. It was also held up to the light and visually examined for haze or lack of clarity. The sample inside the cylinder was swirled to produce a vortex and the bottom of the vortex was examined for particulate matter. The visual clarity was recorded as bright (B) and clear (C).

The sample container was placed in a well-lighted area, avoiding light reflection on the front of the container as much as possible; the bar chart was directly placed behind the container. With the lines towards and parallel with the container bottom, the bar chart was examined through the oil to check whether the narrowest line was at the bottom of the chart. Also, directly facing the containing vessel and viewing the chart through the oil, the bar chart was compared with standard photographs placed next to the sample and similarly lighted. Ignoring colour difference, the photograph with closest appearance to the sample was selected and the number of the photograph recorded as the rating of the appearance of the sample. Any special observation such as a particularly heavy contamination with water or solid or darker than usual colour was observed and recorded.

4.6.3 Flash Point

Approximately 20ml of the oil was filled into the test cup and the temperature was increased. At specified interval, a test flame was passed across the vapour, and the lowest liquid temperature at which application of the test flame caused the vapour of the oil sample to be ignited was taken. The equipment used was Cleveland semi-automatic apparatus.

4.6.4 Pour Point

The pour point of a petroleum product is an index of the lowest temperature of its utility for certain applications. Seta-Lec cloud and pour point refrigerator was used for this test. The test jar was filled with oil to the marked level and closed tightly with a cork carrying the appropriate pour thermometer. The jar was placed into an appropriate hole of the Set-Lec refrigerator and covered. The specimen was observed at interval. The lowest temperature at which the oil was just observed no to be able to flow was taken as the pour point.

4.6.5 Base Number

The quantity of acid, expressed in milligrams of KOH/g of sample that is required to titrate a sample to a specified end point is called Base Number.

About 20g of the oil was weighed into a clean and dry beaker. The potentiograph was adjusted according to the manufacturer's manual and titration was carried out at the speed of 1ml/min. The end point was interpreted from the curve (Appendix B) blank titration was made for each of the titration using 120ml of titration solvent.

4.6.6 Calcium and Zinc content

Some oils are formulated with metal containing additives that act as detergents, antioxidants, and antiwear agents. Some of this additives contain one or more of these metals; barium, calcium, zinc and magnesium. This test provides a means of determining the concentration of these metals that gives an indication of the additive content in the oils.

Samples and standards were diluted with xylene and made to contain approximately 0.3% potassium cyclohexanebutyrate. A 1% potassium solution was prepared by dissolving 5.3g potassium cyclohexanebutyrate and 10ml

2-ethylhexanonic acid in 30ml xylene with heating and diluting with xylene. For each of the sample, 0.1g was measured into 25ml volumetric flask and was made to mark with xylene. 5ml of the above and 3ml of 1%pottssium solution were weighed into 10ml volumetric flask and was made to mark with xylene. This sample were analyzed and read directly using atomic absorption spectrometer.

4.7 Lubricating Oil Test (2^3 – Factorial Design)

Lubricating oils work under certain process conditions. This condition determines the functionality and the efficiency of a given lubricating oil. The ten oil samples were subjected to three process variables namely: temperature, pressure and time; and the effects on the viscosity of oils were investigated. In the lubricating oil test, three process variables were investigated in two ways leading to $2^3 = 8$ levels. Temperature levels of 40 and 100^0C was chosen based on IP240/84, the pressure levels of 1 and 2 bars are within the pressure range of most car engines, and the testing time of 4 and 6 hours. Table 4.2 below shows the lubricating oil test procedure

Table 4.2: Lubricating Oil Test Procedure.

	PROCESS VARIABLES	
Temp (^{0}C)	Pressure (Bar)	Time (Sec)
40	1	4
100	1	4
40	2	4
100	2	4
40	1	6
100	1	6
40	2	6
100	2	6

The result of the test is displayed in Chapter 5. The results were then subjected to statistical analysis to see the significance of the variation of the viscosities at the test conditions and deductions were made.

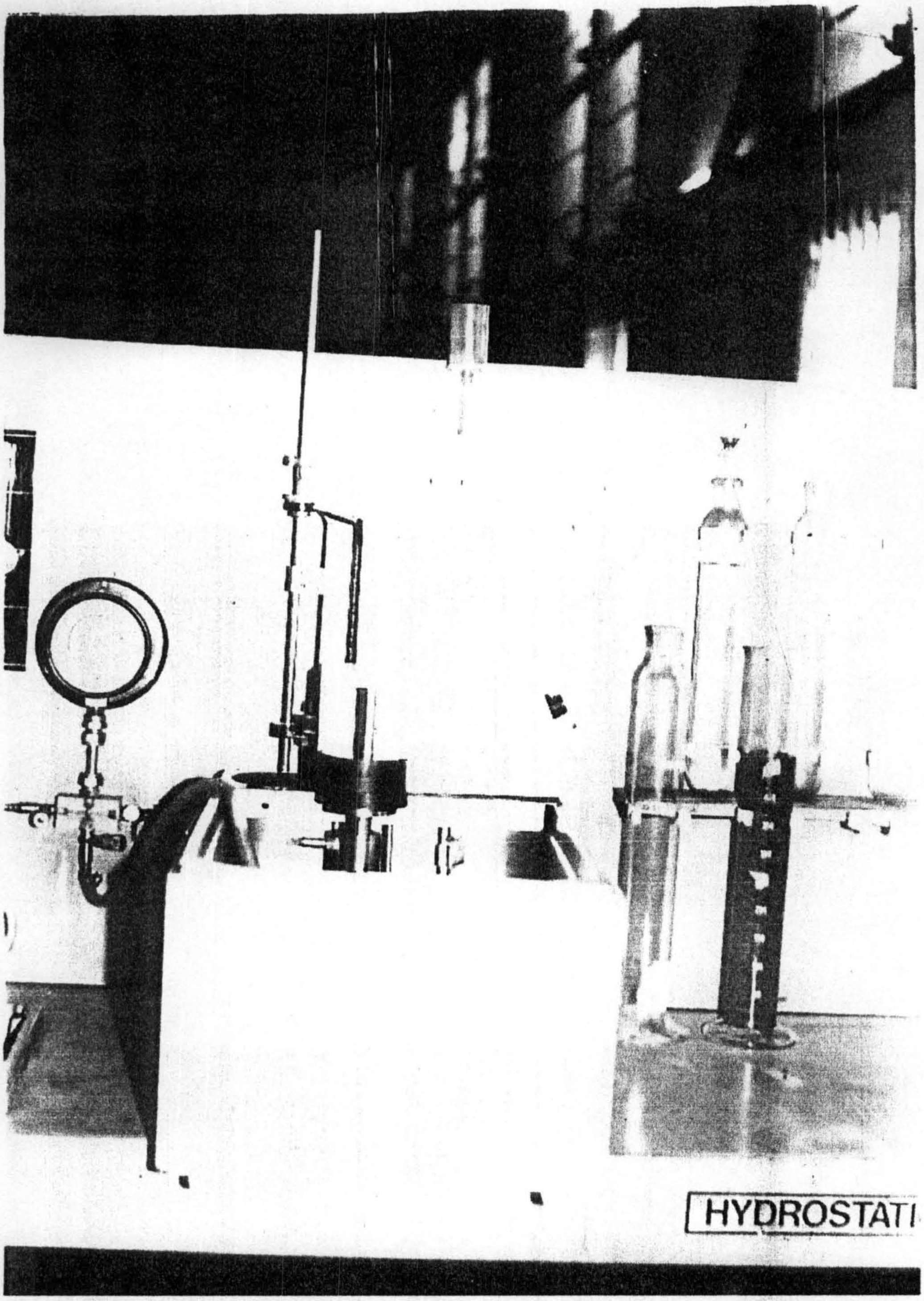


Plate II: Lubricating Oil Test Apparatus Set Up

CHAPTER

5.0 RESULTS AND DICUSSION

5.1 Results

The results of the present study are presented in Tables 5.1 – 5.14

Table 5.1 The Result of Drying.

Stages of drying	Period of Drying at 180^0C (hour)	Weight of castor seeds(g)
1	1	1000
2	1	995.30
3	1	985.80
4	1	975.70
5	1	969.80
6	1	969.40
7	1	964.10
8	1	972.60
9	1	959.90
10	1	959.80
11	1	958.80
12	1	958.60
13	1	958.60

*Initial weight before drying

5.1.1 Physicochemical Properties of castor oil

Table 5.2 shows the physicochemical test results.

Table 5.2: Physicochemical Properties of Castor Oil

Physicochemical Properties	Values
Specific gravity, 25%C/25^{0}C	0.949
Viscosity @ 40^{0}C, cSt	245.34
Viscosity @ 100^{0}C, cSt,	18.98
Viscosity Index	86
Acid Value, mg/KOH/g	3.48
Saponification Number	185.13

5.1.2 Viscosity of Lubricating Oil

The result of the viscosity of the samples of lubricating oil is given in Table 5.3.

Table 5.3: Viscosity of Oil Samples

Oil Sample	Viscometer No.	Viscometer Constants	Time(S)	Viscosity (Cst)
A @ 100^0C	150/778	0.036736	421.91	15.50
@ 40^0C	350/1067	0.54215	202.18	109.61
B @ 100^0C	150/775	0.035972	328.35	11.81
@ 40^0C	300/1724	0.24195	431.91	104.80
C @ 100^0C	150/775	0.035972	438.59	17.40
@ 40^0C	350/1068	0.53477	235.17	125.76
D @ 100^0C	150/778	0.036736	522.10	19.81
@ 40^0C	350/1067	0.54215	260.11	141.02
E @ 100^0C	150/1330	0.042632	469.13	20.00
@ 40^0C	350/1381	0.47487	314.61	149.40
F @ 100^0C	150/766	0.03807	431.84	16.44
@ 40^0C	350/1067	0.54215	220.44	119.51
G@ 100^0C	150/1330	0.042632	387.03	16.50
@ 40^0C	350/1064	0.54215	239.41	129.80
H @ 100^0C	150/766	0.03807	480.45	18.29
@ 40^0C	350/1068	0.55477	247.99	132.62
I@ 100^0C	150/766	0.03807	480.43	18.29
@ 40^0C	350/1068	0.53477	247.99	132.62
J @ 100^0C	150/775	0.035972	527.63	18.98
@ 40^0C	350/1067	0.24195.	452.53	245.34

5.1.3 Appearance of samples

The result of the appearance test is given in Table 5.8. The lubricating oil samples were also free from water or particulate contamination.

5.1.4 Flash Point.

The result of flash point is given in Table 5.4.

Table 5.4: Flash Point of Lubricating Oils

Samples	Flash Point (^{0}C)
A	248
B	230
C	252
D	254
E	256
F	248
G	246
H	249
I	239
J	228

5.1.5 Pour Point

The result of pour point is given in Table 5.5.

Table 5.5: Pour Point of Lubricating Oils.

Samples	Pour Point (^0C)
A	-28
B	-30
C	-28
D	-28
E	-28
F	-28
G	-28
H	-27
I	-30
J	-24

5.1.6 Base Number.

The result of base numbers of the samples is given in Table 5.6.

Details of the calculation are presented Appendix A.

Table 5.6: Base Number of Lubricating Oils

Samples	Titrant value(ml)	Number (mg KOH/g)
A	98	9.35
B	83	9.26
C	119	9.57
D	93	9.92
E	188	9.97
F	115	9.97
G	83	9.36
H	83	9.29
I	82	9.25
J	-	-

5.1.7 Calcium and Zinc Content

The result of the test and analysis of the samples are given in Table 5.7.

Table 5.7: Calcium and Zinc Content of Lubricating Oils

Samples	Calcium content (%)	Zinc content (%)
A	0.18	0.10
B	0.25	0.095
C	0.14	0.095
D	0.32	0.11
E	0.27	0.11
F	0.26	0.11
G	0.24	0.10
H	0.22	0.095
I	0.20	0.095
J	-	-

5.1.8: Summary of the Result of Characterization and Analysis Carried out on Oil Samples

The results of the analyses are presented in Table 5.8

Table 5.8: Test and Analysis Result

Tests samples	A	B	C	D	E	F	G	H	I	J
Appearance	B&C	B&C	B&C	B&C	B&C	B&C	B&C	B&C	B&C	B&C
viscosity@100^{0}C	15.50	11.81	17.40	19.81	20.00	16.44	16.50	18.29	18.29	18.98
@ 40^{0}C	109.61	104.80	125.76	141.02	149.40	119.51	129.80	132.62	132.62	245.34
v.i	1501	101	153	155	155	148	136	154	154	86
Acid number	-	-	-	-	-	-	-	-	-	-
Base number	9.35	9.26	9.57	9.92	9.79	9.72	9.36	9.29	9.25	-
Flash point	248	230	252	254	256	248	246	249	239	228
Pour point	-28	-30	-28	-28	-28	-28	-28	-27	-30	-24
Calcium content	0.18	0.25	0.14	0.032	0.27	0.26	0.24	0.22	0.20	-
Zinc content	0.10	0.095	0.095	0.11	0.11	0.11	0.10	0.095	0.095	-
saponification number	-	-	-	-	-	-	-	-	-	185.13

Table 5.9 ; Analysis of Variance of the Various Lubricating Oil Samples Under Test

Process variables			Viscosity of lubricating oil samples, cSt.									
Temp.(^{0})	Pressure (bar)	Time (hour)	A (x_1, x_2, x_3,) (74.60,3.00,22.40,)	B (x_1, x_2, x_3,) (79.00,4.00,17.00)	C (x_1, x_2, x_3,) (70.60,7.00,22.40)	D (x_1, x_2, x_3,) (72.00,7.60,20.40)	E (x_1, x_2, x_3,) (71.40,8.60,20.00)	F (x_1, x_2, x_3,) (75.20, 5.00,19.80)	G (x_1, x_2, x_3,) (73.80,6.00, 20.20)	H (x_1, x_2, x_3,) (75.20,3.50,21.30)	I (x_1, x_2, x_3,) (78.80,3.20,18.00)	J (x_1, x_2, x_3,) (100.00,0.00,0.0
40	1	4	108.90	103.55	124.94	140.68	149.02	119.19	129.41	132.60	132.21	244.61
100	1	4	15.22	11.55	17.25	19.02	19.78	16.19	16.27	18.17	19.15	18.72
40	2	4	108.55	103.55	124.05	140.28	148.90	118.95	129.03	132.33	133.13	244.22
100	2	4	15.03	11.56	16.96	18.82	19.64	15.98	16.12	18.08	19.09	18.55
40	1	6	108.94	102.90	123.40	140.35	148.63	118.48	128.65	132.20	133.09	243.82
100	1	6	15.17	11.42	16.75	18.71	19.48	15.86	15.97	17.96	18.73	18.38
40	2	6	108.86	102.70	119.47	140.20	148.44	118.04	128.27	132.08	132.97	243.44
100	2	6	15.09	11.20	16.50	18.54	19.42	15.80	15.82	17.88	19.01	18.20

x_1, x_2 and x_3 are the fractions of the base oil, viscosity improver and the additive package respectively.

Table 5.10: Process Conditions' Test for SAE 40

Process Variables			
Temperature (^{0}C)	Pressure (bar)	Time (hour)	(Viscosity of SAE 40 (cSt.)
40	1	4	150.95
100	1	4	15.25
40	2	4	150.98
100	2	4	15.29
40	1	6	150.95
100	1	6	15.25
40	2	6	150.97
100	2	6	15.23

TABLE 5.11: Modeling Equation for Lubricating Oil Samples

						Coefficients					
Bases	A	B	C	D	E	F	G	H	I	J	K
Intercept	171.6633	166.6921	143.9488	222.8375	236.5029	190.7079	207.5033	210.3167	210.2592	397.8792	241.5088
P_1	-1.5563	-1.5440	-0.2996	-2.0253	-2.1610	-1.7400	-1.9048	-1.9132	-1.9024	-3.7829	-2.2626
P_2	-0.7433	- 0.5592	-0.1458	-0.6850	-.02040	-0.4142	-0.5333	-0.5100	-0.6150	-0.5250	0.0142
P_3	0.0017	- 0.3621	13.3046	-0.1775	-0.2713	-0.5713	-0.5333	-2783	-0.1458	-0.5392	-0.0188
P_1P_2	0.0013	0.0039	0.0206	0.0015	0.0009	0.0034	0.0038	0.0020	0.0035	0.0035	-0.0004
P_1P_3	-0.0014	0.0022	-0.1265	-0.0008	0.0014	0.0046	0.0038	0.0011	-0.0009	0.0037	0.0001
P_2P_3	0.0950	0.0125	-0.2445	0.0700	0.0025	-0.0125	-	0.0450	0.0750	-	0.0025

TABLE 5.11: Modeling Equation for Lubricating Oil Samples

						Coefficients					
Bases	A	B	C	D	E	F	G	H	I	J	K
Intercept	171.6633	166.6921	143.9488	222.8375	236.5029	190.7079	207.5033	210.3167	210.2592	397.8792	241.5088
P_1	-1.5563	-1.5440	-0.2996	-2.0253	-2.1610	-1.7400	-1.9048	-1.9132	-1.9024	-3.7829	-2.2626
P_2	-0.7433	- 0.5592	-0.1458	-0.6850	-.02040	-0.4142	-0.5333	-0.5100	-0.6150	-0.5250	0.0142
P_3	0.0017	- 0.3621	13.3046	-0.1775	-0.2713	-0.5713	-0.5333	-2783	-0.1458	-0.5392	-0.0188
P_1P_2	0.0013	0.0039	0.0206	0.0015	0.0009	0.0034	0.0038	0.0020	0.0035	0.0035	-0.0004
P_1P_3	-0.0014	0.0022	-0.1265	-0.0008	0.0014	0.0046	0.0038	0.0011	-0.0009	0.0037	0.0001
P_2P_3	0.0950	0.0125	-0.2445	0.0700	0.0025	-0.0125	-	0.0450	0.0750	-	0.0025

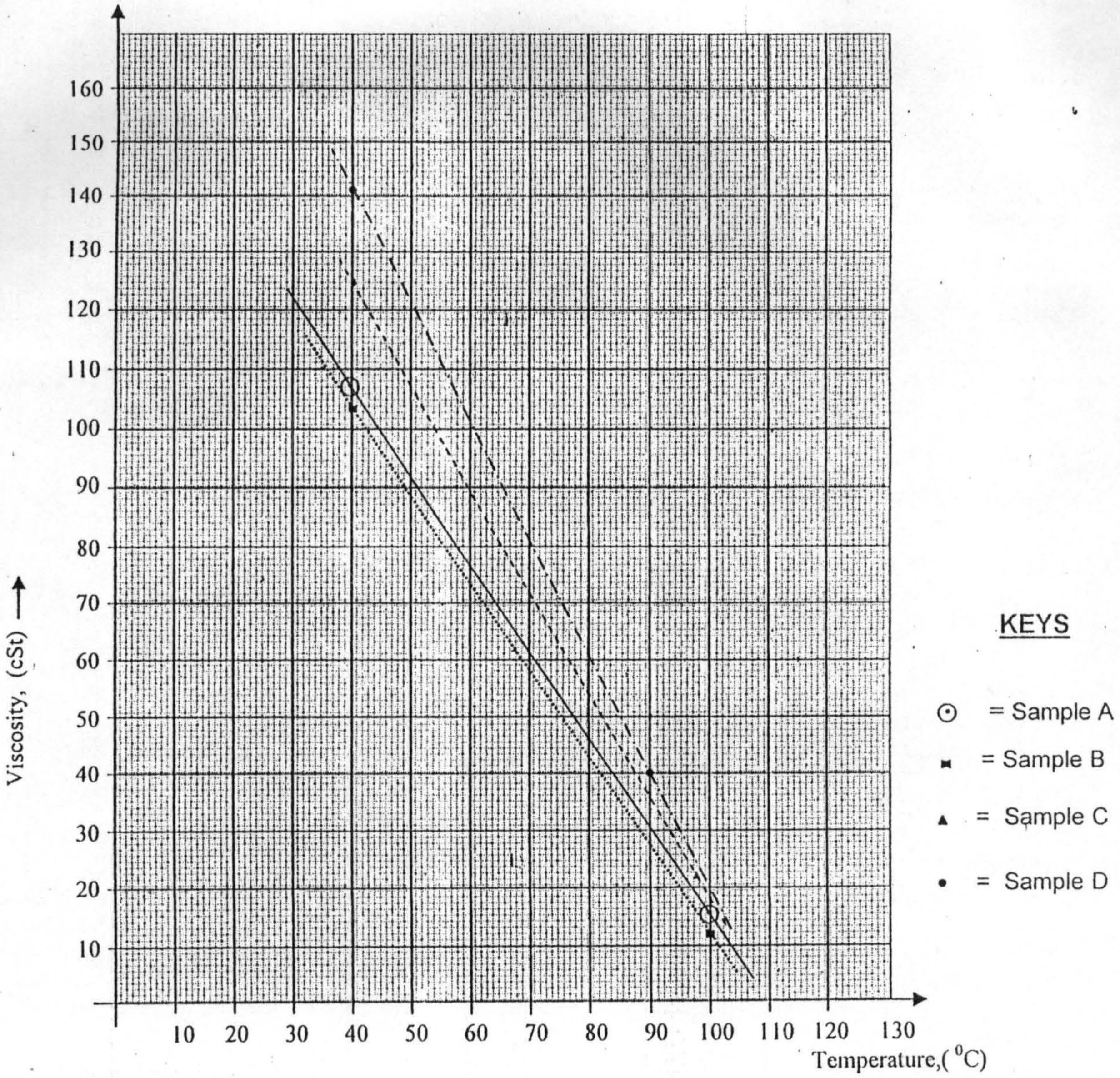


Fig. 5.1; ASTM D341, Viscosity-Temperature Plot for Oil Samples at 1bar

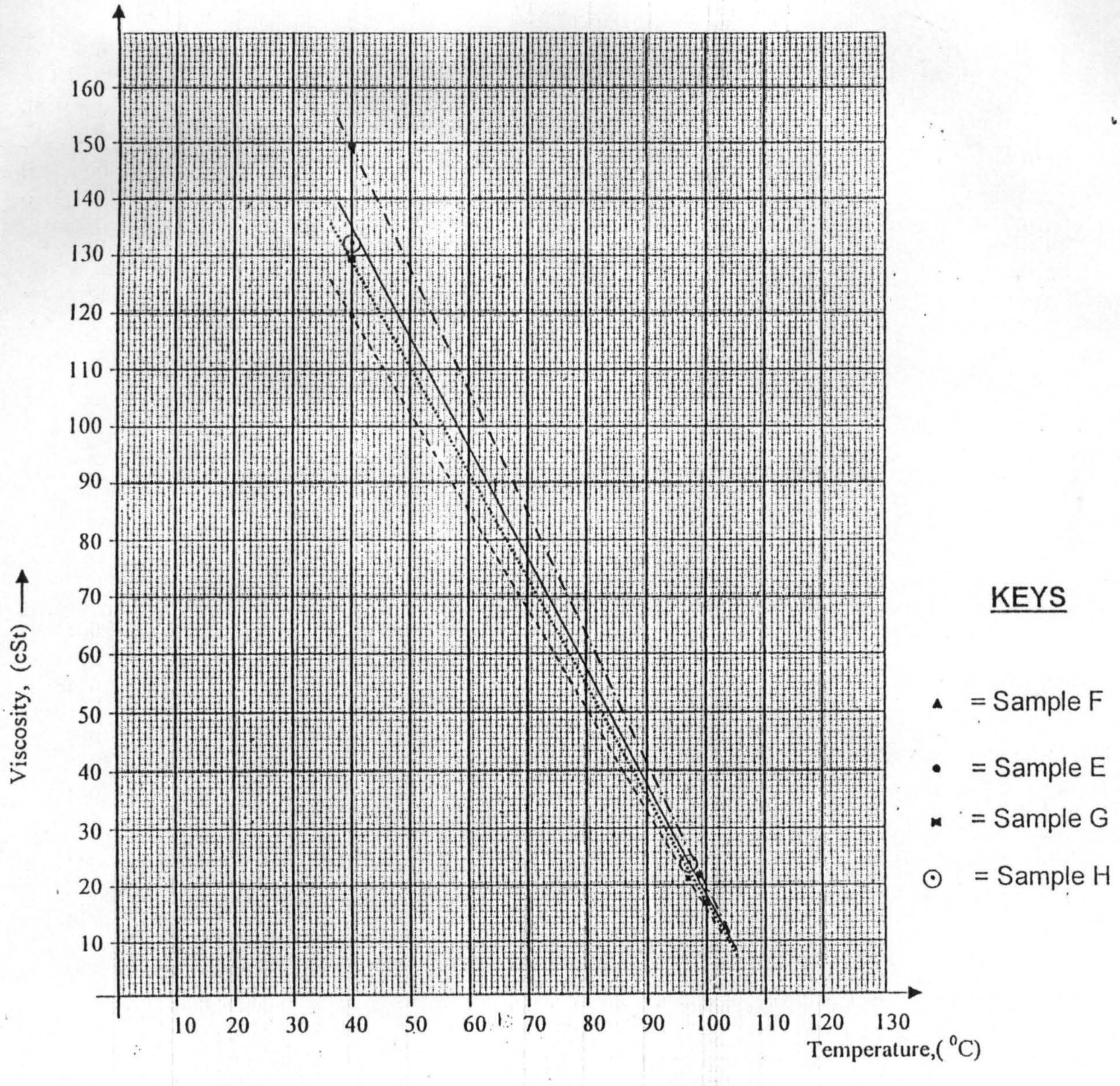


Fig. 5.2; ASTM D341, Viscosity-Temperature Plot for Oil Samples at 1bar

5.1.9 Discussion of Results

Effect of Pre-Drying:

From Table 5.1, it can be seen that the initial weight of castor seeds was 1000 g and the moisture content was 14.14%, but after the drying process, the weight reduced to 958.60 g with approximately zero moisture content. This reduction in weight was due partly to elimination of water molecules from the castor seeds during the drying process.

Castor oil extracted by Soxhlet apparatus was found to have an acid value of 3.48mgKOH/g and specific gravity of 0.949 these values are within the range of standard specifications for castor oil (ASTM D960 – 521952, 1967). The various characteristics of the oil gave it the tendency to combine synergistically with viscosity improver and other additives. An example of such characteristics is the high viscosity of 18.98 and 245.34cSt at 100 and 40^0C respectively (table 5.3).

Effect of Viscosity

The result of characterization carried out on each of the lubricating oil samples revealed that they have good viscosity properties, which fall within the standard specifications of the Society of Automotive Engineers (SAE) and the Nigerian Industrial Standards (NIS). Samples A, B and E have the viscosities and other characteristics that make them correspond to SAE 30, SAE 40 and SAE 20W/50 respectively. The first two grades are mono-grades while the last grade is a multi-grade oil. The multi-grade oil gave a better performance than the mono-grade under the same conditions. The above grades were identified using SAE specifications

(Grove Specification Number 6-829-013433, SAEJ30E DEC95, and NIS370:1997). From Table 5.8, it can be seen that the viscosities of the oil samples at 100 and 40^0C, and hence their viscosity indices are appreciably high. Sample E has highest viscosities of 20 and 149.40cSt at 100 and 40^0C respectively. This made it to emerge as the best sample with the viscosity index of 155. Other samples have lower viscosity indices. This is due to variations in the various proportion of the additives in the formulations.

Effect of Flash and Pour Points

The flash points of the lubricating oil samples are high. Sample E has the highest flash point of 256^0C and Sample J has the lowest flash point of 228^0C. All these values are higher than the Nigerian Industrial Standards (NIS) minimum requirement for flash point for lubricating oils, which given in Table 2.6. This is because castor oil being a vegetable oil is less flammable compared to petroleum oils. The pour points of the oil samples fall within the Nigerian Industrial Standard specification (NIS 370.1997). The pour points are as low as -30^0C, which indicates a good cold starting condition of the oil samples in the engines.

The Effect of Base Number and Metallic Content

The oil samples were also characterized by good base number and metallic content. It can be seen in Table 5.8 that all the oil samples have base numbers of at least 9.25mgKOH/g. These are high enough compared to the 5.0mgKOH/g stipulated by the Nigeria Industrial Standard

(NIS 370.1997). The oil samples also have high metallic contents. Sample E has the highest calcium and zinc contents of 0.27 percent and 0.11 percent respectively. Base number and metallic content of lubricating oil are functions of the percentage of the additives in the oil.

The Effect of Appearance

The result of appearance showed that the oil is bright and clear; and free from water particulate molecules. The major source of contaminants in lubricating oils is the base oil, which in the case of this work was pure.

The Significance of Process Variables Test

Of most importance is the performance of the formulated oils under set process conditions. The most important of the process variables are temperature, pressure and time. It was observed that there are both individual and synergic effects of temperature, and pressure on the viscosity of the lubricating oil over a given period of time. The result of the process variables test is given in Table 5.12. The response of the various grades of the oil has been carried out graphically and shown in Figure 5.1 and 5.2. Comparing the graphical response of the oils with the ASTM standard (ASTM D341), the response is satisfactory.

In order to measure the significance of variation of the process variables, the result of Table 5.12 was subjected to analysis of variance. The result of the analysis is given in Appendix C. In the analysis, which comprised the single level and double levels, the effects of temperature, pressure and time on the oil samples were investigated. The F-test when compared to F-values, shows a high significance i.e. the determined value is higher than the table values. This means a significant P_1 which represents temperature. The other F-values are in fractions.

Also the standard deviations agree with the test result. However, the standard deviation for P_1 and P_2 did not showed much variations as the values increased from 0.0283 for V_1 to 2.9981 for V_7, the standard deviation for the interaction of $P_1$and P_3 i.e. $P_1 * P_3$, representing temperature and time showed a little higher degree of significance in their deviations. This may be due to some errors in the experimental procedures.

The Modelling Equations for Oil Samples

Models were fitted for each of the lubricating oil samples. The result of the statistical modeling is shown in Table 5.10. The major purpose of the modeling is to see clearly the synergy of temperature, pressure and time. The following model equations emerged to be the best models for lubricating oil Samples a, B and E respectively:

For A: $A=171.6633-1.5563P_1-0.7433P_2+0.0017P_3+0.0013P_1P_2-0.0014P_1P_3+0.0950P_2P_3$

For B: $B=166.69321-1.5440P_1-0.5592P_2+0.3621P_3+0.0039P_1P_2-0.0022P_1P_3+0.00125P_2P_3$

For E: $E=236.5029-2.1610P_1-0.2040P_2+0.2713P_3+0.0009P_1P_2-0.0014P_1P_3+0.0025P_2P_3$

The intercept is significant because of the viscosity of each of the oil samples. From the table, it can be seen that almost all the P_1, P_2 and P_3 are negatives. This means that, temperature; pressure and time have effect on the viscosities of the oil samples. The significance of the effects is a measure of the coefficient in each case. Also, from the table, it is clear that the highest effect is from temperature as the highest coefficients were recorded in P_1. This was followed by pressure and time represented by P_2 and P_3 respectively. Comparing the three models above with the model developed for SAE 40 under the same process condition. It is clear that the process condition have similar effect on the viscosity of SAE 40 lubricating oil. Temperature also has the highest effect on the oil. Looking at the effect of the variables on sample J, it can be seen that the highest effect was recorded in P_1 representing temperature. This means sample J have a poor viscosity index, which is due to the fact that it is a pure blend with no additive.

The model equation can also be used as a prediction tool for the viscosity of the oils when the process variables are known. The modeling equation for each of the oil samples are shown in Table 5.13. Each of the equations as earlier mentioned have incorporated into them process variables; temperature: pressure and time and the combinative factors. When the values of temperature, pressure and time are entered, the corresponding viscosity can be determined.

CHAPTER

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The results of this work have proved that castor based formulated lubricant may serve as a potential substitute for that of petroleum based lubricants. All the oil samples which were formulated from castor oil showed a good performance under test, except sample J which is a pure blend.

The resistance of the lubricating oil samples to the applied stress namely temperatures, pressures and time has shown that the oil samples have good performance characteristics compared to that of mineral oil based lubricant. The viscosity index of these samples were also high and the oil samples would perform excellently well with a low rate of deterioration which may be attributed to the presence of antioxidant and the viscosity improver used during the formulation.

6.2 Recommendations

In subsequent work, cold pressing is recommended partly because more quantities of castor oil may be extracted efficiently.

Also in place of combined additive used in the formulation of the lubricating oil, it is recommended that individual compounds and substances

(Propylene glycol, Tryethanol amine, Zinc oxide, Ethanol and Pyrogallol) having the desired properties be used.

The application of the formulated oil samples test should be better carried out using more efficient equipment, such as a cylinder petrol engine. This normally requires larger volume of oil samples which will give reliable result for process variable's test. Also the period for the test should be increased to further see the effect of these variables over a longer period of time.

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APPENDIX A

A1. Moisture content = $\frac{Initialweight - Final\ \text{weight}}{Initialweight} \times 100\%$

A2. Specific gravity (Relative density bottle)

$$\text{specific gravity} = \frac{mass\ \text{of substance}}{\text{mass of an equal valume of water}}$$

$$= \frac{w_1 - w_0}{w_2 - w_0}$$

A3. Viscosity = Time (sec) X C

Where C = Viscometer Constant

Viscosity is in Centistokes

A4. Acid value = $\frac{\text{(Weight of KOH used – blank Volume) N X 56.1}}{\text{Weight of oil samples}}$

Where N = normality of KOH.

Acid value is in Milligram of KOH per gram

A5. Saponification value (S.V.)

S.V. = 56.1 X N (V1 – V_2) /W

Where N = normality of acid, W = grams of sample.

V_1 = Volume of Acid used in blank titration

V_2 = Volume in (m/s) of acid used in titrating the sample

A6. Base Number (B.N.)

B.N = $\frac{(E - F)M_A \times 56.1}{S}$

Where E = volume of $HCLO_4$ solution

F = blank volume

M_A = the molarity of $HClO_4$ solution

S = Sample mass (g)

Base number is expressed in (mg)KOH/g

A7. Flash point

Corrected flash point = C+ 0.06 (760 – P)

Where C = observed flash point in ^{0}C to the nearest 2^{0}C.

P = barometric,mmHg

A8. Viscosity index (For substances whose Kinematic Viscosity at 100^{0}C is less than 70 cSt)

V.I. = L – U

L – H

Where L – H = D.

The values of L, and D are extracts from the tables.

A9. VISCOSITY INDEX

VI = {[(antilog N) – 1]/ 0.00715} + 100

Where N = (Log H – Log U)/Log 7

H is obtained from the table.

Note: method8 is for substance whose V.I is less than 100 and method9 is for substances whose VI is more than 100.

APPENDIX B

Table B1: Analysis of Variance of the Various Lubricating Oil Samples Under Test

Observation	v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8	v_9	v_{10}	p_1	p_2	p_3
1	108.90	103.55	124.97	140.68	149.02	119.19	129.41	132.62	133.21	244.61	40	1	4
2	15.22	11.55	17.25	19.02	19.78	16.19	16.27	18.17	19.15	18.72	100	1	4
3	108.55	103.07	124.05	140.28	148.90	118.95	124.03	132.33	133.13	244.22	40	2	4
4	15.03	11.56	16.96	18.82	19.64	15.98	16.12	18.08	19.09	18.55	100	2	4
5	108.94	102.90	123.40	140.55	140.63	118.48	128.65	132.20	133.09	243.82	40	1	6
6	15.17	11.42	16.75	18.71	19.48	15.86	15.97	17.96	18.73	18.38	100	1	6
7	108.86	102.70	119.47	140.20	148.44	118.04	128.27	132.08	132.97	243.44	40	2	6
8	15.09	11.20	16.50	18.54	19.42	15.80	15.82	17.88	19.01	18.20	100	2	6

APPENDIX B

Table B2: Analysis of Variance (NOVA), Class Level Information

Class	Levels	1st Value	2nd Value
p_1	2	100	40
p_2	2	1	2
p_3	2	1	6

*Number of observation in data set = 8

APPENDIX B

Table B3: Analysis of Variance Procedure for Dependent Variable, v_1

Source	**DF**	**Anova SS**	**Meal Square**	**F - Value**	**Pr > F**
p_1	1	17553.76	17553.76	99999.99	0.00
p_2	1	0.06	0.06	19.14	0.14
p_3	1	0.02	0.02	5.06	0.27
$p_1 * p_2$	1	0.00	0.00	1.00	0.50
$p_1 * p_3$	1	0.01	0.01	4.52	0.28
$p_2 * p_3$	1	0.02	0.02	5.64	0.25

*Number of observation in data set = 8

APPENDIX B

Table B4: Analysis of Variance Procedure for Dependent Variable, v_1

Source	DF	Anova SS	Meal Square	F - Value	Pr > F
p_1	1	16789.37	16789.37	99999.99	0.0
p_2	1	0.19	0.19	3.05	0.33
p_3	1	0.29	0.29	8.77	0.21
$p_1 * p_2$	1	0.03	0.03	0.85	0.53
$p_1 * p_3$	1	0.04	0.04	1.08	0.49
$p_2 * p_3$	1	0.00	0.00	0.01	0.94

*Number of observation in data set = 8

APPENDIX B

Table B5: Analysis of Variance Procedure for Dependent Variable, v_1

Source	DF	Anova SS	Meal Square	F - Value	Pr > F
p_1	1	22517.60	22517.60	193644.78	0.00
p_2	1	3.63	3.63	3.12	0.33
p_3	1	6.32	6.32	5.43	0.26
$p_1 * p_2$	1	2.32	2.32	2.00	0.39
$p_1 * p_3$	1	3.37	3.37	2.90	0.34
$p_2 * p_3$	1	1.10	1.10	0.95	0.51

*Number of observation in data set = 8

APPENDIX B

Table B6: Analysis of Variance Procedure for Dependent Variable, v_1

Source	DF	Anova SS	Meal Square	F - Value	Pr > F
p_1	1	29599.88	29599.88	99999.99	0.0
p_2	1	0.16	0.16	3136.00	0.01
p_3	1	0.80	0.80	1600.00	0.02
$p_1 * p_2$	1	0.02	0.02	361.00	0.33
$p_1 * p_3$	1	0.02	0.02	361.00	0.33
$p_2 * p_3$	1	0.00	0.00	16.00	0.16

*Number of observation in data set = 8

APPENDIX B

Table B7: Analysis of Variance Procedure for Dependent Variable, v_1

Source	DF	Anova SS	Meal Square	F - Value	Pr > F
p_1	1	33368.48	33368.48	99999.99	0.0
p_2	1	0.03	0.03	11.56	0.18
p_3	1	0.23	0.23	83.42	0.07
$p_1 * p_2$	1	0.000	0.000	0.54	0.59
$p_1 * p_3$	1	0.01	0.01	4.84	0.27
$p_2 * p_3$	1	0.00	0.00	0.00	0.96

*Number of observation in data set = 8

APPENDIX B

Table B8: Analysis of Variance Procedure for Dependent Variable, v_1

Source	**DF**	**Anova SS**	**Meal Square**	**F - Value**	**Pr > F**
p_1	1	21097.66	21097.66	99999.99	0.0
p_2	1	0.11	0.11	7.37	0.22
p_3	1	0.57	0.57	37.04	0.10
$p_1 * p_2$	1	0.02	0.02	1.37	0.45
$p_1 * p_3$	1	0.15	0.15	10.06	0.19
$p_2 * p_3$	1	0.00	0.00	0.02	0.91

*Number of observation in data set = 8

APPENDIX B

Table B9: Analysis of Variance Procedure for Dependent Variable, v_1

Source	DF	Anova SS	Meal Square	F - Value	Pr > F
p_1	1	24884.57	24884.57	7963.06	0.01
p_2	1	4.56	4.56	1.47	0.44
p_3	1	1.04	1.04	0.33	0.67
$p_1 * p_2$	1	3.73	3.73	1.19	0.47
$p_1 * p_3$	1	2.08	2.08	0.67	0.56
$p_2 * p_3$	1	3.13	3.13	1.00	0.50

*Number of observation in data set = 8

APPENDIX B

Table B10: Analysis of Variance Procedure for Dependent Variable, v_1

Source	DF	Anova SS	Meal Square	F - Value	Pr > F
p_1	1	26122.12	26122.12	99999.99	0.0
p_2	1	0.04	0.04	13.14	0.17
p_3	1	0.15	0.15	45.56	0.09
$p_1 * p_2$	1	0.01	0.01	2.25	0.37
$p_1 * p_3$	1	0.01	0.01	2.64	0.35
$p_2 * p_3$	1	0.00	0.00	1.27	0.46

*Number of observation in data set = 8

APPENDIX B

Table B11: Analysis of Variance Procedure for Dependent Variable, v_1

Source	DF	Anova SS	Meal Square	F - Value	Pr > F
p_1	1	26039.90	26039.90	99999.99	0.0
p_2	1	0.00	0.00	0.00	0.97
p_3	1	0.08	0.08	4.21	0.28
$p_1 * p_2$	1	0.02	0.02	1.22	0.47
$p_1 * p_3$	1	0.01	0.01	0.34	0.67
$p_2 * p_3$	1	0.01	0.01	0.64	0.57

*Number of observation in data set = 8

APPENDIX B

Table B12: Analysis of Variance Procedure for Dependent Variable, v_1

Source	DF	Anova SS	Meal Square	F - Value	Pr > F
p_1	1	101754.63	101754.63	99999.99	0.0
p_2	1	0.16	0.16	3136.00	0.01
p_3	1	0.64	0.64	12768.98	0.01
$p_1 * p_2$	1	0.02	0.02	441.00	0.03
$p_1 * p_3$	1	0.10	0.10	1936.00	0.01
$p_2 * p_3$	1	0.00	0.00	0.00	1.00

*Number of observation in data set = 8

APPENDIX C

Table C 1: Standard Deviation for Regression Analyses

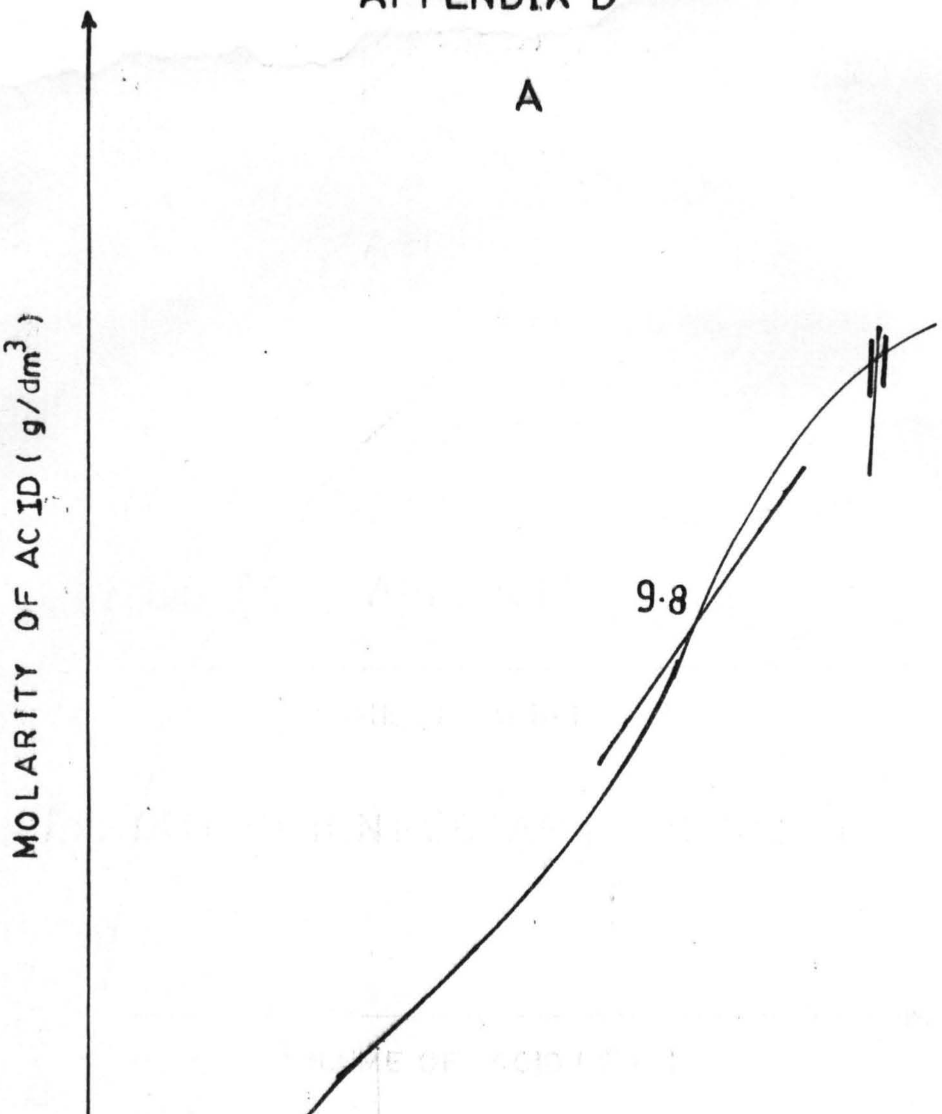
Process Variables		Lubricating Oil Samples									
P_1	P_3	I	II	III	IV	V	VI	VII	VIII	IX	X
100	4	0.1344	0.0071	0.2051	0.1414	0.0990	0.1485	0.1061	0.0636	0.0424	0.1202
100	6	0.0566	0.1556	0.1768	0.1202	0.0424	0.0424	0.1061	0.0566	0.1980	0.1273
40	4	0.2475	0.3394	0.6505	0.2828	0.0849	0.1697	3.8042	0.2051	0.0565	0.2758
40	6	0.0566	0.1414	2.7789	0.2475	0.1344	0.3111	0.2687	0.0849	0.0849	0.2687

APPENDIX C

Table C 2: Standard Deviation for Regression Analyses

Process Variables		Lubricating Oil Samples									
P_1	P_2	I	II	III	IV	V	VI	VII	VIII	IX	X
100	1	0.054	0.0919	0.3536	0.2192	0.2121	0.2333	0.2121	0.1485	0.2970	0.2404
100	2	0.0424	0.2546	0.3253	0.1980	0.1556	0.1273	0.2121	0.1414	0.0566	0.2475
40	1	0.0283	0.4596	1.1102	0.0919	0.2758	0.5020	0.5374	0.2970	0.0849	0.5586
40	2	0.2192	0.2616	3.2385	0.0566	0.3252	0.6435	2.9981	0.1768	0.1131	0.5515

APPENDIX D



Fig· D(1): POTENTIOGRAPH FOR SAMPLE A·

APPENDIX D

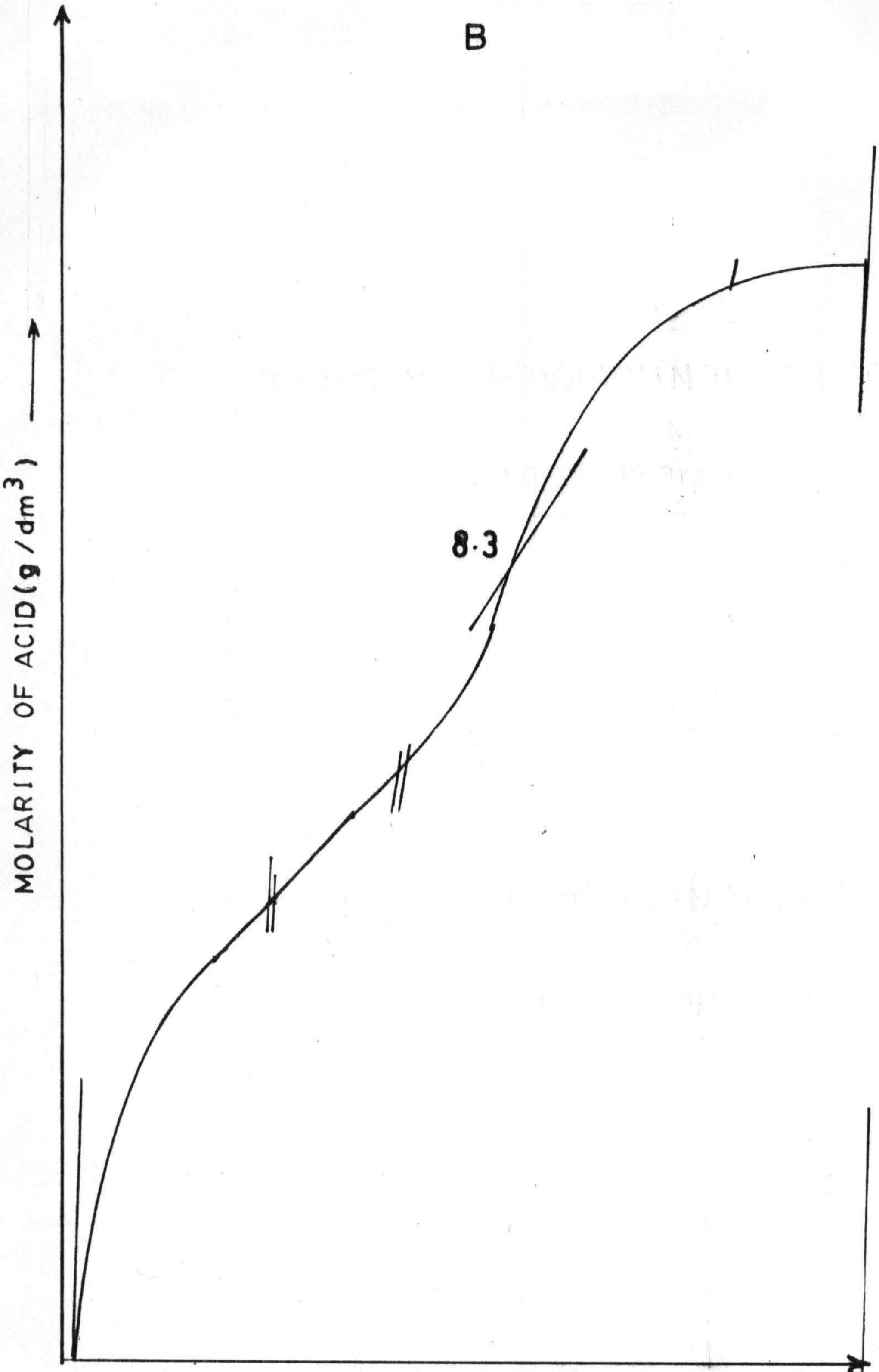


Fig. D(2) : POTENTIOGRAPH FOR SAMPLE B.

APPENDIX D

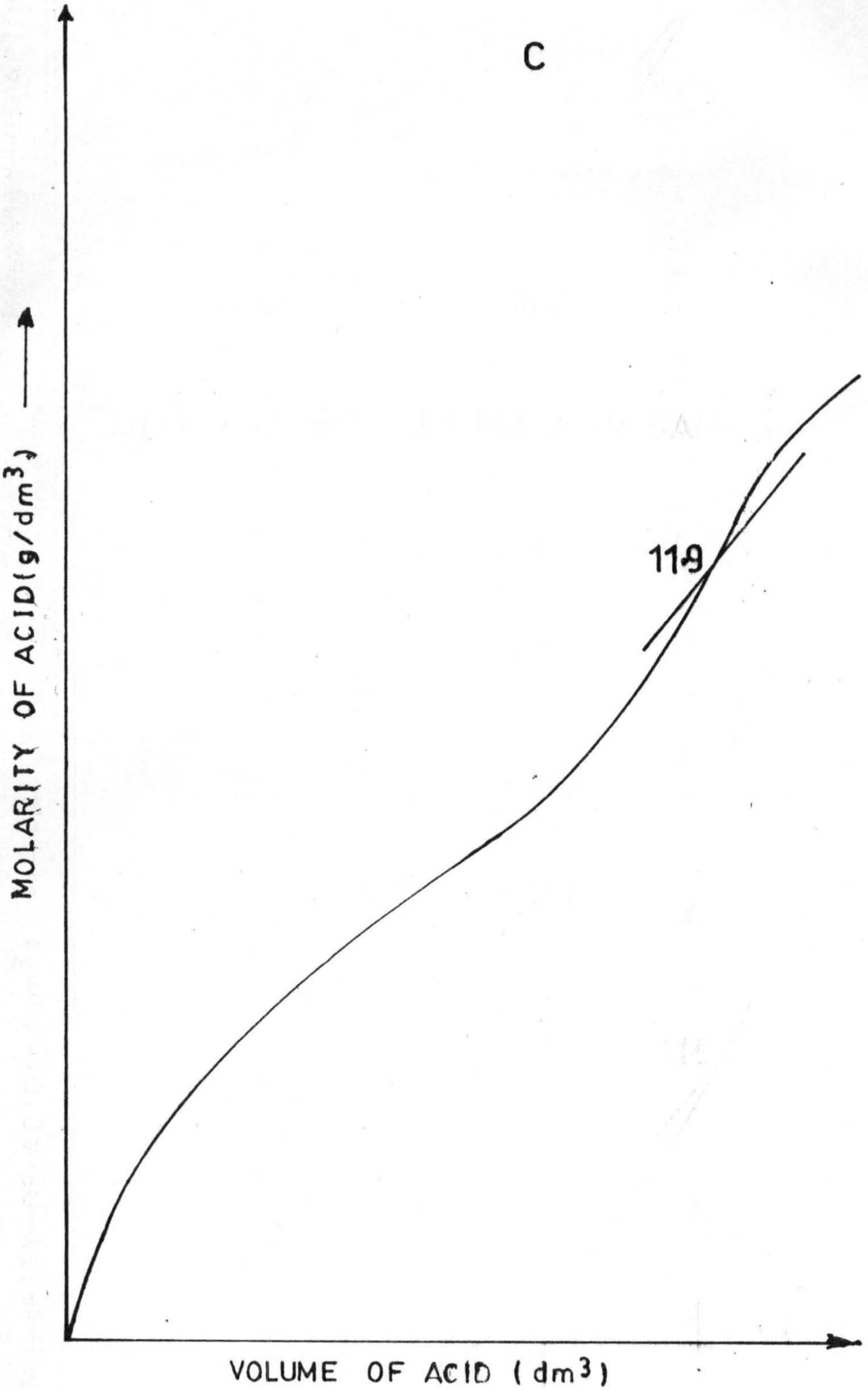


Fig D(3) POTENTIOGRAPH FOR SAMPLE C.

APPENDIX D

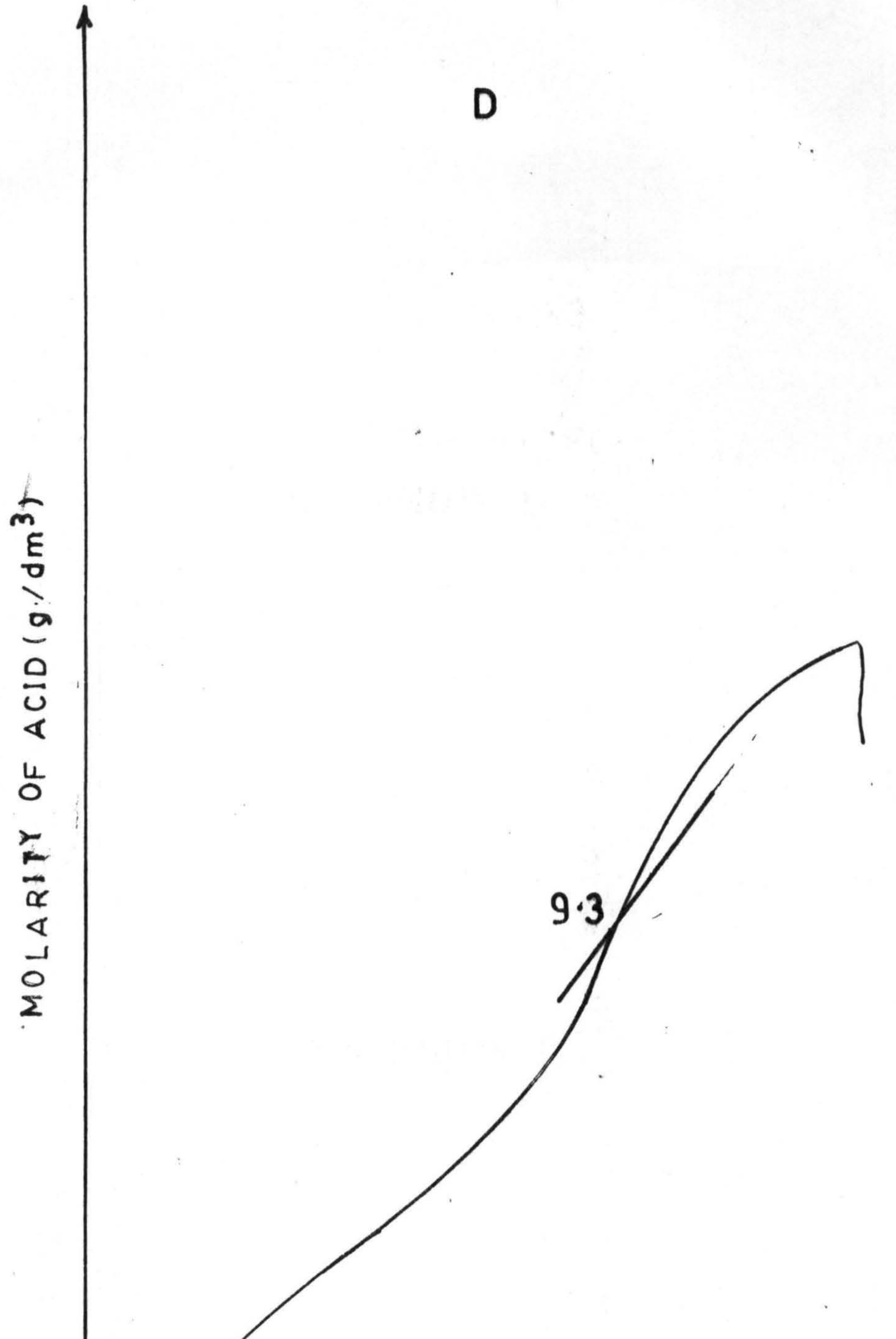
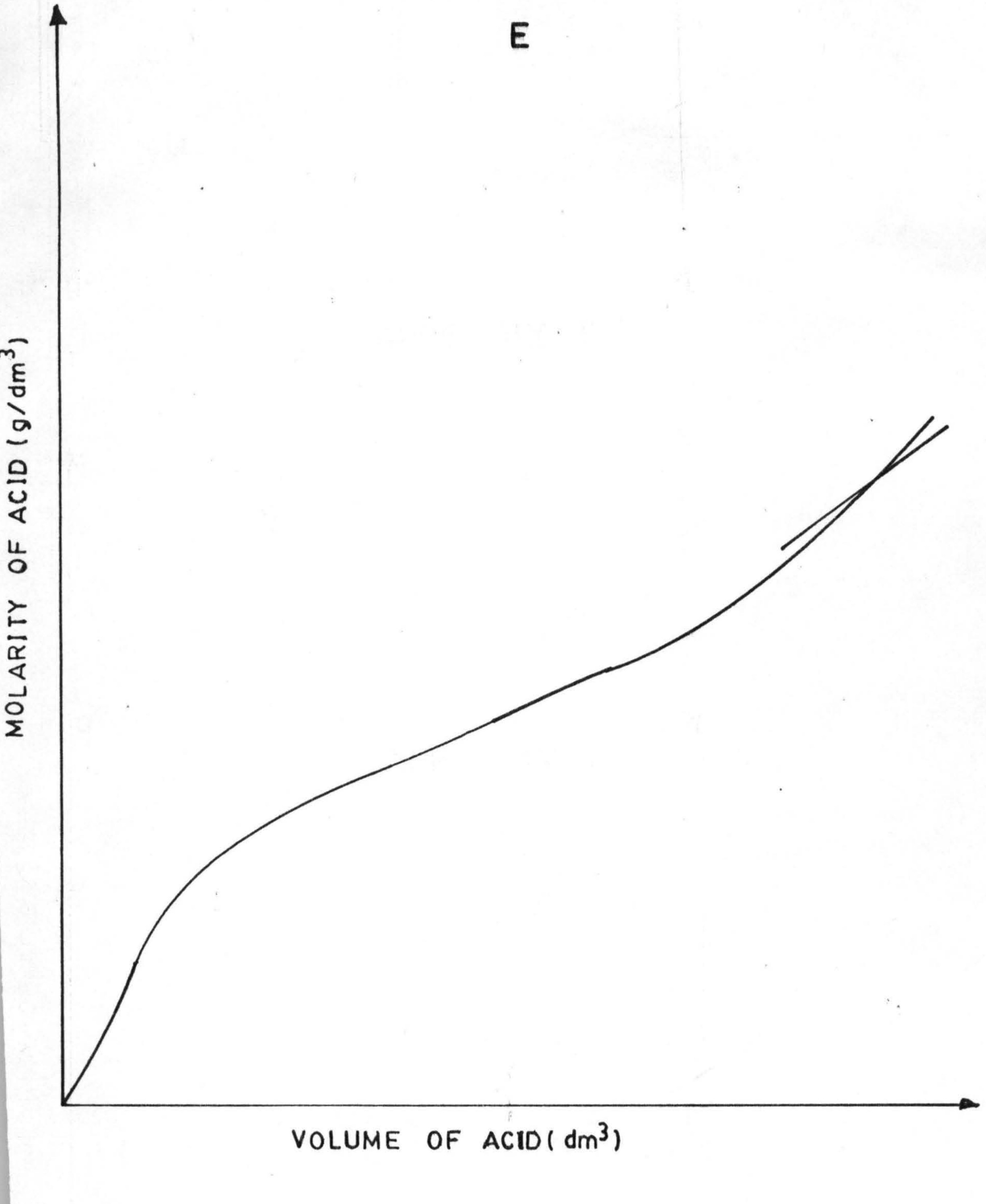


Fig. D(4): POTENTIOGRAPH FOR SAMPLE D.

APPENDIX D



Fig·D(5): POTENTIOGRAPH FOR SAMPLE E.

APPENDIX D

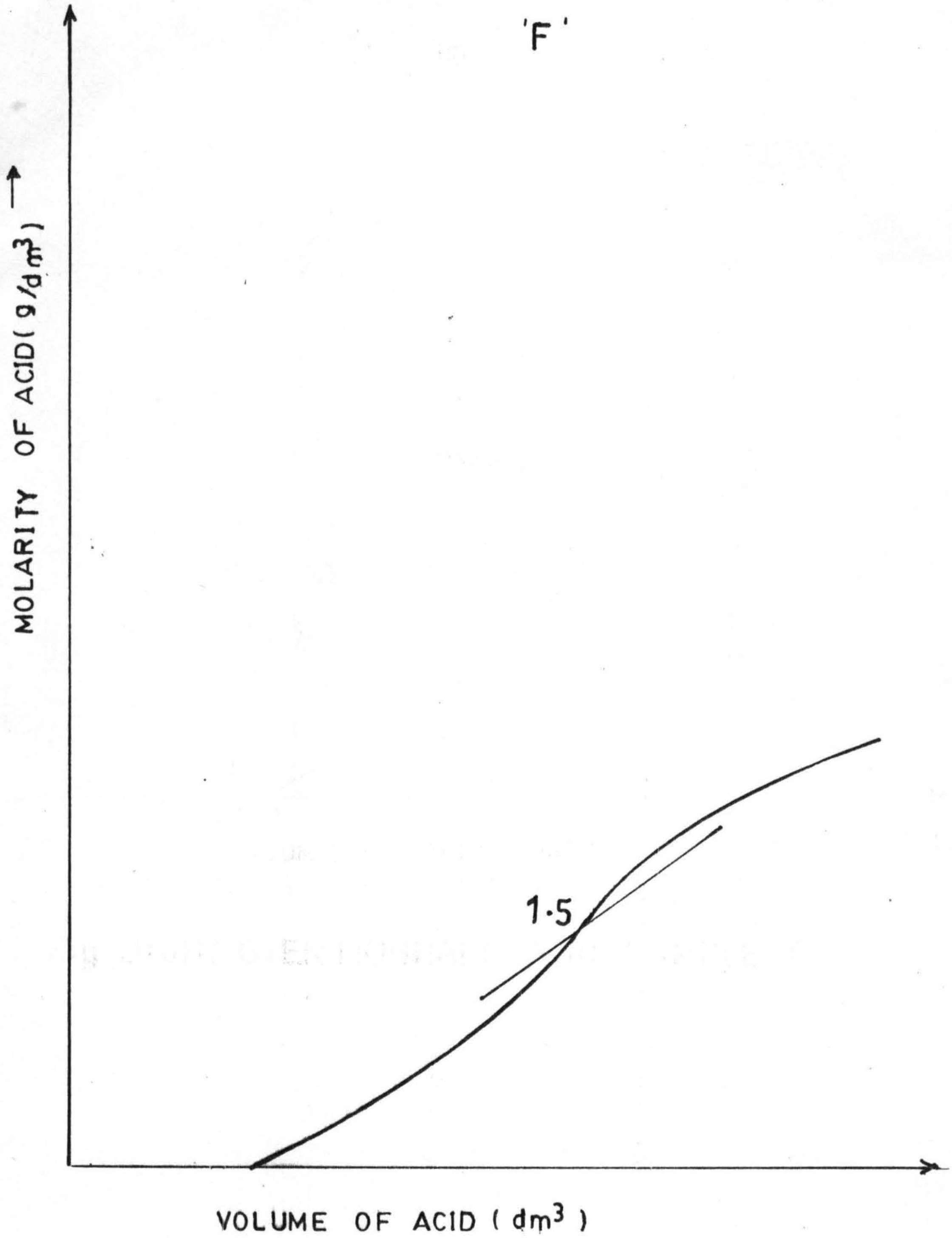


Fig. D(6): POTENTIOGRAPH FOR SAMPLE F.