PREPARATION AND CHARACTERIZATION OF VEGETABLE OIL POLY AMIDES FROM CASTOR Ricinus communis AND THE OIL-PALM *Elaeis guineansis* OILS

BY

MOOREY, BINBUT DALEN

JUNE, 1999

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BY

MOOREY, BINBUT DALEN

B.Sc. CHEMISTRY (A.B.U.)

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AHMADU BELLO UNIVERSITY

ZARIA - NIGERIA

JUNE, 1999

DECLARATION

I hereby declare that this thesis contains the report of my research and has not been presented in any previous application for a higher degree. All information from other sources have been acknowledged by means of references.

.....

MOOREY BINBUT DALEN

5/7/99

.....

DATE

CERTIFICATION

This thesis entitled "Preparation and Characterization of Vegetable Oil Polyamides from Castor *ricinus communis* and the Oil-Palm *Elaeis guineansis* oils" by MOOREY, Binbut Dalen, meets the regulation governing the award of the degree of Master of Science of the Ahmadu Bello University, Zaria, Nigeria and is approved for its contribution to knowledge and literary presentation.

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Date

DEDICATION

This research work is dedicated to the memory of my late father Mr. Dalen Wazhi-Moorey who died on June 12th, 1997 as a result of a flood disaster during which this work was being carried out, and to my brothers and sisters who are labouring to acquire knowledge.

ACKNOWLEDGMENT

To everything that has a beginning it must also have an end. Praise be to the Almighty for this wonderful end. I wish to express my profound and sincere gratitude to my supervisor, Prof. J. Y. Olayemi, who despite his tight schedule, gave fatherly and academic assistance, kind suggestions and constructive criticisms throughout the course of this work.

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Finally and above all, I am immensely grateful to Almighty God for the strength, health, patience and wisdom He bestows on me to accomplish this study.

ABSTRACT

This study investigated the synthesis and application of polyamides from three Nigerian vegetable oils, castor, palm kernel and palm oils obtained in Zaria, Kaduna State and Jos, Plateau state.

Physical and chemical characterisation of the filtered oils yielded the following results, CO = RV (1.380), RI (1.4712), %ffa (3.6), SV (179.3), IV (76.2), PKO = RV (1.068), RI (1.4552), % ffa (0.75), SV (265.8), IV (17.75) and PO = RV (1.139), RI (1.4612), % ffa (7.7), SV (228.0), IV (41.11).

The oils were alkaline refined with appropriate strengths and amounts of lyes of NaOH calculated from each oil's % ffa; followed by earth bleaching.

Mixed fatty acids of the refined oils were obtained from the acid hydrolysis of their soaps. Urea fractionation of the mixed fatty acids yielded unsaturated fatty acid fractions as follows; CO (63.4 %), PKO (9.7 %), PO (36.9 %).

Reactions occuring at the double bonds of the unsaturated fatty acid fractions obtained, led to the formation of fatty acid dimers. The progress of the dimerisation reactions with time was monitored by variations in iodine values and relative viscosities. The average rates of dimerisation calculated from plots of changes in iodine values were found to be; CO (110), PO (8.0), PKO (2.3) g iodine/100g/l hr. Furthermore, measurements of shifts in band

intensities from IR spectral runs of the main functional group, -CH= CH- with time of dimerisation laid claims for the formation of saturated linkages from unsaturated centres.

Polycondensation reactions between the difunctional dimer acids and ethylenediamine yielded fatty acid polyamides. The progress of the reactions were followed by measurements of variations of acid values with time at average rates in the order, PKO (0.8), PO (0.2), CO (0.11) mg KOH/min.In addition, plots of the Carothers equation for a non-catalysed polycondensation reaction yielded maximally the following parameters;

PO = DP (3.5), Mn(2,058.00), p (71.42%) at t = 30 mins,

CO = DP (5.0), Mn(2,940.00), p (80.00 %) at t = 60 mins.

PKO = DP (7.8), M/7(4,752.29), p(87.14%) at t = 70 mins.

Furthermore, intercept values from the plots of the Carothers relationship showed positive deviations above unity for PO and CO, while calculated k values are in the order; CO > PO >PKO.

Characterisation of the fatty acid compounds prepared, by IR spectroscopy and solubility tests gave encouraging evidences of the formation of polyamides.

Finally, formulated spray-coat trials on leather surfaces showed good to excellent dry and wet rubfastness ratings between 30 - 150 circles for PO and PKO coats compared to standard coats used in the leather industry. However, CO coat appeared tacky.

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Glossary

CO = Castor oil or its compounds

PO = Palm oil or its compounds

PKO = Palm kernel oil or its compounds

RV = Relative viscosity

RI = Refractive index

SV = Saponification value

% ffa = Free fatty acid

IV = Iodine value

SLTC = Society of Leather Technologists and Chemists

J.AOCS = Journal of American Oil Chemists Society

IR = Infra-red

$\overline{Mn}$ = Number average molecular weight

DP = Degree of polymerisation

p = Extent of reaction

k = Rate constant

CHAPTER ONE

1.0 INTRODUCTION

The three groups of naturally occurring organic compounds which are of fundamental importance in both animal and vegetable worlds are oils/fats, carbohydrates and proteins (Brian, 1977). These are termed essential nutrients without which life would have not been possible (Hill. 1992).

Oils and fats belong to a large group of naturally occurring substances called lipids which are a diverse group of compounds that have little in common except that they are soluble in organic solvents and insoluble in water and most are derivatives of fatty acids(Gunstone, 1967; Hill, 1992). The lipid family therefore has been conveniently classified according to their hydrolysis products as follows (Gunstone, 1967):

a). Glycerides

b). Waxes

c). Phosphoglycerides

d). Glycoglycerids

e). Sphingomyelins

f). Spingolipids

g). Plant phosphosphingolipids.

Groups (a - d) are essentially fatty acid esters of an alcohol, most commonly glycerol, while the groups (e - g) occur as fatty amides of long chain organic bases related to sphing-4-enine (Hilditch, 1964). Appendix A further elaborates the various hydrolysis products of the various lipid groups.

For the purpose of elaboration and understanding, discussions on the various classes of lipids and their chemical nature would be made as follows:

1.1 Triglycerides

Triglycerides are described as fats when solid and as oils when liquid at ordinary temperatures, and are laid down by plants and animals mainly as energy reserves (Kirk-Othmer, 1965; Bhati et. al., 1980).In nutritive terms, they supply about 9 3 kcal/g, over twice that of proteins and carbohydrates (Cornelius, 1977; Hill, 1992). In addition, they serve as source of energy as ingested and as stored in the body as well as carriers for fat-soluble vitamins A and D, and E, aiding their absorption from intestinal tract (Rackis, 1974). Moreover, they are the sources of poly-unsaturated and other essential fatty acids required for structural development of tissues and prevention of the fat-deficiency disease which manifests itself in man as eczema(Dollear, 1978; Hamilton et. al., 1980).

Furthermore, when triglycerides are hydrolysed, only mixtures of long-chain fatty acids and glycerol are obtained (Hilditch, 1964; Gunstone, 1967).

$$\begin{array}{l} CH_2OOCR^1 \\ | \\ CHOOCR^2 \\ | \\ CH_2OOCR^3 \\ \text{(triglycerides)} \end{array} \xrightarrow[\text{Acid/Enzymes}]{\text{hydroysis}} \begin{array}{l} R^1COOH \\ R^2COOH \\ R^3COOH \\ \text{(fatty acids)} \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{(glycerol)} \end{array} \qquad \ldots..(1.1)$$

where R^1, R^2 and R^3 are long chain aliphatic hydrocarbon parts which may be the same or different (Robert, 1974). However, natural oils/fats are always mixed triglycerides, each molecule containing more than one type of fatty acid and usually contain small quantities of a variety of combined fatty acids; although normally two or three predominate (Cornelius,

1980). Furthermore, all oils/fats contain a proportion of combined unsaturated fatty acids and saturated fatty acids, the degree of each varies with the source and type of oil or fat (Morgan, 1982).

The liquid triglycerides (oils) are essentially and mainly obtained from vegetable sources, and contain often always predominantly unsaturated fatty acids, while the solid fats are mainly from the animal sources and contain often predominantly saturated fatty acids (Gunstone, 1967; Hilditch, 1964; Cornelius, 1980). Generally, oils and fats are found mainly in fruit-coats, seeds, nuts and to a lesser extent in leaves, barks and roots of plants; in the animal kingdom they are found in the adipose tissues such as the heart, kidney, lungs, liver and other subcutaneous layers (Dollear, 1978; Reid, 1978; Fasina, 1983). However, the concern in this research is with the vegetable oils, therefore, emphasis is laid in this direction. Consequently, Appendix B shows the fatty acid composition of some vegetable oils (Fasman, 1975).

Appendix B indicates that triglycerides are composed of both saturated and unsaturated fatty acids in varying proportions which can be further grouped as follows-

Lauric/myristic acid groups

These are C_{12} and C_{14} saturated fatty acids respectively which occur mainly in coconut, palm kernel oils and other nut oils (Hilditch, 1964; Fasina, 1983).

Palmitic acid group

This is a C_{16} saturated fatty acid which is present in practically every fat/oil examined to date (Hilditch, 1964). The chief sources include the vegetable fats/oils of Chinese tallow (60 - 70%), palm oil (40%), cotton seed oil (22 -28%) (Gunstone, 1967; Paquart, 1979).

Stearic acid group

This is a C_{18} saturated fatty acid which occurs in most vegetable fats/oils but only a major component in only few (Paquart, 1979). Two principal grades available are the commercial or pressed acid and the distilled or solvent recrystallised acid (Cornelius, 1980).

On the other hand, the unsaturated fatty acid groups of vegetable origin include the C_{18} aliphatic acids such as oleic, linoleic, linolenic having one, two and three double bonds in that order, and their derivatives (Hilditch, 1964; Appendix B). In this regard, these acids have been conveniently grouped into three (Syed, 1976).

i) Those containing only one unsaturated centre such as oleic acid, its isomers and its derivatives (Mohammad et. al., 1977; Simpson, 1977; Gupta, 1985), Such derivatives include ricinoleic acid, a 12-hydroxy octadec-cis-9-enoic acid which is the main acid of castor oil (Naughton, 1974). The hydroxy group on the chain makes the acid to have low solubility in petroleum ether and increase solubility in alcohol and organic polar solvents (Terill et. al., 1975).

ii) Non-conjugated poly unsaturated acids; these occur in both plants and animals as well as in microorganisms (Hilditch, 1964; Gunstone, 1967) However, in plants they are restricted to the c_{18} members (Fasman, 1992), usually the unsaturation is interrupted by methylene groups (Skipski, 1969). Some prominent members include linoleic, linolenic acids and their derivatives (Raie, 1976; Robertson et. al., 1979; Morgan, 1982). These acids are usually characterised by high iodine values and are therefore high drying properties (Naughton, 1974; Kor, et. al., 1980).

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iii) Conjugated poly unsaturated acids; these are the C_{18} poly unsaturated fatty acids most of plant sources, of which some contain additional oxygenated functions (hydroxy and keto compounds) attached to carbon adjacent to the unsaturated system (Hilditch, 1964). Furthermore, the conjugated systems contain mainly two or three unsaturated centres which start at carbon 2, 8, 9, 10, or 12 with the olefinic groups both in cis and trans configuration (Fasman, 1992). However, the interest here is on C_{18} unsaturated fatty acids of oleic, linoleic, linolenic and ricinoleic. In addition, brief discussion on the other classes of lipids would be made to bring out the structural differences between them (Baum, 1970).

1.2 Waxes

Waxes as classified here are esters of aliphatic acids with long chain monohydric alcohols, other than glycerol (Baum, 1970; Thorstensen, 1993). The acids and alcohols normally found in waxes have chains of the order of 12 to 34 carbon atoms in length (Simpson, 1977) and are easily-melted solids found in both plant and animal matter usually as protective coatings (Baum, 1970). Examples include bees wax, wool wax, carnauba wax, to mention a few.

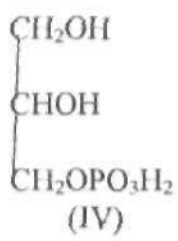
$C_{25}H_{51}C(=O)OC_{30}H_{61}$ (I) — myricyl cerotate (plant wax)

$C_{15}H_{31}C(=O)OC_{30}H_{61}$ (II) — myricyl palmitate (bees wax)

$C_{15}H_{31}C(=O)OC_{16}H_{33}$ (III) — cetyl palmitate (animal wax)

1.3 Phosphoglycerides

The term phosphoglyceride is used to describe all derivatives of glycerophosphoric acid containing at least O-acyl or related group (Kates, 1970; Khor, 1980).



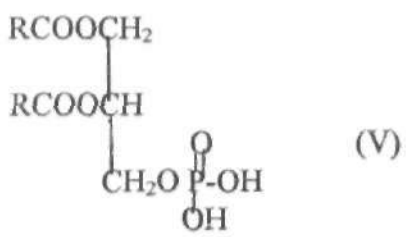
glycerophosphoric acid

(IV)

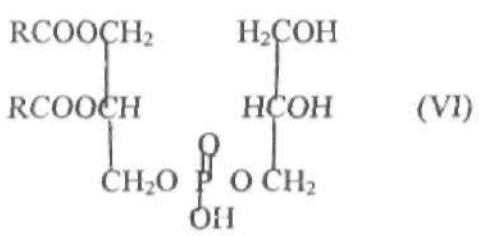
This group of lipids occurs widely in both plants and animals and usually the two free glycerol OH groups are acylated by long-chain fatty acids (Britchard, 1975). Furthermore, the phosphoric acid moiety is usually attached to some other compounds such as amino alcohol or inositol (VIII) (Gunstone , 1967).

Based on the above, they are identified as phosphotidic acids (V), phosphatidyl glycerols (VI), phosphatidic esters (VII) and phosphatidic inositide (VIII). Details have been documented

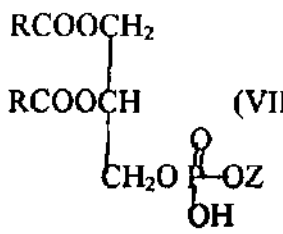
(Gunstone, 1967; Skipski, 1969; Kates, 1970; Baum, 1970; Fasman, 1992).



(V)

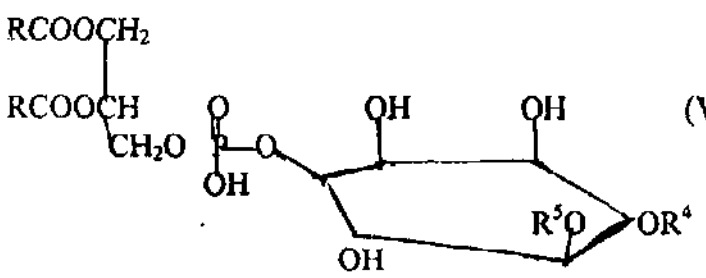


(VI)



(VII)

Z = $-CH_2CH_2N^+Me_3OH^-$ (3-phosphatidyl choline)
= $-CH_2CH_2NH_2$ (Ethanolamine)
= $-CH_2CH(CO_2H)NH_2$ (serine)

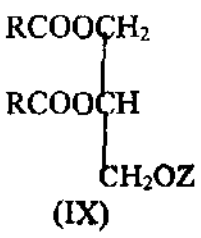


(VIII)

If $R^4 = R^5 = H$ ⟶ Inositol-1-phosphate
$R^4 = PO_3H_2$, $R^5 = H$ ⟶ Inositol-1,4-diphosphate
$R^4 = R^5 = PO_3H_2$ ⟶ Inositol-4,5-triphosphate

1.4 Glycoglycerides

These are present in plants and some microorganisms and are essentially diglycerides attached through primary hydroxyl group to a range of carbohydrate units (Baum, 1970; Khor, 1980)



(IX)

where Z = galactose, glucose, etc

1.5 Sphingolipids

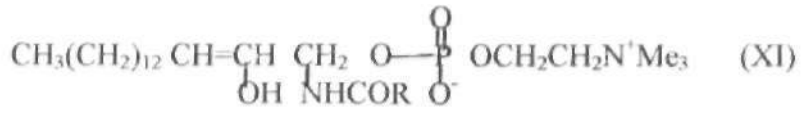
In contrast to the waxes, glycerides, and phosphoglycerides, in which fatty acids are combined as esters, the sphingolipids are amides of fatty acids with long chain bases such as sping-4-emine (sphingosine, (X),) in which the OH group is esterified with glucose or galactose (Finar, 1967).



(X)

1.6 *Phosphosphingolipids (sphingo myelins)*

They are present in brain and nervous tissues alongside cerebrosides and phosphoglyceride (sections 1.3 and 1.5). They are structurally represented as shown below (Baum, 1970)



(XI)

In summary, lipids can be grouped broadly into three main classes:

1. Simple lipids which include fats and oils and waxes
2. Compound lipids which comprise phosphosphingolipids and glycosphingolipids
3. Derived lipids which include the sterols and the steroids family (Gunstone, 1967).

1.7 Uses of vegetable oils

Vegetable oils, like most animal oils and fats have found useful applications in the industry and commerce and as edible oils in several food preparations (Ekpenyong, 1989) Industrially, they are used for example in foams, paint and other surface coatings, lubrications, adhesives, plasticizers, textile dyes, pharmaceutical and cosmetic formulations and many others (Terill et. al., 1975; Burgess, 1994).

1.8 Objectives of the present research

1. To obtain or extract oils from palm and castor seeds, such oils as palm oil, palm kernel oil and castor oil
2. To determine the physical and chemical characteristics of the oils after vacuum filtration

3. To purify the oils by alkaline refining and earth bleaching
4. To produce mixed fatty acids through hydrolysis of the refined oils.
5. To isolate/separate the unsaturated fatty acids from the mixed fatty acids.
6. To synthesise fatty acid dimers from the unsaturated fatty acids obtained in (5) above
7. To synthesise fatty acid polyamides from the dimer acids obtained in (6) above
8. To characterise the polyamides prepared in (7)
9. To attempt formulation of surface coating (lacquer) using the polyamides and any other.

CHAPTER TWO

2.0 LITERATURE SURVEY

One of the fundamental issues of development is economic development which according to Meier (1976), is a process of cumulative change that results from positive forces that raise productivity (Edozium, 1979). Accordingly, one of the development forces in economic theory of production is availability/distribution of scarce raw materials for the manufacturing industry (Wells, 1970). Generally, industrial raw materials whether organic or inorganic have been grouped into the following classes (Wells, 1970; Scott, 1985):

a) Agricultural sources

b) Fossil sources

c) Inorganic sources

Brief mention will be made of each class.

2.1 Agricultural sources of industrial raw materials

These are animal and vegetable (plant) matter, products and by-products such as meat, hides/skins, milk from the animal matter and wool, gums, resins, tannins, fats/oils from vegetable matter to mention a few (Tedder et.al., 1975; Mohammad, 1981).

2.2 Fossil sources of industrial raw materials

Fossils are the dead bodies of animals and plants that have been buried in the desert or frozen ice or covered by sand or mud in ponds or at the bottom of the sea (Hatchi et. al., 1977). Various chemical reactions take place for several years leading to the formation of petroleum, associated gas and coal from which various chemicals and petrochemicals are obtained to feed other industries (NNPC Pub, 1995). Details have been described in Etete, 1995 and NNPC Pub, 1995).

2.3 Inorganic sources of industrial raw materials

These are the mineral elements and their compounds obtained from the earth crust. They also the gases from the atmosphere (Parker, 1978). The include; iron, copper, tin, columbite, aluminum to mention a few while from the atmosphere such gases as CO_2, O_2, N_2 are obtained (Hill, 1992).

Generally, the agricultural and the fossil sources of raw materials provide the bulk of raw materials for the process and manufacturing industries (Chang, 1975; Mounts et. al., 1978). Thus the focus of this research on vegetable oils is justified.

2.4 World production of vegetable oils

Vegetable oils have traditionally been products of southern climates and have contributed immensely to the growth of the economies of many developing nations (Southerland et. al., 1986). While olive oil remains a factor in the agricultural economies of Greece, Spain and Italy as palm oil and castor oil in the domestic and export economies of West Africa, Malaysia, Brazil and India (Terill, et. al., 1975, Oil palm news, Market Review, 1980). Details have been documented (Sparnaw, 1980 and Appendices C and D).

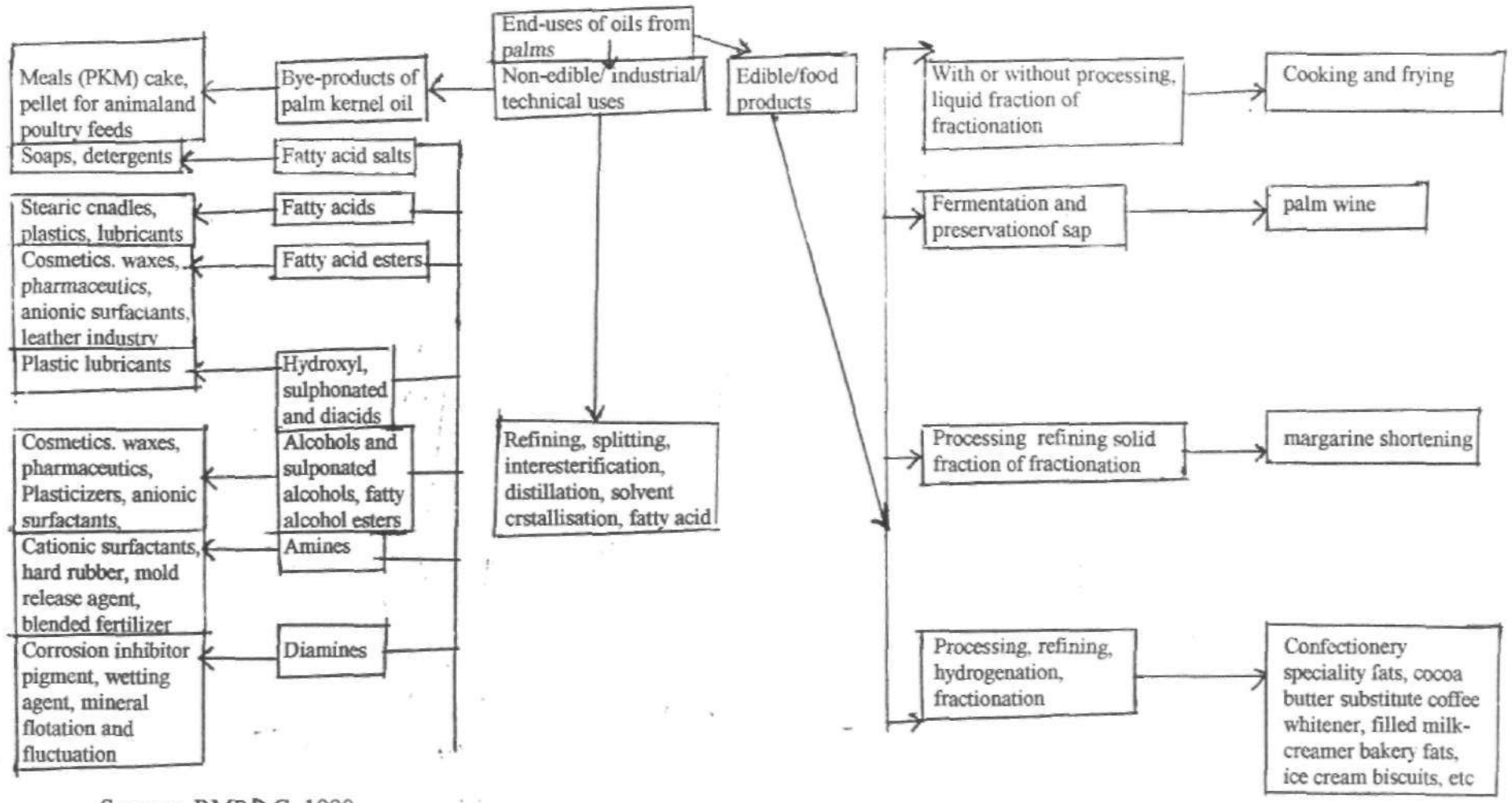
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2.5 The Oil-palm (Elaeis guineansis)

This tree was first grown in West Africa and is now one of the World's main sources of edible and soap-making oils, yielding more oil per year than any oil-bearing plants (Sparnaaij, 1980). The oil-palm produces two types of oils namely, palm oil from the outer mesocarp of the fruit and palm kernel oil from the inner hard nut (Khan et. al., 1972; Khor et. al., 1980). Details of its morphology, cultivation, varieties and uses have been described (Purseglore, 1972; Cornelius, 1975; Birkill, 1985; Appendix C and Fig. 2.1).

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Fig. 2.1:- Major end uses of oils from palms



Source:- RMRDC, 1990.

2.6 The Castor (Ricinus communis)

Castor oil, from the seed of the castor bean plant is widely distributed in tropical and semi-tropical countries (Morgan, 1982; Appendix D). Essentially the castor plant is a native of India (Naughton, 1974).

The oil obtained from the seeds either by expression or solvent extraction has been known since antiquity and was used by the Egyptians as a constituent of embalming fluid (Ramannamuthy, 1975). Earlier, in Mesopotamia (in present day Iraq), the Sumerians of Ur used the oil along with palm oil to produce a crude soap by boiling with alkali (Terill et al., 1975). Although, most widely known for its medicinal properties, such use accounts for only a minute fraction of the total (Naughton, 1974). It has long been known as an article of commerce and its industrial uses are many and varied, including protective coatings, greases, fatliquors, soaps, to mention a few (Mraz et. al., 1972; Fram, 1972; Mohammad, 1981).

Castor oil is one of the few naturally occurring glycerides that approaches being a pure compound as the fatty acid portion is about 90% ricinoleic acid with the chemical structure

$$CH_3(CH_2)_5\underset{\underset{OH}{|}}{CH}CH_2CH{=}CH(CH_2)_7COOH$$

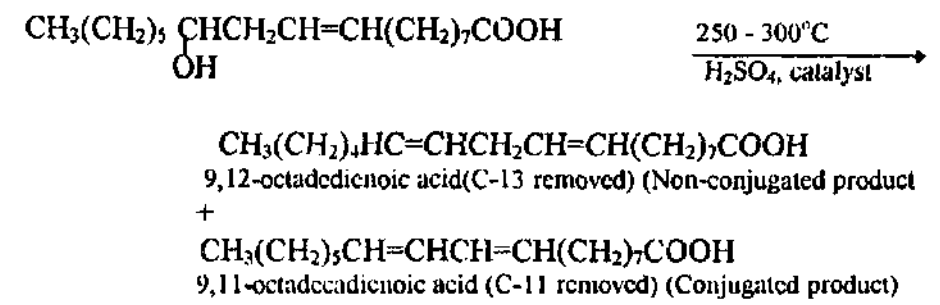
The oil is readily distinguishable from other oils by its high specific gravity, viscosity and acetyl value (Appendix F; Deokar, 1977). In fact the presence of -OH group on the main fatty acid, the double bond and -COOH group are the functional groups responsible for the large number of reactions of industrial importance (Fig. 2.2; Naughton, 1974). Dehydration occurs at the -OH group by the removal of the OH-group and an adjacent hydrogen atom at

Fig. 2.2:- Chemical reactions at three basic points of functionality of castor oil

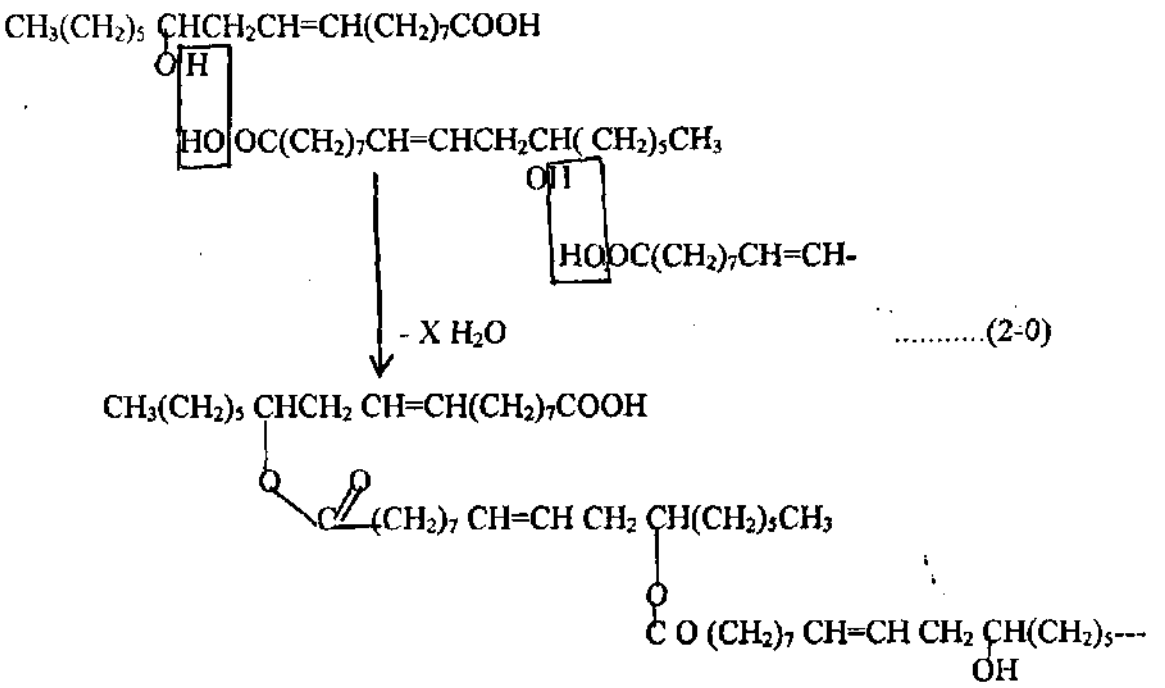
Functional group	Nature of reactions	Added reactants	Type of products
Ester linkage	1. Hydrolysis	Acids, enzymes, twitchell reagent catalysts	Fatty acids
	2. Esterifcation	Monohydric alcohols	Esters
	3. Alcoholysis	Glycerol, glycols	Mono, diglycerides, monoglycols, etc
	4. Saponification	Alkalis, alkali plus metallic salts	Soluble soaps, insoluble soaps
	5. Amidation	Alkylamines, alkanolamines etc	Amine salts, amides
	6. Halogenation	Sulphonyl chloride ($SOCl_2$)	Fatty acid halogens
Double bond	7. Oxidative polymerisation	Heat, air, oxygen	Polymerised oils
	8. Hydrogenation	H_2, moderate pressure	Hydroxystearates
	9. Epoxidation	Hydrogen peroxide	Epoxidised oils
	10. Halogenation	Cl_2, Br_2, I_2	Halogenated oils
	11. Addition reactions	Sulphur, maleic acid	Polymerised oils
	12. Sulphonation	H_2SO_4	Sulphonated oils
Hydroxy group	13. Dehydration	Catalyst plus heat	Dehydrated castor oil
	14. Caustic fusion	NaOH	Sebacic acid and capryl alcohol
	15. Halogenation	Pcl_5, $POCl_3$	Halogenated castor oil
	16. Pyrolysis	High heat	Undecylenic acid, heptaldehyde
	17. Alkoxylation	Ethylene and or propylene oxide	Alkoxylated castor oils
	18. Esterification	Acetic, maleic, phthalic anhydrides	Alkylated castor oils
	19. Amination	Oxidation plus NH_3	12-amino oleate
	20. Sulphonation	H_2SO_4	Sulphated castor oil (Turkey red oil)
	21. Urethane reaction	Tolylenediisocyanate	Urethane polymers

Source:- Journal of American Oil Chemists Society, Vol 51 No. 3, 1994, p.66.

C-11 or C-13 in the ricinoleic portion of the triglyceride (Bennett, 1955; Morgan, 1982). The reaction is represented as



Dehydrated castor oil is excellent for protective coatings. It has been observed that the catalytic dehydration of ricinoleic acid results in a side reaction in which the OH-groups react with -COOH groups to form estolides or polyricinolesies (Naughton, 1974; Burgess, 1994) represented as;



Other important reactions are outlined in Fig. 2.2 above.

World production of castor beans is shown in Appendix D.

2.7 Extraction of oils

The separation of oils and fats from oil-bearing animals and vegetable materials constitutes a distinct and specialised branch of fat technology (Hubbard et. al., 1977). The widely differing characteristics of fatty materials from diverse sources have given rise to the extraction processes such as rendering, pressing and solvent extraction (Swern et. al., 1964). All extraction processes, however, have certain objects in common which include, obtaining the oil uninjured and free as much as possible from undesirable impurities; secondly to obtain the oil in high yield consistent with the process economies and thirdly, to produce an oil cake or residue of the greatest possible value (Hamilton et. al., 1980).

Vegetable materials, unlike animal materials, contain a large proportion of solid materials associated with the oil. Therefore, careful reduction of the material followed by heat treatment and application of heavy pressure is required to obtain an efficient separation of the oil from the solids (Swern et. al., 1964). Even after the most efficient pressing, an oil cake will retain an appreciable amount of absorbed oil, usually amounting to 2.5 to 5% by weight. However, low oil-bearing seeds may contain about 15 to 20% oil in the cake (Hubbard et. al., 1977).

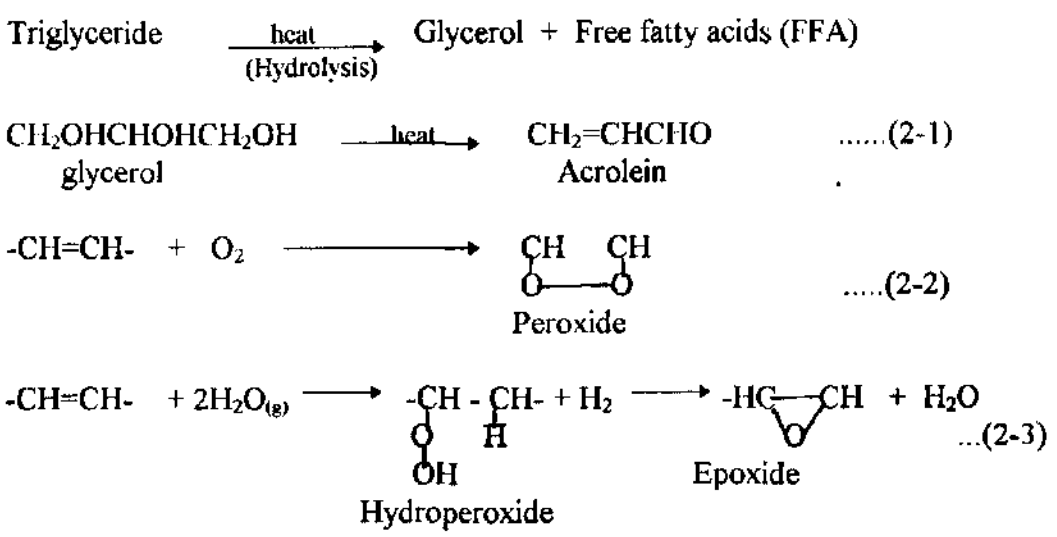
For the processing of low-oil seeds, solvent extraction is particularly valuable since it will reduce residual oil in the extracted seeds to less than 1% (Morgan, 1982). The chief disadvantages of solvent extraction are the high cost of the equipment, integration of some oil seeds under the influence of the solvent which consequently becomes difficult to handle and the Risks of fire and explosion from volatile solvent among others (Swern et. al., 1964; Robert, 1974). However, solvent extraction remains the efficient method for recovery of oil

from any oil-bearing materials in terms of yield and other qualities (Hamilton et. al., 980; Hill, 1992). Some common solvents used are n-hexane, petroleum ether, chlorinated hydrocarbons, to mention a few (Hubbard et. al., 1977).

Oils, whether obtained by mechanical expression or solvent extraction, the oil-bearing seed is cleaned and freed as completely as possible from foreign matter and other seeds by screening and winowing as the case may be before subjecting to the following operations; crushing, heating, pressing, expelling or solvent extraction (Swern et. al., 1964). Details have been described (Swern et. al., 1964; Hamilton et. al., 1980; Morgan, 1982).

2.8 Purification of vegetable oils

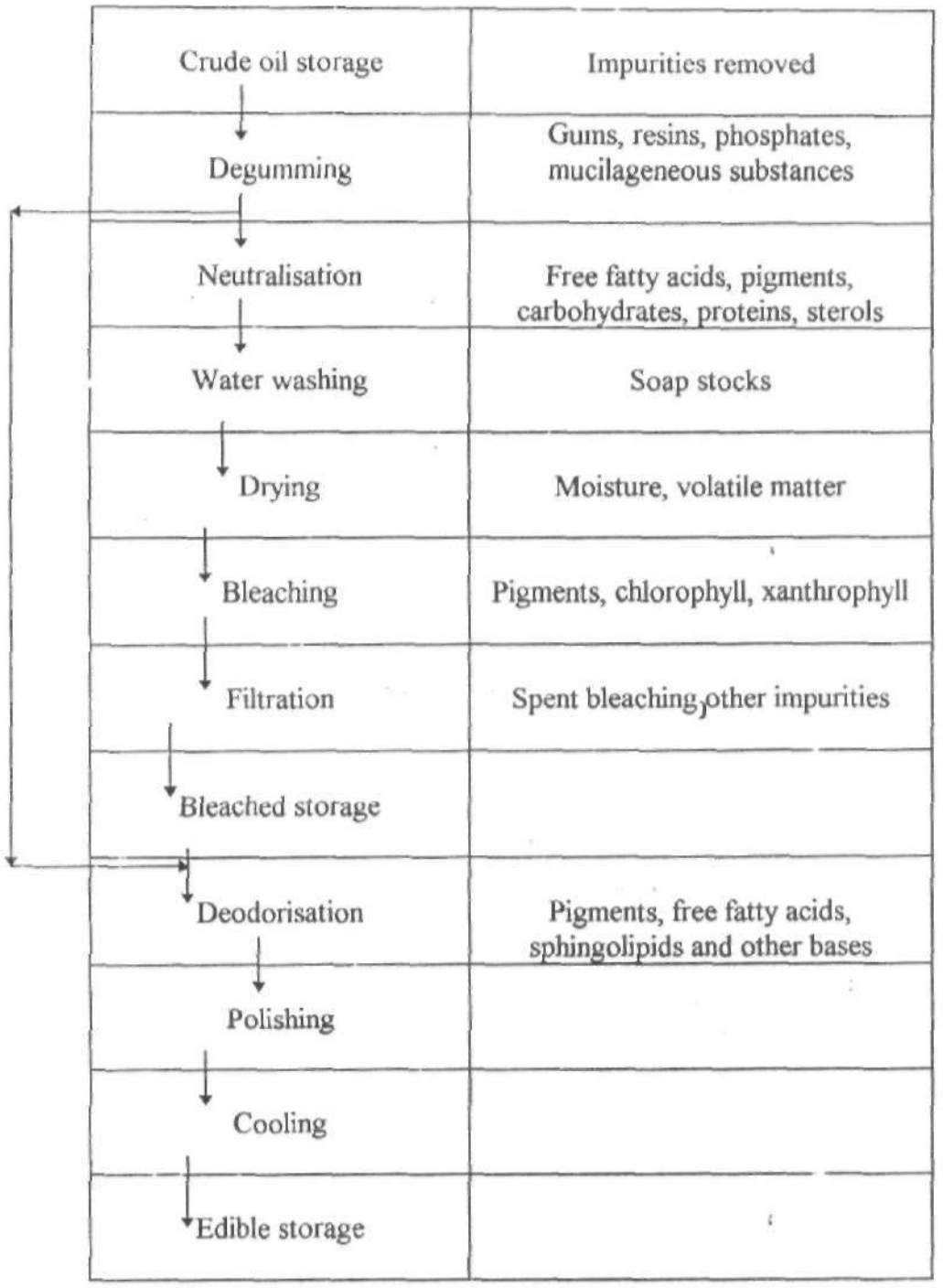
Crude fats and oils produced by rendering, expression or solvent extraction contain variable amounts of non-glyceride impurities (Swern et. al., 1964). The impurities in high-grade animal fats and some vegetable oils such as coconut and palm kernel oils consist principally of free fatty acids which can easily undergo both oxidative and hydrolytic rancidity, giving off-flavours, thus making the oils to have poor keeping qualities (Carter et. al., 1975; Pritchard, 1975).



Equation (2-1) gives rise to hydrolytic rancidity while equations (2-2) and (2-3) give rise to oxidative rancidity. The off-flavours are due largely to the aldehydes formed (equation 2-1) as well as short chain saturated carboxylic acids, hydroperoxides (equation 2-3) while the foaming in an oil is due to hydrolytic rancidity (equation 2-1) (Pritchard, 1975)

Most of the impurities are objectionable because they render the oil dark-coloured, cause it to foam or smoke or are precipitated when the oil is heated in subsequent processing operations (Selke et. al., 1977). According to Jamieson and Baughman, 1926, the following impurities are in most oils/fats; raffinose, pentosans, resins, proteoses, peptones, phosphates, inosites, chlorophyll, phytosterols, phosphotide, xanthophyll, mucilugeneous substances and free fatty acids among others (Kates, 1970). However, not all impurities in oils are undesirable. For instance, the sterols are colourless and heat stable and inert while the tocopherols protect the oil against oxidation (Burgess, 1970; Bastic, 1977). Therefore the object of purification (refining) is to remove the objectionable impurities in the oil with the least possible damage to the glycerides and the tocopherols and other desirable impurities with the least possible loss of oil (Moijboom et. al., 1979; Warner 1978). In refining, both physical and chemical methods have been employed. The physical methods include filtration, degumming, deodorisation and bleaching, which remove one type of imputity or the other while the chemical method is the alkaline refining (Swern et. al., 1964; Morgan, 1980). However, both physical and chemical methods are used together to obtain the desired result. In a nutshell, the stages involved are shown below and described in details in Swern et. al., 1964.

Fig. 2.3 Crude oil refining stages



Source: Halmilton et. al., 1980.

One main physical method of refining is bleaching, especially earth-bleaching. This is an adsorption process specifically physorption on certain surfaces (Swern et. al., 1964; Morgan, 1982). The most important adsorbents used in the bleaching of fats and oils are bleachning earhts or clays; one of which is the Fullers' earth (Benett, 1955; Swern et. al., 1964). It comprises various earths or clays consisting basically of hydrated aluminum silicate which has suitable surfaces of appropriate energies for the adsorption of pigments either disolved in the oil or present as colloidal dispersed particles (Swern et. al., 1964; Carter et. al., 1975).

Besides the clays, another adsorbent used to some extent on fats/oils is activated carbon. However, because of its relatively high cost and high oil retention, it is rarely used alone (Carter et. al., 1975). Most refiners use mixture of clay and activated carbon in the ratio 20 :1 in that order which is more effective than bleaching clay alone (Swern et. al., 1964) Activtaed carbon is very effective in removing "brown" caused by traces of mineral oil in vegetable oils. The mineral oil may increase the apparent red colour of an oil considerably. Activated carbon is also an adsorbent for traces of soap in alkaline refined oil (Hamilton et. al., 1980).

The amount of adsorbent required for any bleaching operation depends on the nature of adsorbent, its activity, that is its efficiency, the variety of oil and the colour of the oil, and the colour requirements of the end-users (Hamilton et. al., 1980). For instance, palm oil is intensely coloured deep-orange-red due to its high carotenoid pigments which are readily adsorbed (Pritchard, 1975). Therefore, for palm oil and other highly coloured oils, about

10% of the adsorbent is normally used while for other less coloured oils, about 3-5% are used; percentages are based on the weight of the oil (Swern et. al., 1964; Hamilton et. al., 1980).

Generally, for earth bleaching, bleaching times of about 30-60 minutes and temperatures of 80-90°C have been employed to effect colour removal at minimal refining losses (Cocks et. al., 1973). Earth bleaching generally removes phosphates and other mucilagenous material referred to as "gums", "slimes". etc (Swern et. al., 1964).

Chemically, alkaline refining involves the use of alkalis to react with the free fatty acids in the oil ordinarily called "neutralisation" (Fig 2.3). This effects the complete removal of free fatty acids which are converted into oil-insoluble soaps (Hamilton et. al., 1980).

$$\underset{\text{free fatty acids}}{RCOOH} + \underset{\text{alkali}}{NaOH} \longrightarrow \underset{\text{soap}}{RCOONa} + H_2O \qquad \text{.....(2-4)}$$

Other acidic substances likewise combine with the alkali and there is complete removal of impurities from the oil by adsorption on the soap formed. Furthermore, all substances which become insoluble upon hydration are also removed (Ekpa et. al., 1996).

The alkali employed mostly is caustic soda because it is more effective in its decolourising action than weaker alkalis such as soda ash, sodium bicarbonate and ethanolamine (Epka et. al., 1996). However, caustic soda has the disadvantage of saponifying a small proportion of the neutral oil in addition to the reaction with free fatty acids, leading to higher refining losses (Cocks et. al., 1973). Oils, particularly those intended for use in paints are sometimes "acid refined" by treatment with strong acids such as H_2SO_4. Acid refining does not reduce

the free fatty acids, but chars and precipitates phosphatides and similar impurities (Thorpe, 1975). Consequently, for the purpose of this research, alkaline refining is employed using caustic soda of appropriate lyes to minimise refining losses and to avoid sulphation/ sulphonation reactions if H_2SO_4 is used (Swern et. al., 1964). However, the selection of appropriate strength of lye for refining is based on the % free fatty acids (Swern et. al., 1964; Cocks et. al., 1973).

The strengths of the lye solutions have been measured in terms of their specific gravity expressed in degrees Baume as shown in Appendix E. Ordinarily, the refiner uses the lye containing a sufficient amount of NaOH to produce the colour desired in the oil and the strength of lye which will produce the lowest refining loss with the desired colour (Cocks et. al., 1973).

2.9 Physical characterisation of vegetable oils

Physical constants of oils have been employed in the quality analysis and identification of individual oils, amongst which are colour, specific gravity, refractive index, viscosity, slip point, flash point among others (Cocks et. al., 1973). However, specific gravity, refractive index and relative viscosity are discussed below:

2.9.1 Specific gravity

This is the ratio of the weight of a specified volume of oil relative to the weight of an equal volume of water at the same temperature (Morgan, 1982), using a gravity bottle and given by the formula below;

$$\text{Specific gravity} = \frac{W_2 - W_o}{W_1 - W_o} \qquad \text{.....(2-5)}$$

W_o = weight of empty, dry gravity bottle

W_1 = weight of bottle filled with water

W_2 = weight of bottle filled with oil

2.9.2 Refractive index

The refractive index of an oil or fat is the ratio of the sine of an angle of incidence to the sine of the angle of refraction when a ray of wavelength of 589.3 mμ (the mean of D lines of sodium) passes from air into the oil and is represented as η_D^t, where t = temperature (Cornelius, 1975). Thus a refractive index is a function of temperature and for vegetable oils, refractive index increases with unsaturation and decreases with the molecular weight of the fatty acids (Cocks et. al., 1973).

2.9.3 Viscosity of oils

All liquids flow when a force is applied, however, some liquids flow more readily than others, for instance, thin limpid liquids like water or white spirit are said to possess a low viscosity whilst high viscosity is a characteristic of stand (polymerised) oils (Morgan, 1982). Hence, viscosity can be simply defined as the resistance to flow.

Generally water has been used as the standard as it has a viscosity of 0.01005 poise or 1.005 centipoises (unit named after Poiseuit) at 20°C (Gallagher et. al., 1977). However, in common use is the relative viscosity, which has no unit as described in Bodor, 1991. There are four methods in use for the measurement of viscosity of oils by which they can be compared either directly or indirectly with distilled water; these apparatuses/methods include; Ostwald (U-tube) viscometer, falling sphere viscometer, bubble tube and efflux (Ubbelohde) viscometer (Fig. 3.1). Amongst these, the Ubbelohde viscometer is the most employed (Collins et. al., 1973).The efflux viscometer measures the relative viscosity which

is a ratio of the viscosity of the solution to that of solvent and is related to their efflux times by the expression below(Collins et. al., 1973);

$$\frac{\eta_2}{\eta_1} = \frac{t_2}{t_1} \qquad \text{.....(2-6)}$$

η_2 = viscosity of solution

η_1 = viscosity of solvent

t_2 = efflux time of solution

t_1 = efflux time of solvent

The above expression is valid for laminar flow of newtonian fluid if measurements are made at the same temperature (Bodor, 1991) assuming that the densities of the two liquids are practically equal (Collins et. al., 1973).

2.10 Chemical characteristics of vegetable oils

2.10.1 Acid value

This measures the free fatty acids content of oils and fats (Pritchard, 1975). The acid value of an oil or fat is defined as the number of milligrams (mg) of potassium hydroxide required to neutralise 1 g of the oil/fat (Cocks et. al., 1973; Koslowky, 1975). The Dutch Standard (1961) specifies a solvent mixture of two parts benzene and one part ethanol and a 0.1 M ethanolic KOH and 3 g of oil/fat in the determination (Cocks et. al., 1973).

In commercial and industrial practice, the acid value of an oil/fat is a quality control parameter (Pritchard, 1975), which measures the degree of hydrolytic rancidity in the

oil/fat. Usually this value is expressed in percentage free fatty acid (section 3.3.1) based on oleic acid (Cocks et. al., 1973).

2.10.2 Saponification value

The saponification value of an oil/fat denotes the weight of potassium hydroxide expressed in milligrams required to saponify completely the free and combined (esters, lactones)fatty acids in 1 g of oil/fat (Cocks et. al., 1973). The saponification value relates indirectly to the molecular weight of the fact or oil (Pritchard, 1975).

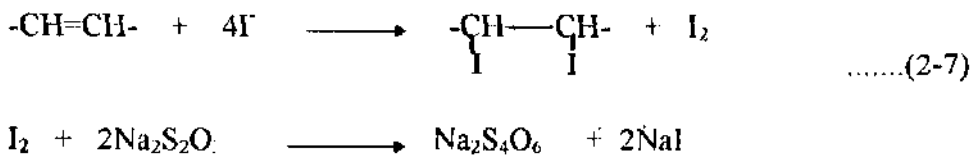
2.10.3 Iodine value

This is a measure of the level of unsaturation in an oil or fat and is the number of halogen expressed in terms of iodine which combines with 100 g of oil or fat under the conditions of the determination at 20°C (Koslowsky, 1975). The determination of olefinic unsaturation was developed primarily for the analysis of animal and vegetable fats and oils which are expressed by iodine number or bromine number (Koslowsky, 1975).

Several methods have been developed for the measurement of olefinic unsaturation in oils/fats, however, the Hanus and Wjis methods are the most employed (Hilditch, 1964). The Hanus method employs iodine monobromide and chloroform as the main reagent and solvent respectively while the Wjis method utilizes iodinetrichloride and carbon tetrachloride as the principal reagent and solvent in that order. However, both methods use sodium thiosulphate solution as the titrant (Vogel, 1971).

Generally, the principle of iodine value determination is that the Hanus or Wjis reagents generate sufficient iodine to react with the double bonds of the oil and the excess of this

iodine is back titrated with sodium thiosulphate solution as shown below (Vogel, 1971; Bastic, 1977; Appendix F).



$$-CH{=}CH- + 4I^- \longrightarrow -\underset{I}{CH}-\underset{I}{CH}- + I_2 \qquad \text{.....(2-7)}$$

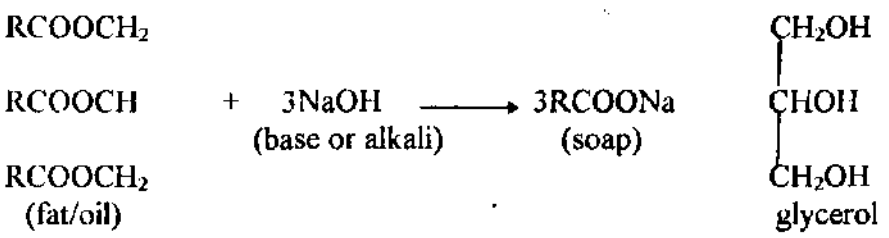
$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

2.11 Hydrolysis of oils and fats

Much have been reported on the hydrolysis of fats and oils into fatty acids and glycerol (equation 1-1, Ekpenyong, 1989). Some of of the methods discussed range from steam treatment to catalytic stripping, acid and alkaline hydrolysis (Hubbard, 1977). Furthermore, a number of reported studies have identified such catalysts as paratoluene sulphonic acid in methanol; Pd/Al_2O_3,; $PdCl_2$/alkali chlorides; $SnCl_4/NaCl/CH_3COOH$; to mention a few (Ekpenyong, 1989). Details of stripping of vegetable oils/fats have been described in Thorpe, 1975; Pritchard, 1975; List et. al., 1978). However, alkaline hydrolysis is discussed in details below.

2.11.1 Alkaline saponification: preparation of water-insoluble fatty acids

Alkaline hydrolysis is essentially saponification where an oil or fat is treated with a solution of a base or alkali in the preparation of soaps (section 2.10.2). The soaps of the individual oils or fats are prepared from their saponification values and subsequently acidulated with concentrated hydrochloric acid to give the fatty acids (Cocks et. al., 1973, Olayiwola, 1994).



$$\begin{array}{l} RCOOCH_2 \\ RCOOCH \\ RCOOCH_2 \\ \text{(fat/oil)} \end{array} + \underset{\text{(base or alkali)}}{3NaOH} \longrightarrow \underset{\text{(soap)}}{3RCOONa} + \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \\ \text{glycerol} \end{array}$$

cyclization and esterification at the double bonds (Paulose et. al., 1978). Thus, molecular distillation is employed in the isolation of some highly unsaturated fatty acids and is particularly valuable in polymer studies to separate monomeric, dimeric and polymeric materials (Selke et. al., 1977).

2.12.2 Crystallisation

Crystallisation is another classical procedure used to separate fatty acids. In general, solubility decreases with increasing chain length and increases with increasing unsaturation (Hilditch, 1964). Furthermore, solubility is affected by the position of double bonds and by their configuration, trans-acids are less soluble than cis-isomers and those with conjugated unsaturation are less soluble than their isomers with non-conjugated unsaturation (Hilditch, 1964). Most unsaturated acids are liquids or low-melting solids with high solubility in most solvents at ordinary temperatures which makes it easy for them to be separated by crystallisation at subnormal temperatures or after conversion to some less soluble derivative from which the unsaturated acids are easily generated (Hilditch, 1964; Gunstone, 1967). These treatments include:

i) Crystallisation of lead salts

This provides a satisfactory method of separating saturated and unsaturated acids when only C_{16} and C_{18} members are present (Simpson, 1975). In one standard procedure, a mixture of fatty acids and lead acetate is crystallized from 95% ethanol containing a little acetic acid (1.5%), the crystalline lead salts are almost solely saturated and the mother liquor consists almost solely of salts of unsaturated acids, both of which can be regenerated from the salts by reacting with mineral acids (Simpson et. al., 1977). A reasonable amount of each group of acids is separated in this way.

ii) Crystallisation of lithium salts

When mixtures of fatty acids and lithium hydroxide in 95% acetone are crystallised, the salts of .saturated and monoethenoid acids separate and the salts of polyethenoid acids remain in solution (Hilditch, 1964; Gunstone, 1967). This method is used mainly to separate highly unsaturated oils such as fish oils rich in poly-unsaturated acids (Ackman, 1974).

iii) Low temperature crystallisation

This method was developed by J.B. Brown in 1935 and has been used since then in laboratories and industries (Hilditch, 1964). The method employed temperatures as low as -70°C which makes it possible to crystallise very soluble acids which may be liquid at room temperature (Hilditch, 1964; Simpson et. al., 1977). This method has several advantages because it is a non-chemical procedure, effected at low temperatures, which can be applied safely to the highly unsaturated acids which oxidize and polymerise so easily (Simpson et. al., 1977). In addition, given a suitable refrigerant such as solid carbon dioxide, the procedure is simple, direct and readily adaptable, for by suitable modification of solvent and temperature, any number of fractions can be collected, especially as saturated, monoethenoid and ployethenoid acids (Hilditch, 1964; Gunstone, 1967).

However, the efficiency of separation is subject to three limiting factors and separation is not always complete, as dissolved acids act as excellent solvents for those which should crystallise, cooled solutions come to equilibrium very slowly and must be held at the crystallising temperature for several hours, complete separation of mother liquor from crystals is incomplete even after thorough washing with cold solvent (Gunstone, 1967).

This method has been widely employed and is still used in industry with such solvents as methanol, ether, petroleum ether and acetone, usually at a dilution of 10 cm^3 of solvent per gram of acids. Separation of saturated and monoethenoid acids from one another and from polyethenoid acids is good, separation of polythenoid acids from one another is less satisfactory (Hilditch, 1964; Gunstone, 1967).

2.12.3 Urea fractionation

Pure urea normally crystallizes in tetragonal form, but in the presence of certain aliphatic compounds, it forms hexagonal prisms containing some of the aliphatic compounds(Simpson et. al., 1975) These crystals are built up from urea as six molecules forming a unit cell of 11.1 A° long and 8.2 A° in diameter and contain a channel in which an aliphatic molecule may be found so long as it fulfils certain dimensional qualifications, it must not be too short or it will not be held within the channel, and it must not be too wide if it is to fit into the free space, variously estimated at between 4.0 and 6 A° (Simpson et. al., 1977). Many straight chain fatty acids and their derivatives satisfy these conditions and thus readily form complexes or inclusion compounds with urea (Gunstone, 1967; Simpson et. al., 1977).

Accordingly, saturated fatty acids form soluble complexes more readily than the unsaturated acids and oleic acid enters into these inclusion compounds more readily than do the poly unsaturated acids (Gunstone, 1967). In practice, mixed fatty acids or esters are dissolved in methanol and treated with varying amounts of urea and subsequently cooled to room temperature or below. However, the amount of urea consumed is three times the weight of the fatty acids treated (Hilditch, 1964). The complexes formed are readily decomposed on addition of warm water to regenerate the fatty acids. Thus by this method,

separation of saturated fatty acids, followed by monoethenoid acids and lastly polyethenoid acids are achieved in that order, just as in the case of low-temperature crystallisation of fatty acids or their lead and lithium salts (Hilditch, 1964; Gunstone, 1967; Simpson et. al., 1977).

2.12.4 Chromatographic methods

The most important advances in separation procedure are concerned with chromatographic methods which can be classified according to whether adsorption or partition is the major factor in separation; whether separation is effected in a column, thin film or layer or on the adsorbents and solvents used (Stahl, 1990). Most of those procedures extensively used to separate fatty acids and their simple derivatives include partition chromatography on columns, paper chromatography, thin layer chromatography, gas liquid chromatography which have been described (Pecsok et. al., 1976; Meiboom et. al., 1979; Stahl, 1990).

Having mentioned the various methods of separating individual fatty acids either pure or as their derivatives, the determination of their chemical nature, that is knowing the number and position of functional groups becomes expedient.

2.13 Methods of structure determination

Before a fatty acid of unknown structure can be identified, it must be isolated in pure state or at least in highly concentrated form, by one or other of methods just described above (Stahl, 1990). Gas liquid chromatography will almost certainly be used in conjunction with other isolation procedures and the carbon number one or more stationary phases will provide useful structural information. It may be possible to discover the chain length, the extent of unsaturation, the relative position of double bonds and the presence and nature of additional functional groups, but new fatty acids cannot usually be identified by gas liquid

chromatography alone. Other physical and chemical evidence is required (Jack et. al., 1975; Kemp, 1991).

In common with other groups of natural products, physical methods of structural identification have become increasingly important, as chemical investigations are relatively becoming less important (Pecsok et. al., 1976; Raie, 1976). These physical methods include: infra-red spectroscopy, nuclear magnetic resonance spectroscopy, X-ray crystallography, mass specstroscopy, ultra-violet spectroscopy among others (Kemp, 1991). Some of these are described below especially those that are concerned with fatty acids.

2.13.1 Infra-red spectroscopy

Infra-red spectroscopy is of particular value in the recognition of usual functional groups and in the study of fatty acids with trans double bonds (Hamilton et. al., 1980). This method has been used to recognise certain functional groups in most oils containing usual mixtures of saturated and unsaturated acids (Seyd, 1976). Such functional groups as OH, -COOH, NH_2, $CONH_2$ et certra, absorption characteristics are shown in Appendices I and J.

Appendices I and J indicate absorption frequencies of some functional groups found in fatty acids and their derivatives. However these frequencies are not absolute as they are affected by other parameters such as H-bonding, neighbouring groups, vibrational couplings, molecular associations, conjugation of multiple bonds, and the solvents in which these samples are dissolved (Richardson et. al., 1974). For instance, H-bonding and other molecular association, conjugation tend to lower vibrational frequencies especially for

alcohols, carboxylic acids and diene, triene conjugated acids in that order (Pecsok et. al., 1976).

2.13.2 Nuclear magnetic resonance spectroscopy (NMR)

This is one of the most versatile methods of structural determination that distinguishes hydrogen atoms in different environments, both qualitatively and quantitatively (Hamilton et. al., 1980). For instance, the spectrum of methyl stearate ($C_{17}H_{35}COOCH_3$) shows four peaks corresponding to hydrogen nuclei in the end methyl group, the ester methyl group and the methylene group adjacent to the carbonyl and all other methylene groups (Medsen, 1976). Further details are described in Pecsok et. al., 1976; Robertson et. al., 1979, in which other methods such as mass spectroscopy, electron spin resonance are discussed. Furthermore, any method so chosen depends on the information required and the accuracy, sensitivity and precision of the procedure for the determination (Selke et. al., 1977).

2.14 Chemical reactions of fatty acids

Fatty acids like their parent triglycerides undergo chemical reactions through their basic functional groups; -COOH, -C=C- and OH groups where present (Naughton, 1974). The products of these reactions have useful application in the industry (Burgess, 1994). One of the very important reactions of fatty acids is polymerisation through the olefinic double bonds to form dimers, trimers, tetramers and so on depending on the reaction conditions (Nelson et. al., 1975).

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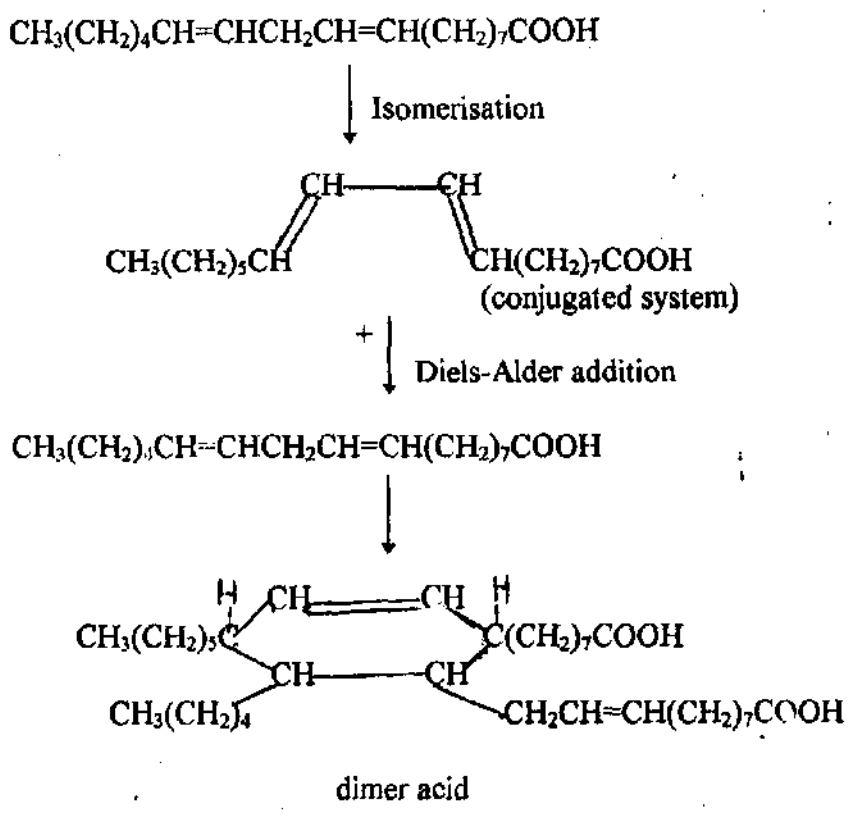
2.14.1 Polymerisation (dimerisation) of fatty acids

The treatment of fatty acids or oils especially the ones containing high degree of unsaturation with a catalyst at 220°C gives dimer and trimer acids (Nelson et. al., 1975). The catalysts usually employed are clay catalysts such as bentonite and BF_3 and certain organo-metallic compounds (Pryme, 1975; Ault, 1975).

The dimer acid is a cyclic dicarboxylic acid having a total of 36 carbon atoms if the reaction is with the C_{18} unsaturated fatty acids, while the trimer acid is a tricarboxylic acid having a total of 54 carbon atoms (Peerman, 1969; Terill et. al., 1975).

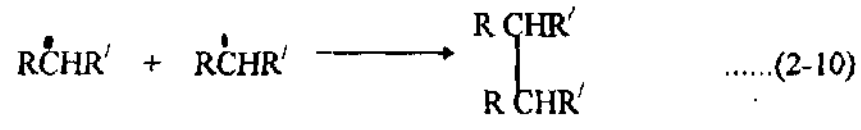
Various theories and mechanisms have been put forward for the formation of these acids among which are the following;

i) The acids may be formed by isomerisation of two double bonds in linoleic acid to a conjugated system followed by a Diels-Alder addition to an isolated double bond of a second fatty acid molecule to produce a tetra-substituted cyclohexene (dimer) (Cowan, 1962; Nelson et. al., 1975; Bellamy, 1974).



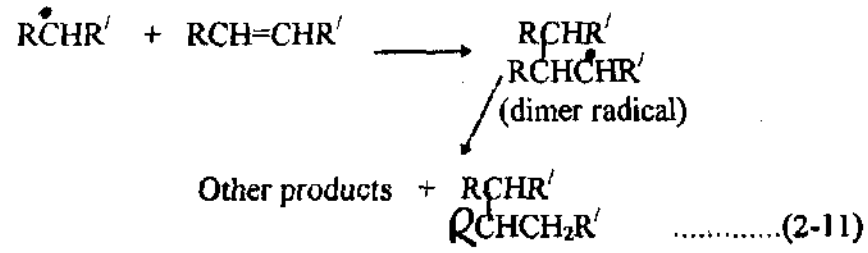
dimer acid

ii) These dimers can also be formed by union of two radicals to give non-cyclic dimer (Cowan, 1962; Gunstone, 1967).



.....(2-10)

iii) They can also be formed by addition of a free radical to a double bond to give a dimeric radical which stabilises itself by hydrogen abstraction from another molecule or by disproportionation (Nelson et. al., 1975). Furthermore, intramolecular cyclization can presumably occur by the operation of the second (ii) or third (iii) process (Gunstone, 1967; Bellamy, 1974).

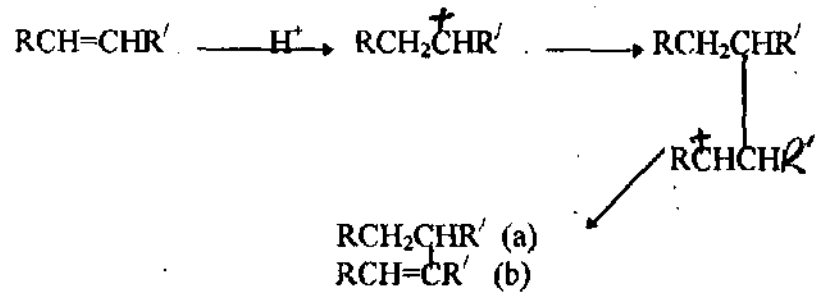


.....(2-11)

R′ = Part that contains -COOH group
R = Hydrocarbon part of the fatty acid chain.

iv) The polar reaction in which such catalysts as BF_3 and HF have been employed (Kohlhase et. al., 1977). The reaction presumably proceeds via carbonium ion intermediate to the products (equation 2-12, Gunstone, 1967). According to current theory, the carbonium ion would probably undergo prototropic change so that the linkage in the (a) part of the molecule below would not be restricted in C-9 and C-10 in the case of oleic rich oil (Gunstone, 1967) as shown in equation (2-12) below.

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In considering these reactions, one has to distinguish those polymerisations which occur through the agency of heat alone, those in which air is present and oxidation plays a dominant role and those which occur under the influence of radical or polar catalysts (Gunstone, 1967). In addition, certain clays such as bentonite can also introduce the above reactions (2-9) - (2-12) as it acts both as a dehydrogenating and isomerisation catalyst, however, the exact mechanism has not been established (Gunstone, 1967; Pryme, 1975).

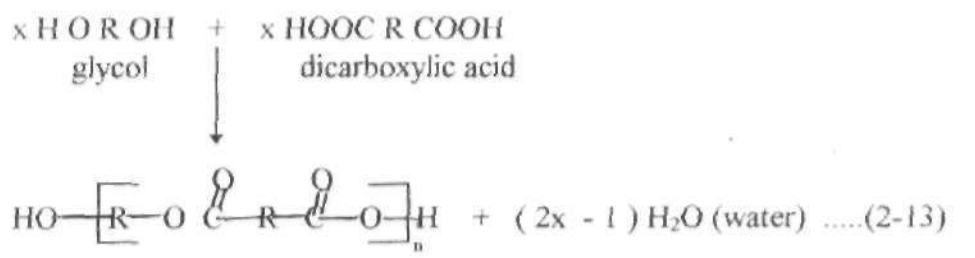
Generally, these reactions occur with increases in viscosity until a clear thick liquid is formed (Cowan, 1962). This readily observable change is accompanied by a decrease in iodine value and increases in density, refractive index, average molecular weight, and more often, for poly unsaturated fatty acids reactions as in equation (2-9), there is an increase in the content of conjugation (Ault, 1975; Turill et. al., 1975). Thus such parameters as iodine value, viscosity, refractive index can be used to monitor these reactions, since polymerised fatty acids or oils are used in variety of applications such as surface coating formulations, lubricants among others (Richardson et. al., 1974).

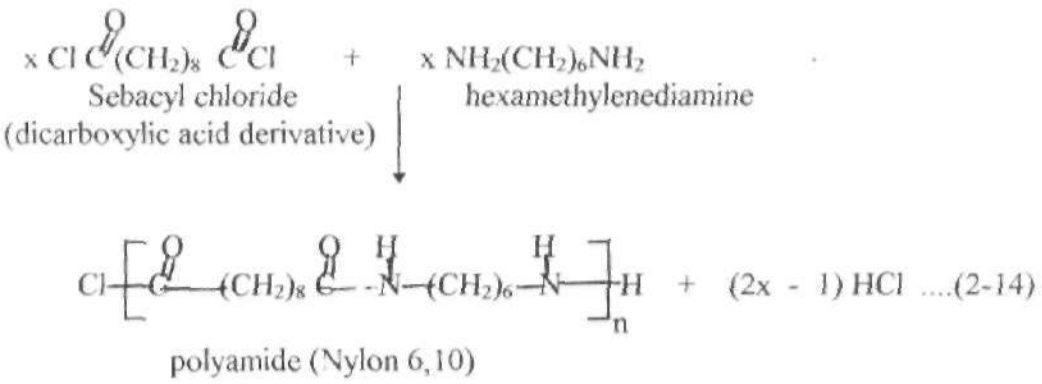
2.15 Polymerisation mechanisms

There are basically three mechanisms through which polymers are synthesised. These include the following, polycondensation, addition polymerisation and co-ordination polymerisation (Cowie, 1973; Billmeyer, 1984).

2.15.1 Condensation polymerisation

This became established by the works of the Carother brothers in 1929, in which polymers are prepared by step-wise condensation reactions of monomers (Dyson, 1992; Hill, 1992). The resulting molecular formula of the repeat unit of the polymer lacks certain atoms present in the monomers from which it was formed (Dyson, 1992; Hill, 1992). For instance, the formation of a polyester from a glycol and dicarboxylic acid and a polyamide formed from a reaction of a diamine and dicarboxylic acid are cases in point (Collins et. al., 1973). However, there are certain condensation reactions in which no simple molecule is released, for instance, the urethane reaction (Billmeyer, 1984).





where x and n are integers. In the above two examples, water and HCl are eliminated from the reaction mixture, typically in polyamide and polyester formation (Bodor, 1991).

2.15.2 Addition polymerisation

In this mechanism, the loss of a small molecule does not take place. The most important group of addition polymers are those derived from unsaturated vinyl monomers (Cowie, 1973). For instance, poly(ethylene), poly(vinyl) chloride and so on which are polymers formed from different mechanisms from polycondensation (Cowie, 1973).

The mechanisms of addition polymerisations include; free radical, ionic and co-ordination polymerisation which have been discussed in details by Cowie, 1973, Collins et. al., 1973, Rabeks, 1980, Billmeyer, 1984, Bodor, 1991. Furthermore, all the modes of polymerisation mechanisms have different reaction kinetics, however, the stages of initiation, propagation and termination are the same (Dyson, 1992). In this regard, kinetics of polycondensation is discussed below for the concern of this research.

2.16 Kinetics of polycondensation

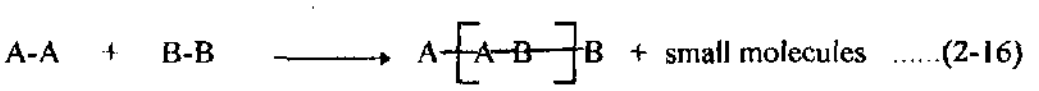
The kinetics of polycondensation reactions follow the same general scheme but differ sharply from the kinetics of free radical polymerisation in which the propagation stage proceeds by a chain reaction mechanism initiated by a single active radical or ion (Billmeyer, 1984). The treatment of kinetics of polycondensation is the same as those of the simple condensation reactions of simple organic molecules (Cowie, 1973; Billmeyer, 1984). Furthermore, a condensation becomes a polycondensation when the functionality (the average number of functional groups per molecule of the reactants equals or exceeds two).

For instance, the functionality of the reaction of a diacid/dimer and a diamine (equations 2-13 and 2-14) is given by equation (2-15) (Cowie, 1973).

$$\text{Functionality} = \frac{½(2) + ½(2)}{1} = \frac{2}{1} \quad \text{or} \quad \frac{0.5(2) + 0.5(2)}{1} = \frac{2}{1} \qquad \text{.....(2-15)}$$

Where (0.5) represents the number of moles of reactants and (2) represents the functional groups on the comers and (1) is the total number of moles (0.5 + 0.5) in the system (Cowie, 1973). Therefore the functionality is 2.

The kinetics of polycondensation became established by the work ofCarother brothers in which the concept of functional group reactivity is considered independent of the molecular weight (Collins et. al., 1973; Cowie, 1973). Thus the formation of polyesters, polyamides, polyurethanes may be taken as examples. Accordingly, considering an A-A and B-B systems for diacid and diamine respectively (equations 2-13; 2-14). where the two polyfunctional monomers taking part in the reaction each possessing only one distinct type of functional groups, the model below is used (Cowie, 1973; Bodor, 1991).



.....(2-16)

Let us consider the Carothers equation which relates the number average chain length (Xn) (or the degree of polymerisation (Dp)) to the extent of reaction (p). Let N_o be the number of molecules (functional groups) originally present in the system. Therefore considering an A-B system, let N' be the number of functional groups remaining after time t. The difference $N_o - N'$ equals to the total number of functional groups that have reacted

after time t (Cowie, 1973; Rabeks, 1980). Thus the extent of reaction (p) or percentage conversion is given by

$$p = \frac{N_o - N'}{N_o} \text{ and } N' = N_o(1 - p) \qquad \text{.....(2-17)}$$

It then follows that

$$Xn(DP) = \frac{N_o}{N'} = \frac{1}{(1-p)} \qquad \text{.....(2-18)}$$

Similarly, $$\bar{Mn} = \frac{M_o}{1-P} = M_o DP \qquad \text{.....(2-19)}$$

where p = Extent of reaction or percentage conversion

N_o = Number of molecules (functional groups) originally present)

N' = number of molecules (functional groups remaining after time t)

Xn(DP) = Degree of polymerisation or number average chain length

Mn = Number average molar mass

M_o = Mass of repeat unit

The reaction between a diacid and diamine or diol is catalysed by acids (Cowie, 1973). In the absence of added strong acid, a second molecule of the acid acts as a catalyst (Cowie, 1973). Accordingly, in the non-catalysed system, the rate of condensation equals to the rate of disappearance of carboxyl functional groups which can be monitored titrimetrically as a function of time t (Cowie, 1973; Collins et. al., 1973). Hence a rate law is proposed as follows,

$$-\frac{d[COOH]}{dt} = k[COOH]^2[NH_2] \qquad \text{.....(2-20)}$$

k = rate constant

Generally, stepwise polymerisation typically involves equilibrium reaction of the type (Billmeyer, 1984).

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D \qquad \text{.....(2-21)}$$

where rates of the forward and reverse reactions are $k_f[A][B]$ and $k_r[C][D]$ respectively (Billmeyer, 1984). At equilibrium, these rates are equal;

$$\text{where } K = \frac{k_r}{k_f} = \frac{[C][D]}{[A][B]} \qquad \text{.....(2-22)}$$

If the system is far from equilibrium as in the initial stages of polymerisation, the reverse reaction is negligibly slow and changes in the concentrations of the reactants may be considered to result from the forward reaction alone as in equation (2-20) above (Cowie, 1973). Since the reaction is stoichiometric, the concentrations of carboxyl and amino groups are equal, (Cowie, 1973), hence equation (2-20) becomes

$$-\frac{dC}{dt} = kC^3 \quad , \text{ C = concentration} \qquad \text{.....(2-23)}$$

Thus integrating equation (2-23) becomes

$$kt = -\left[\frac{C^{-2}}{-2}\right]_{C_0}^{C} \qquad \text{.....(2-23b)}$$

hence

$$2kt = \frac{1}{C^2} - \frac{1}{C_0^2} \qquad \text{.....(2--23c)}$$

where C = concentration at time t

C_0 = initial concentration

Therefore, introducing the extent of reaction (p) from equation (2-17) into equation (2-23c), noting that,

$$p = \frac{N_o - N'}{N_0} = \frac{C_0 - C}{C_0} \qquad \text{.....(2-24)}$$

and

$$N' = N_0(1 - p) = C = C_0(1 - p) \qquad \text{.....(2-24b)}$$

hence, substituting C from equation (2-24b) into equation (2-23c) and rearranging becomes:

$$2C_0^2kt = \frac{1}{(1-P)^2} - 1 \qquad \text{.....(2-25)}$$

Rearranging,

$$\boxed{\frac{1}{(1-p)^2} = 2C_0^2kt + 1} \qquad \text{.....(2-26)}$$

A plot of $\frac{1}{(1-p)^2}$ *vs* t gives a straight line graph with intercept = 1 and slope = $2C_0^2k$.

Equation (2-26) is the Carother's equation for a non-catalysed polycondensation (Cowie, 1973; Collins et. al, 1973 Billmeyer, 1984).).

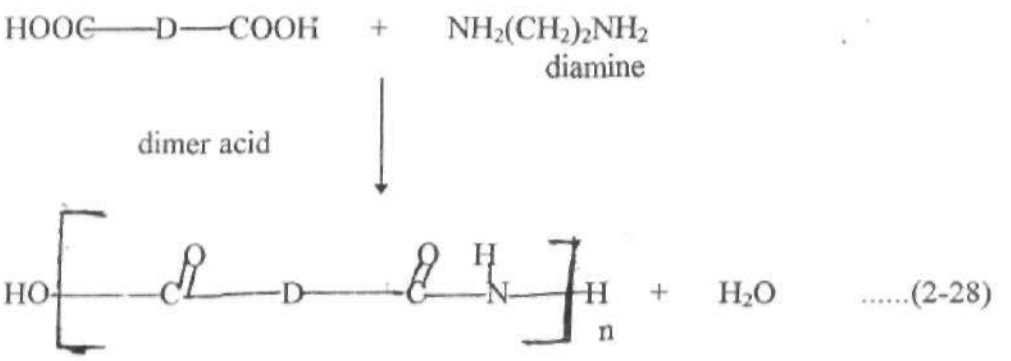
If only bifunctional reactants are present and no side reactions occur, the number of unreacted carboxyl groups equals the total number of molecules N in the system (Billmeyer, 1984). If acid or amino groups separately (not in pairs), are defined as structural units, the initial number of carboxyl groups present is equal to the total number N_0 of structural units

iv) Emulsion polymerisation; the system include water emulsifier initiator, buffer and monomer. Mild is agitation is needed and the latex formed is spray-dried to give the polymer (Bodor, 1991). The initiator must be soluble in water and the buffer serves to control the pH of the emulsion formed (Bodor, 1991). The polymer formed are ultimate powder sizes (McCafery, 1970; Bodor, 1991).

In all, polymer purity is in the order Bulk > Suspension > Solution > Emulsion (Cowie, 1973). In any . case, most polycondensation reactions employ the bulk technique especially for such polymers as polyamides and polyesters (Collins et. al., 1973).

2.18 Fatty acid polyamides

Fatty acid polyamides are condensation products of di- or polyfunctional amines and di- or polybasic acids by the polymerisation of unsaturated vegetable oil fatty acids or their esters (Billmeyer, 1984). Unlike the nylons which are prepared from well characterised chemical entities (equation 2-14), the fatty acid polyamides start with a prepolymerisation of the unsaturated fatty acids to produce what are termed "dimers" (section 2.14.1; equations 2-9 - 2-12; Richardson et. al., 1974). These polybasic acids or "dimers" are actually mixtures of materials, mainly dibasic acids (dimers) and other mono and poly-basic fractions (Perman, 1969). The fatty acid polyamides derived their distinctive physical properties from the dimer acids used in their production (Perman, 1969; Richardson et. al., 1974)



(2-28)

D = Hydrocarbon chain residue of the dimer acid

Their reactions with ethylenediamine gives low-molecular weight, film forming thermoplastics which are materials that form high-gloss, flexible films with good adhesion, weatherability and impact strength (Billmeyer, 1984).

In addition to the simple polyamides from the condensation of the polymerised vegetable oil fatty acids and simple di or polyamines, many copolymers are possible (Richardson et. al., 1974). The properties of the polyamides are modified by adding other dibasic or mono-basic acids to the dimer acids (Sumrell et. al., 1978). Similarly, diamines, polyamines and amino-alcohols are used to modify the character of the polyamides (Sumrell, 1978). The amide copolymers thus produced are not easily represented structurally, however, the dimer acid is represented as, HOOC -D- COOH, the -D- between the carboxylic groups represents a C34 divalent radical or there about (Peerman, 1969).

Furthermore, compared with the conventional nylons, the fatty polyamides are more soluble in lower alcohols, are lower in melting point, non-structural and have lower average molecular weights, as well as a greater compatibilty with other chemicals, resins and other modifiers and greater flexibility (Chang et. al., 1975). It has been observed through X-ray spectroscopic data that fatty acid polyamides have very low order of crystallinity compared with the nylons (Simpson et.al., 1975). This can be explained on the basis of their structures, the nylons are linear condensation polymers which can easily pack into their crystal lattices, while the conformation of the fatty acid dimers does not favour easy packing as the cis-formation is dominant (Taylor et. al., 1973). Thus the nylons are drawn into fibres while the fatty acid polyamides are essentially resinous.

The progress of the polyamide formation can be monitored by the measurement of acid or amine numbers, changes in viscosity, refractive index and the amount of water eliminated (equation 2-28; Mccafery, 1970). From these changes, other parameters such as extent of reaction and degree of polymerisation can be determined (equations 2-24 - 2-27).

The low molecular weights of these polymers favour their applications in areas in which low viscosity, high solubility and easy application, such as hot-melts are required, since viscosity rather molecular weight is the more useful criterion in adhesives, coatings and other applications, it is more of practical significance than molecular weight (Peerman, 1969).

2.19 Uses of fatty acid polyamides

As mentioned above, these polymers are used in the formulation of surface coatings, such as lacquers, vanishes, thixotrophic paints in addition to their thermoplastic, lubricant and adhesive uses (Billmeyer, 1984; George, 1984). However, the lower molecular weight products which are liquids at room temperature serve as curing agents for epoxy resins (Billmeyer, 1984).

Coating or impregnation of surfaces serve to cover surface imperfections, aesthetic appeal, durability of the article, thereby adding value and beauty to the material (Sarkar, 1991). Thus, such formulations as lacquers, varnishes, latex system and paints among others serve these functions (Morgan, 1980). Furthermore, a coating formulation must certainly have the following basic properties; adhesion, film forming properties, flexibility and durability (Thorstensen, 1993).

Adhesion of a coat onto a surface of a substrate is dependent upon the condition of the substrate such that when a coat is applied it should stick; for this reason the substrate surface must be "wettable" (Thorstenten, 1993). Similarly, the coat so applied must be flexible to withstand flexing, as coats that do not have good adhesion and flexibility will peel and crack (George, 1984). Therefore the choice of resins and other materials is dependent to a great extent on the intended use of the substrate (Billmeyer, 1984; Sharphouse, 1989; Eckhart, 1993).

Substrates may be exposed to extreme environmental conditions such as temperature, heat and so on, hence the film must have a wide range of temperature over which it is soft and pliable and it must also be hard enough to maintain the high gloss which is required (Thorstensen, 1993). Furthermore, the polyamide resins has self plasticizing effects with good water proofness properties in addition to making the substrate to stand up to a reasonable amount of both wet and dry abrasion (Eckhart, 1993; Burgess, 1994). Consequently, some of these coating systems are discussed in brief below.

2.19.1 Lacquer systems

The formation of a film in a lacquer system is based on the evaporation of the solvent containing a film forming material (George, 1984). For instance dissolving a fatty acid polyamide in alcohol or spirit and applying this to a surface either by spraying or brushing, as the solvent evaporates, a thin film is formed on the substrate surface giving high gloss and beauty (George, 1984; Billmeyer, 1984). Other lacquer systems include shellac, nitrocellulose, et certra (Sharphouse, 1989).

2.19.2 Drying oil system (varnishes)

Natural drying oils such as linseed and tung oils and any material, which undergoes polymerisation upon drying to form films are called varnishes (Thorstensen, 1993). A varnish is therefore different from a lacquer system in that setting up (curing) of the film is not simply a deposition of high molecular weight material, rather it is a chemical reaction taking place between the dissolved film forming materials and atmospheric oxygen (Morgan, 1982). Other film forming materials include condensation and latex system (Sarkar, 1991; Eckhart, 1993).

2.19.3 Review of reported work

A number of work on the synthesis of vegetable oil polyamides from dimer acids as curing agents for liquid epoxy resins and fo. protective coatings have been reported (Richardson et. al., 1974). Another type of fatty acid dimer acid has been described that depends upon cationic copolymerisation of a conjugated fatty esters with styrene which may be used for producing polyamide resins (Nelson et.al., 1975).

Several publications describe the analyses of polymerised fatty acids in which dimer acids and mono-acids ratios are determined by GLC and mass spectrometry (Hase et. al., 1974).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Sample collection

i) Palm oil:- This was purchased at Kwararafa market in Jos, Plateau State

ii) Palm kernel oil:- This was purchased at Katako market in Jos, Plateau State

iii) Castor oil:- The seeds were purchased from Korai and Tundun Sarki villages of Jama'a District, near Samaru-Zaria. The seeds were ground and extracted with n-hexane to give an oil yield of about 45%.

3.2 Physical characterisation of the oils

The oils were vacuum filtered at 35 °C after which their specific gravities, refractive indices were determined respectively using the expressions:

$$\frac{W_2 - W_0}{W_1 - W_0} \quad \text{and} \quad \frac{\sin i}{\sin r}$$

where W_2 = weight of density bottle filled with oil

W_1 = weight of density bottle filled with water

W_0 = weight of empty dry density bottle

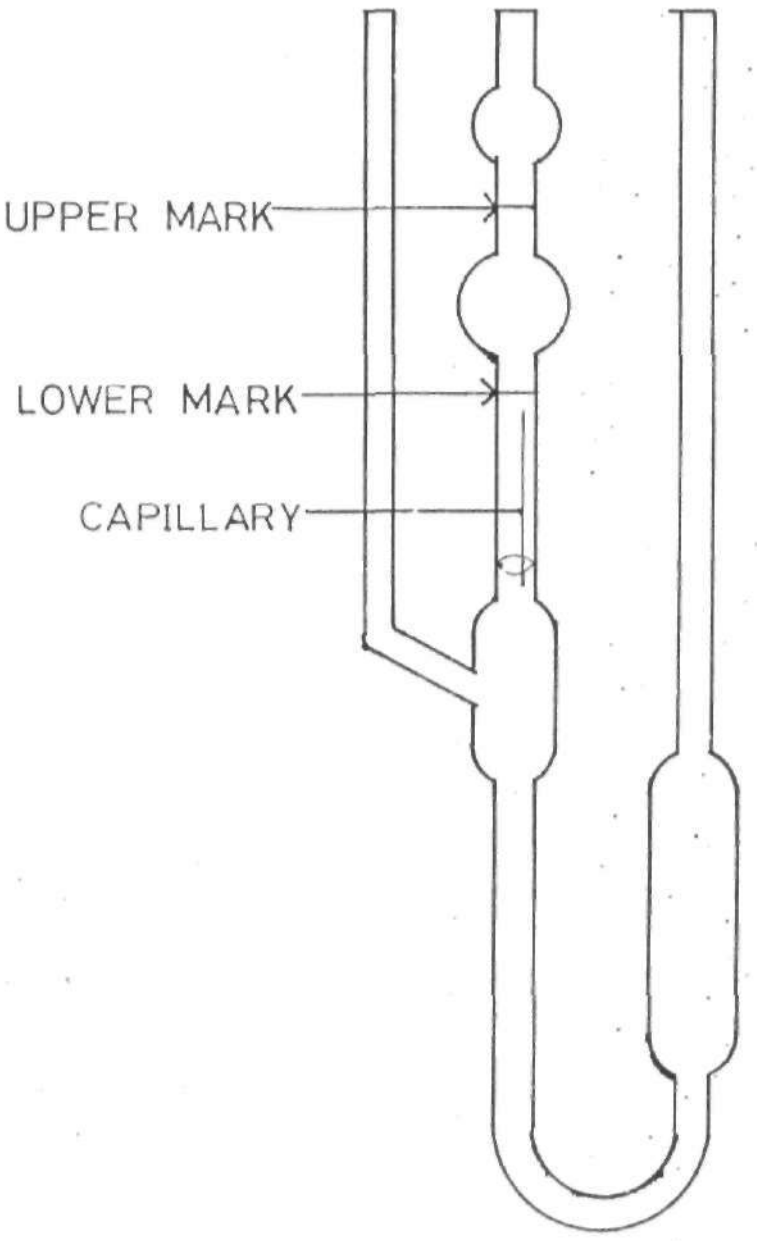
i = incidence angle

r = angle of refraction

3.2.1 Relative viscosities of the oils

The Ubbelohde viscometer was employed in this measurement (Fig. 3.1) which was done in a water bath at 30 °C. Toluene was employed as the solvent and the procedure of Collins et. al., 1973 was used.

Fig 3·1 UBBELOHDE VISCOMETER



3.3 Chemical characterisation of the oils

The acid values, saponification and iodine values were determined according to the methods of Cocks et. al., 1973.

3..3.1 Acid values of the oils

Method: About 3.0 g of the oil in each case was weighed into a 250 cm^3 conical flask and 40 cm^3 of mixed solvent (2 parts benzene and 1 part ethanol vol/vol) was added. This was warned on a water bath to dissolve. It was cooled and titrated rapidly with 0.1 M ethanolic KOH to phenolphthalein end point. Similarly, a blank titration (without oil sample) was concurrently run. The acid values were calculated from the expression;

$$\text{Acid value} = \frac{56.1 \times M(a-b)}{W}$$

From the above expression, the free fatty acid percentage (% ffa) were determined by

$$\%\ \text{ffa} = \frac{56.1 \times M(a-b)M_f \times 100}{W \times 1000}$$

where a = volume of KOH (in cm^3) for blank

b = volume of KOH (in cm^3) for test

M = molarity of KOH

W = weight of oil sample (g)

M_f = 2.82, factor based on oleic acid.

KASH...

3.3.2 Saponification values of the oils

Method:- About 4.0 g of the oil in each case was weighed into a conical flask and 50 cm^3 of 0.5 M ethanolic KOH was added and 4 drops (2 cm^3) of phenolphthalein indicator were added. The mixture was refluxed for about 40 minutes after which it was titrated rapidly

with 0.5 M HCl to a colourless end point. A blank titration was also concurrently run. The saponification values were calculated by the following expression;

$$\text{Saponification value} = \frac{56.1 \; x \; M(V_2 - V_1)}{W}$$

where W = weight of oil sample (g)

V_1 = volume (cm^3) HCl used in test

V_2 = volume (cm^3) HCl used in blank

M = molarity of HCl

3.3.3. Iodine values of the oils

Reagents

Hanus reagent:- This was prepared by dissolving 13 g of iodine and 8 g of bromine with glacial acetic acid in a 1-litre volumetric flask, making it to the mark. The solution was stored in an amber coloured bottle. 10% KI solution was prepared by dissolving 10 g of KI with distilled water and making up to the mark in a 100 cm^3 volumetric flask. 0.1 M $N_2S_2O_3.5H_2O$ solution was prepared by dissolving 24.808 g of the thiosulphate with distilled water in a 1-litre volumetric flask and making it to the mark and stored in an amber coloured bottle. 2% (W/V) starch solution was prepared by dissolving 2 g of starch in 100 cm^3 solution. Chloroform:- Analytical grade reagent.

Oil quantities: Oil sample quantities were weighed according to their reported iodine values from literature (Cocks et. al., 1973; Appendix F). Accordingly, 0.4 g of castor oil, 0.8 g palm oil and 0.8 g of palm kernel oil were weighed.

Method:- To a weighed sample of an oil in a stoppered flask was added 10 cm^3 of chloroform with shaking to dissolve the oil. Next 25 cm^3 of Hanus reagent prepared was then added from a burette. A blank (without oil sample) was concurrently prepared. Both the test and the blank were allowed to stand in the dark (cupboard) for at least 1 hour to allow complete reaction between the double bonds of the oil and the liberated iodine (Cocks et. al., 1973; section 2.10.3) The excess of the liberated iodine was then titrated as follows; to the mixture were added 15 cm^3 of 10% aqueous KI solution and 50 cm^3 of distilled water. This was then titrated with 0.1 M $Na_2S_2O_3.5H_2O$ solution to a pale yellow colour and at this point, a few drops of 2% starch indicator solution was added. Meanwhile, the thiosulphate solution was added dropwise until the blue colour that developed on addition of indicator disappeared. The same treatment was given to the blank. The iodine values of the oils were calculated using the expression;

$$\text{Iodine value} = \frac{126.9 \times M(a-b) \times 100}{W \times 1000}$$

where 126.9 = molar mass of iodine

M = molarity of thiosulphate

a = volume (cm^3) of thiosulphate used for blank

b = volume (cm^3) of thiosulphate used for the test

100/1000 = multiplication factor as defined for iodine value

3.4 *Purification of the oils* (Swern et. al., 1964)

3.4.1 Alkaline refining

From the acid values of the oils calculated in section 3.3.1 and presented in Table 4.1, appropriate volume of lyes of sodium hydroxide were calculated using the expression;

$$\text{Volume of lye required in cm}^3 \text{ for 100 g of oil} = \frac{Acid\ \ value}{NaOH\ (g)}\ x\ 100$$

Based on the above formula and using the acid values of the oils (Table 4.1), the following lyes were selected whose strength are expressed in terms of their specific gravity in degrees Baume at 15 °C.

18 °Baume (12.68% W/V NaOH) for palm oil

12 °Baume (8.0% W/V NaOH) for castor oil

10 °Baume (6.56% W/V NaOH) for palm kernel oil

Thus, 24.1 cm^3, 17.5 cm^3 and 4.3 cm^3 of the respective lyes were used for palm oil, castor oil and palm kernel oil in that order.

Method:- To 100 g of oil was added dropwise from a burette the appropriate volume of lye with constant agitation with one drop (0.5 cm^3) in excess to ensure complete removal of free fatty acids. This was subsequently boiled on a water bath for about 30 minutes with stirring. It was then allowed to stand overnight in the cold. The following day, it was observed that the soaps formed had settled at the bottom of the container and the supernatant (oil) was carefully decanted and washed several times with warm distilled water in a separating funnel, each time the aqueous layer was run off. This was done until all the traces of soap were completely removed to foamless aqueous layer. The oil layer was allowed to stand for about 6 hours to allow all traces of residual water to drain to the bottom. The water was drained off after decanting the oil. The oil recovered was weighed and the % loss in oil due to refining was calculated using the formula;

$$\text{\% loss in oil due to refining} = \frac{100 - yield\ in\ \%\ of\ neutralised\ oil}{\%\ ffa\ of\ crude\ oil}$$

3.4.2 Earth bleaching

Method:- A mixture of Fuller's earth and activated carbon in the ratio of 20 : 1 W/W was thoroughly mixed for the bleaching operations. Activated carbon is employed here because it is a better adsorbent than Fuller's earth, however, it introduces acidity to the neutral oil hence a limited amount is required (Cocks et. al., 1964).

Based on the initial colours of the oils, the following quantities of the bleaching mix were used.

palm oil; 10 % W/W of bleaching mix

castor oil; 5% W/W of bleaching mix

palm kernel oil; 5% W/W of bleaching mix

To 500 g of the alkaline refined oil was added an appropriate quantity of the bleaching mix and warmed over water bath with constant agitation for about 30 minutes. Thereafter, it was removed and allowed to cool sufficiently and filtered under vacuum through a sintered glass.

3.5 Alkaline saponification (hydrolysis) of the oils

3.5.1 Preparation of soaps of the oils

In order to strip the mixed fatty acids from the oils(triglycerides) (Appendix H), the soaps of the oils were prepared using 50% W/V NaOH solution. The quantity of NaOH solution added was obtained using the formula;

Volume (cm^3) of NaOH solution required for 100 g of oil =

$$\frac{Saponification\ value\ of\ oil}{Weight\ (g)\ of\ NaOH\ in\ solution} \times 100$$

Method:- To 500 g of oil was added the calculated amount of the 50% W/V NaOH solution dropwise from a burette with constant agitation. An excess of a drop (0.5 cm^3) was added to ensure complete saponification. Furthermore, the soap solution formed was warmed over a steam bath with stirring for about 30 minutes and thereafter kept overnight in cold to solidify and subsequently dried in the open.

3.6 Preparation of water-insoluble mixed fatty acids from the soaps

To 100 g of the soap prepared above was added 100 cm^3 of warm distilled water and the resulting solution was heated over water bath with constant stirring for 30 minutes. Then 20 cm^3 of concentrated HCl acid (density 1.18 g/cm^3) was added gradually and stepwisely with stirring until it gave an acidic pH (yellow colour) with universal indicator paper. There was instant fatty acid layer on top and the aqueous layer at the bottom (section 2.11.1). The aqueous layer contains glycerol and sodium salt (section 2.11.1).

The two layers were shakened in a separating funnel and allowed to stand after which the aqueous layer was drained off. Thereafter, warm distilled water was used to wash the fatty acid layer several times, each time the resulting aqueous layer was drained off, until it tested foamless and neutral to pH paper. The fatty acid layer was then allowed to stand for about 3 hours to ensure complete removal of residual water which was subsequently drained off. The pure fatty acid was recovered. The acid numbers (values) of the pure fatty acids were determined as before (section 3.3.1), from which the degrees of hydrolysis or stripping or conversions of soaps to fatty acids were calculated by the expression;

$$\text{Degree of conversion of soap to fatty acids} = \frac{\textit{Acid value of mixed fatty acids}}{\textit{Saponification value of the oil}} \times 100$$

3.7 Urea fractionation of mixed fatty acids

Commercial urea fertilizer purchased in Zaria was determined for its elemental composition and purity by the Institute of Agriculture Research Samaru-Zaria. Elemental analysis indicates;

Nitrogen (N)	=	46%
Carbon (C)	=	19.7%
Oxygen (O)	=	26.3%
Hydrogen (H)	=	6.6%
Total	=	98.6%

The difference may be due to water and other impurities. To this end, the urea was dried in an oven at 102 ± 2 °C and weighed at intervals of 1 hour to a constant weight to remove volatile matter and other impurities.

Method:- A mixing ratio of 3:3:1:1 proposed by Hilditch, 1964, of urea, water, methanol and mixed fatty acids in that order was employed as follows; 100 g of mixed fatty acids was dissolved in 100 cm^3 of methanol. Next, 300 g of urea was dissolved in 300 cm^3 of distilled water and warmed over water bath until a clear solution resulted which was filtered through a filter paper to remove any particulates present. The fatty acid solution prepared was then mixed with the urea solution and warmed over water bath with stirring for about 30 minutes to ensure complete solubilisation of the mixture.

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The mixture was removed and allowed to cool and later cooled under running water. It was subsequently transferred carefully into a one-litre separating funnel and corked. The body of the funnel was cooled under running water and later ice-block to aid crystalisation of urea (section 2.12.3). The funnel under this condition was allowed to stand for about 3 hours after which two distinct layers were observed with one more intense and cloudy. The two layers were run off seaprately into two different containers.

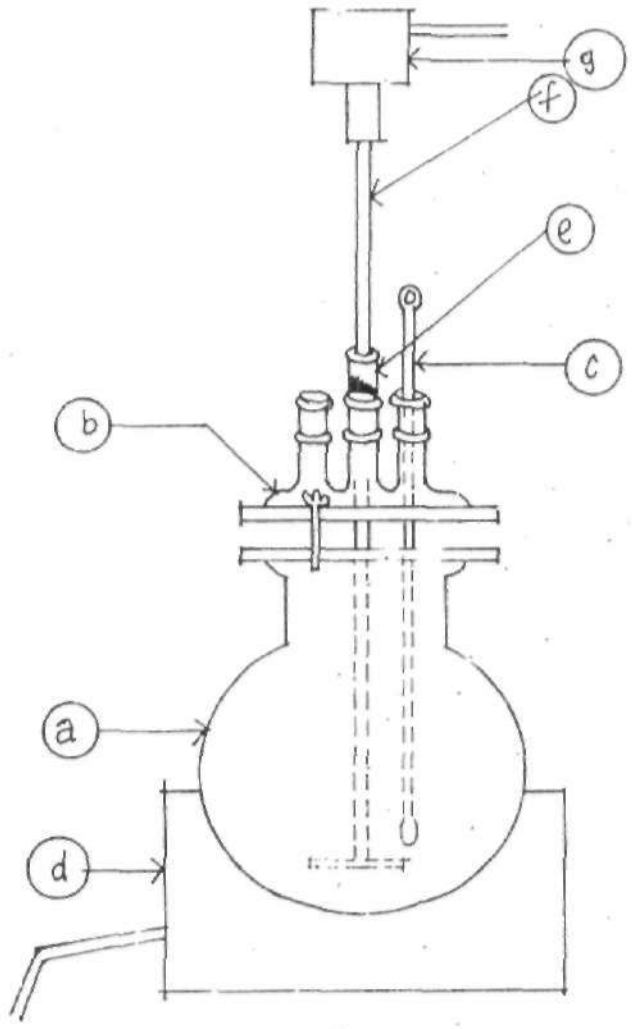
Accordingly, each of the layers was transferred to a 250 cm^3 separating funnel. They were then individually shakened with warm distilled water several times, each time, the aqueous layer was drained off to remove urea from the urea-fatty acid complex (section 2.12.3). The resulting fatty acid layers were left in the funnels for at least 30 minutes to 1 hour to drain off the residual water traces which were subsequently run off. The fatty acid layers were then transferred through the mouths of the funnels into two separate preweighed bottles and their weights determined by difference. The above process was repeated to get large quantity of each fraction.

From section 2.12.3, the lower layer of urea fraction composed of complexes of urea with saturated fatty acids while the upper layer contained the unsaturated fatty acid complexes fraction. The infra red spectral analysis of both the unsaturated fraction and the whole (mixed) fatty acids were done to ascertain the level of separation. Furthermore, the iodine values of the unsaturated fractions were determined as before (section 3.3.3).

3.8 preparation of fatty acid dimers

The principle and theory are stated in section 2.14.1. Unsaturated fatty acids were obtained from the urea fractionation of mixed fatty acids (section 3.6).

Fig 3·2 Set up for dimerisation reaction



KEY:

a Reaction kettle
b Reaction kettle top
c Thermometer
d Heating mantle
e Stirrer bushing (guard)
f Stainless steel stirrer
g Stirrer socket connection to a motor

Method - 200 g of the unsaturated fatty acids was charged into a reaction vessel coupled with a mechanical agitator, thermometer and condenser as shown in Fig. 3.2 above. 2 g of bentonite powdered clay (BDH chemical) catalyst was added and stirred properly. The resin kettle was then mounted over an oil-bath heated at a temperature of 220 - 230 °C. For effective cooling of the reflux system, the condenser was connected to a Churchill circulator that utilised glycerol as coolant.

The progress of the reaction was monitored right from the beginning by withdrawing aliquots at time intervals and determining the following characteristics:

i) Relative viscosities

ii) Iodine values

iii) Infra-red spectral analysis

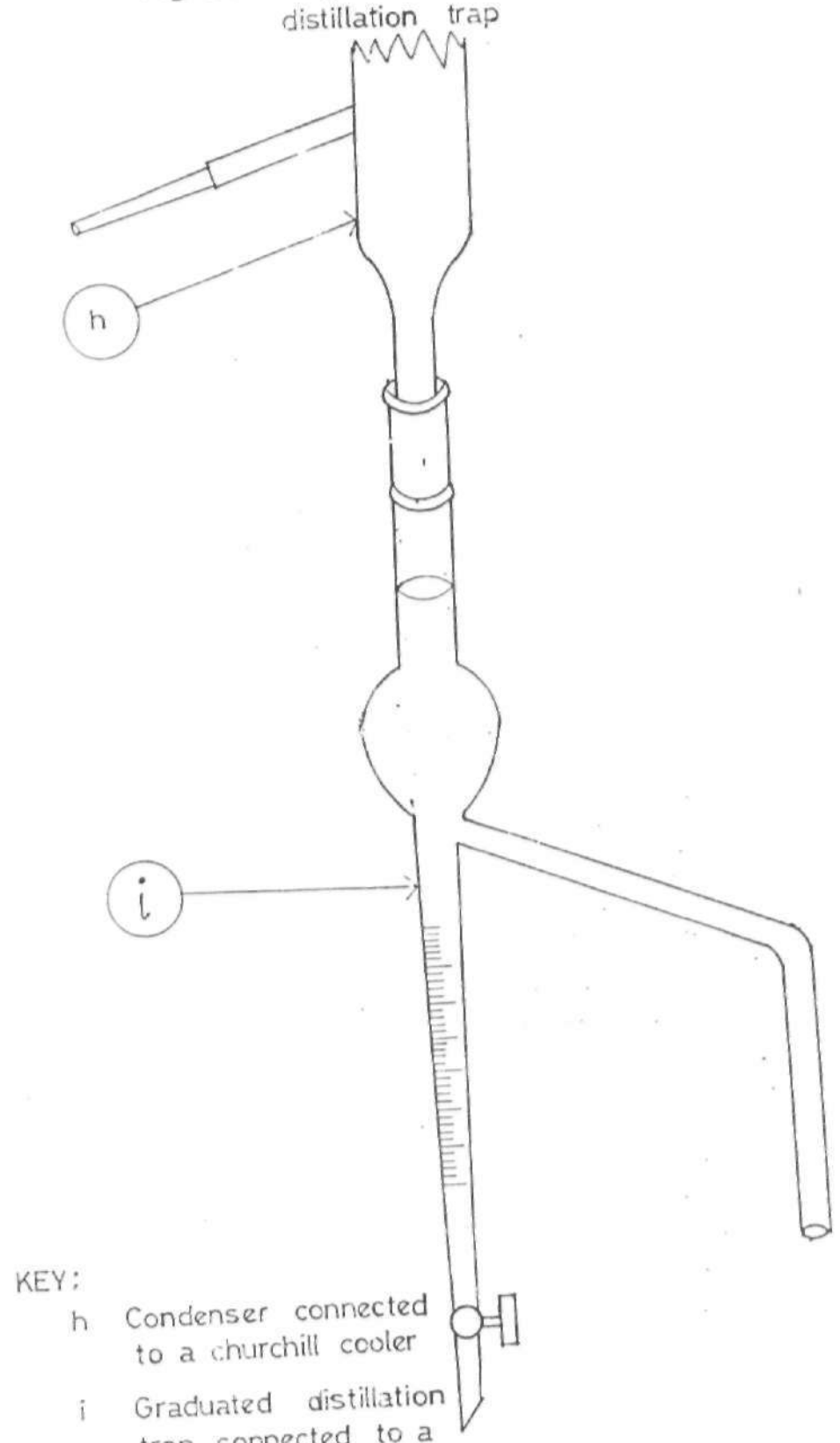
The reaction continued for about 4 hours and the above physical and chemical characteristics were determined just as in the case of the oils. The above steps were carried out on all samples of the unsaturated fatty acids of the three oils and the results recorded.

3.9 Preparation of fatty acid polyamides

Method:- Polycondensation through the bulk technique was employed (section 2.17) on the liquid dimer acids in section 3.8 and liquid monomer ethylenediamine (AR grade).

250 g of fatty acid dimers (0.5 mole, calculated based on the molecular weight of oleic dicarboxylic acid) was charged into a resin kettle equipped with accessories just as shown in Fig. 3.2, except that the position of the condenser was replaced with a graduated distillation trap (Fig. 3.3). However, the condenser this time topped the trap and connected

Fig 3·3 Diagram of graduated distillation trap



KEY:

h Condenser connected to a churchill cooler

i Graduated distillation trap connected to a kettle top and condenser

as described in section 3.8. The system was heated to a temperature of 200 °C with stirring for 5 minutes. Next, 33.5 cm^3 of ethylenediamines of density 0.902 g/cm^3 equivalent to 30 g (0.5 mole) was added through a dropping funnel and immediately a timer was started.

The progress of the reaction was monitored by the amount of water eliminated into the distillation trap (Fig. 3.3) and measurement of acid values as a function of time (sections 2.15, 2.18). About 2.0 g from aliquots withdrawn at time intervals of 10 minutes were dissolved in 10 cm^3 of chloroform and titrated with 0.8 M methanolic KOH to phenolphthalein end point. The reaction can be represented as

$$HOOC{-}D{-}COOH + \underset{\text{ethylenediamine}}{NH_2(CH_2)_2NH_2} \xrightarrow{200\ ^\circ C}$$

$$HOOC{-}D{-}\underset{\text{amide}}{CO\,N\,(CH_2)_2NH_2} + \underset{\text{water}}{H_2O}$$

$$\downarrow + KOH$$

$$KOOC{-}D{-}CO\,N\,(CH_2)_2NH_2 + H_2O$$

where D = fatty acid chain residue.

3.10 Characterisation of fatty acid compounds prepared in 3.9

3.10.1 Infra-red spectral studies

Samples of the fatty acid compounds were run neat on a Fourier Transform infra-red spectrophotometer. and such functional groups as OH, C=O, $CONH_2$ were correlated with those reported from literature (Appendices I and J).

3.10.2 Solubility tests

Solubility tests were carried out on the samples in such solvents as toluene, methanol, ethanol, water, benzene, chloroform, carbon tetrachloride, acetone and 1,1,1-trichloroethane at room temperature. The purpose of these tests is to ascertain the following;

i) If the fatty compounds were polymers, dissolution would occur in three stages; absorption of solvent molecules, swelling occurs and finally solution results if there are favourable solvent-polymer interactions (Olabisi et. al., 1979).

ii) Suitability, availability , cost implications or otherwise of these liquids as solvents for these fatty compounds in commercial and industrial applications.

3.10.3 Melting range

This was determined on a melting point apparatus.

3.11 Formulation of spray coats

To 10 g of polyamide sample was added 10 cm^3 of kerosene to dissolve. This was followed by 90 cm^3 of chloroform with vigorous agitation for complete dissolution. The resulting solution was filtered through a nylon cloth to remove suspended particles

3.12 Spray-coat trials on wood and leather surfaces

3.12.1 Preparation of surfaces

Plywood samples were cut into 4 x 4 cm of 3 cm thick. Their surfaces were sandpapered to give smooth grains. Similarly, leather samples (chrome retan shoe uppers) were cut into 4 x 4 cm of 1.6 mm thick and their grain surface smoothened on a hot-plating machine at 50°C.

3.12.2 Method of spraying formulated coats

The prepared grain surfaces of the wood and leather samples were sprayed with the formulated coats by a means of a spray-gun utilising compressed air. Three each of leather and wood samples were sprayed with each of the three polyamide types. The samples were then allowed to dry in a spray-cabinet after which the grains surfaces were smoothened on a hot-plating machine at 50 °C.

3.13 Dry and wet rubfastness testing

Both the leather and wood samples spray-coated were tested for rubfastness both in wet and dry conditions using "SATRA" rubfastness tester, a machine that simulates the flexing actions of materials and other treatment conditions in use (Sharphouse, 1989).

Method:- A sample in each case was introduced into the rubfastness tester and clamped at both ends. A wet felt (in the case of dry rubfastness test) and a dry felt (in the case of wet rubfastness test) was plugged into the finger of the tester. The tester was then set to give to and fro motion of 30 circles, after which observations on change in shade of sample and staining of felt were made and assessed on standard Gray Scales. The to and fro motions were then increased to 50, 100 and 150 circles at different parts of the sample with different felts and changes in shades of sample and staining of the different felts were assessed as before.

Similar tests were carried out on leather samples. Samples sprayed with standard coats utilized in the leather industry and assessments and comparisons were made with test

samples. The changes in shade and staining of felts were assessed on standard Gray scales (JSLT, IUP/20, 1996) as follows;

1	=	Very poor finish
2	=	Poor finish
3	=	Good finish
4	=	Very good finish
5	=	Excellent finish

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CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Physical and chemical characteristics of the oils

Specific gravities, refractive indices and relative viscosities of the oils are in the order; castor oil > palm oil > palm kernel oil. These results arise from the differences in the thickness of the oils, chain lengths of their constituent fatty acids (Appendices B, F, G, H, Fasman, 1975). Furthermore, the results of specific gravities and refractive indices (Table 4.1) agree appreciably with what are reported in literature (Appendices B and G).

Chemical characteristics of the oils show that their % ffa are in the order; palm oil > castor oil > palm kernel oil (Table 4.1), indicative of the level of hydrolytic rancidity in the oils (section 2.8) and therefore relative stabilities which are in the reversed order (Cocks et. al., 1973). According to Cocks et. al., 1973, the hydrolytic emzymes and level of stabilisers (tocopherols) in an oil determines its relative stability against rancidity. Tocopherols which are fat soluble vitamin E are essential natural stabilisers in vegetable oils (Burger, 1970). Generally for edible oils, % ffa of 2.5% and below is acceptable and any value above 2.5% is unacceptable (Pritchard, 1975). Thus from the results in Table 4.1 only palm kernel oil has % ffa value below 2.5.

The saponification values are in the order; palm kernel oil > palm oil > castor oil which agree appreciably with literature (Appendix F). However, saponification values above 200 give good quality soaps while those below form soft soaps; that is, soft to touch (Khan et. al., 1972). Oils containing high levels of short chain (C12 and C14) saturated fatty acids have high saponification values compared to those having high levels of C18 saturated or unsaturated fatty acids (Appendices F, H, Cocks et. al., 1973).

The degrees of unsaturation measured by iodine values are in the order; castor oil > palm oil > palm kernel oil. However, all the values fall below 100, hence these oils are categorised under non-drying oils (Morgan, 1982). Generally, oils having iodine values below 100, are non-drying; those having values between 100 and 130 are semi-drying, while those having values above 130 are termed "drying oils" (Gunstone, 1967; Morgan, 1982; Appendix F).

Table 4.1: Some physical and chemical characteristics of the oils

Oil type	Specific gravity	Refractive index	Relative viscosity	Acid values	% free fatty acid	Saponification values	Iodine values
Castor oil	0.960	1.4712	1.380	14.03 →	3.60	179.3	76.20
Palm oil	0.924	1.4612	1.139	30.50 →	7.7	228.0	41.11
Palm kernel oil	0.866	1.4552	1.068	2.96 →	0.75	265.8	17.75

Key

Specific gravity (25°C); Refractive index (29°C); Relative viscosity in toluene (30°C); Acid values (mg KOH/g oil); % ffa calculated from acid values; Saponification values (mg KOH /g oil); Iodine values (g iodine/ 100 g oil)

4.2 Alkaline refining and earth bleaching

Alkaline refining apart from removing the free fatty acid contents of the oils also lightens their colours. This results from the adsorption of pigments and other surface active agents in the oils on the surfaces of the soap-stocks formed (section 3.4.1, List et. al., 1978).

Similarly, earth bleaching further removes pigments, phosphatides and other "impurities" in the oils (Fig 2.3; Burger, 1970). Refining losses calculated for the oils indicate a higher % loss for palm kernel oil due to partial saponification of the neutral triglyceride by the lye used (Table 4.2).

Table 4.2:- Results of alkaline refining and earth bleaching

Parameter/oil type	Palm kernel oil	Castor oil	Palm oil
Degrees Baume at 15 °C	10°	12°	18°
% W/V NaOH content	6.57	8.0	12.68
Actual Vol (cm^3) of NaOH used/100g oil	4.5	17.5	24.1
% refining loss	29.1	5.6	3.1

4.3 Alkaline saponification (hydrolysis) of the oils

The soaps of the oils prepared (section 3.5.1) show hardness to touch in the order; palm kernel oil > palm oil > castor oil. This is in line with the differences in their saponification values (section 4.1). The exact volume (cm^3) of 50% W/V NaOH solution required for saponification of each oil is determined by the expression stated in section 3.5.1.

Table 4.3:- Results of alkaline saponification (hydrolysis) of the oils

Oil type	Saponification Value in (g) NaOH/100g oil	Volume (cm^3) of 50% W/V NaOH/100g oil	Remark
Palm kernel oil	26.6	53.2	Hard soap
Palm oil	22.8	45.6	Hard soap
Castor oil	17.9	35.9	Soft, creamy soap

4.4 Preparation of water-insoluble mixed fatty acids

The degrees of acid hydrolysis for all the soaps are less than 100% due to alkaline refining, earth bleaching which remove the free fatty acid content and other non-triglycerides in the parent oil (section 3.4.1). Furthermore, comparing the acid values of the mixed fatty acids (table 4.4) to those of the crude oils (Table 4.1) confirms the presence of more -COOH groups in the mixed fatty acids (Cocks et. al., 1973).

$$\underset{\text{soap}}{RCOONa} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{fatty acid}}{RCOOH} + \underset{\text{salt}}{NaCl}$$

Table 4.4:- Results of water-insoluble mixed fatty acids

Weight of soap(g)	Vol(cm^3) of distilled water	Vol(cm^3) of conc HCl	Acid value for mixed oil	Saponification value	% degree of hydrolysis soaps
100g soap from PKO	100	20	224.4	265.8	84.5
100g soap from PO	100	20	170.6	228.0	74.8
100g soap from CO	100	20	144.6	179.3	80.7

PKO = palm kernel oil; PO = palm oil; CO = castor oil

4.5 Urea fractionation of mixed fatty acids

The results of urea fractionation of mixed fatty acids in Table 4.5 indicate that % yields of the unsaturated fatty acid fractions are in the order; castor oil > palm oil > palm kernel oil which is in line with literature (Appendix H). However, the values obtained are correspondingly lower than those from literature. The reasons may be explained as follows;

i) handling losses

ii) ineffective temperature control under the existing laboratory conditions

iii) some of the unsaturated fatty acids especially oleic acid might have entered the inclusion complex of the urea unit cell together with the saturated fatty acids or immediately after them (Simpson, et. al., 1975).

Generally, the modes of entry into the unit cell of urea are in order; saturated fatty acids; mono-unsaturated fatty acids; then poly-unsaturated fatty acids (2.12.3; Simpson, et. al., 1977). It therefore follows that palm kernel oil mixed fatty acid entered the complex easily, followed by palm oil mixed fatty acids and lastly those of castor oil (section 2.12.3; Appendix H). Furthermore, iodine value determinations and infra-red spectral studies of both the mixed and unsaturated fatty acid fractions provide evidences that urea fractionation is efficient (Appendices K and 1 - 12).

Table 4.5:- Results of urea fractionation of mixed fatty acids

Mixed fatty acid type	Wt of mixed fatty acid (g)	% unsaturated fatty acid fraction A	% saturated fatty acid fraction B	% loss due to handling 100-(A+B)
C.O. mixed fatty acids (g)	100	63.37	24.74	11.89
P.O. mixed fatty acids (g)	100	36.89	37.65	25.46
P.K.O. mixed fatty acids	100	9.65	69.52	20.83

4.6 Dimerisation reactions

The progress of each dimerisation reaction was monitored by measurements of the following parameters as a function of time (hr);

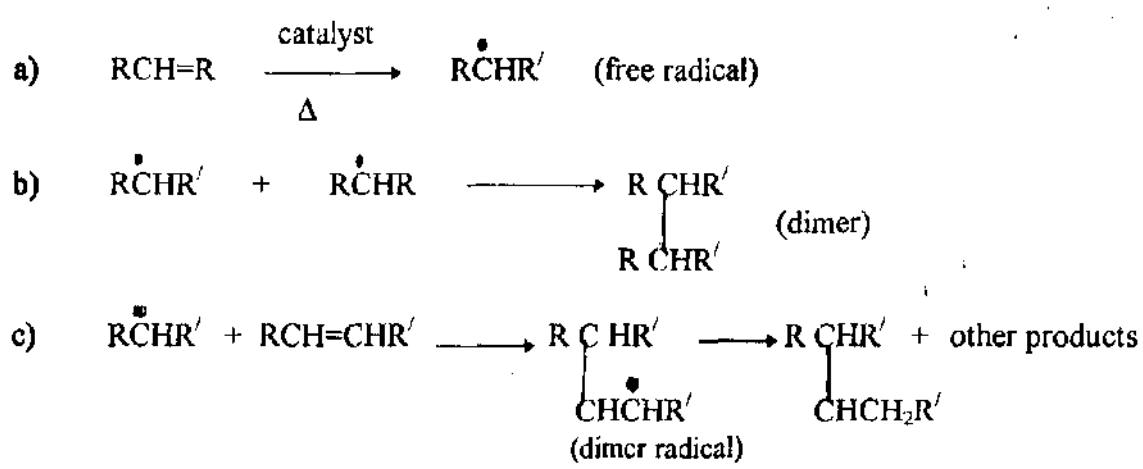
i) changes in iodine values

ii) changes in relative viscosities

iii) infra-red spectral studies (section 2.14.1)

The results of changes in iodine values and relative viscosities indicate decreases and increases in these values respectively as a function of time (Appendix K). Plots of iodine values with time show slight but smooth decreases in iodine values with time of dimerisation (Fig. 4.1). From the slopes of the plots of iodine values in Fig. 4.1, the average rates of dimerisation are in the order; castor oil unsaturated acids > palm oil unsaturated acids > palm kernel oil unsaturated acids (Fig. 4.1). The observed differences in average rates of dimerisation may be due to the relative level of unsaturation in the parent oils (Appendix H).

The progressive increases and decreases in relative viscosities and iodine values respectively with time of dimerisation for each unsaturated fatty acid type are in the order; castor > palm oil > palm kernel oil (Fig. 4.1; Appendix K). This suggests that dimerisation reactions occur at the double bonds as follows; (section 2.14.1; Simpson et. al., 1977).



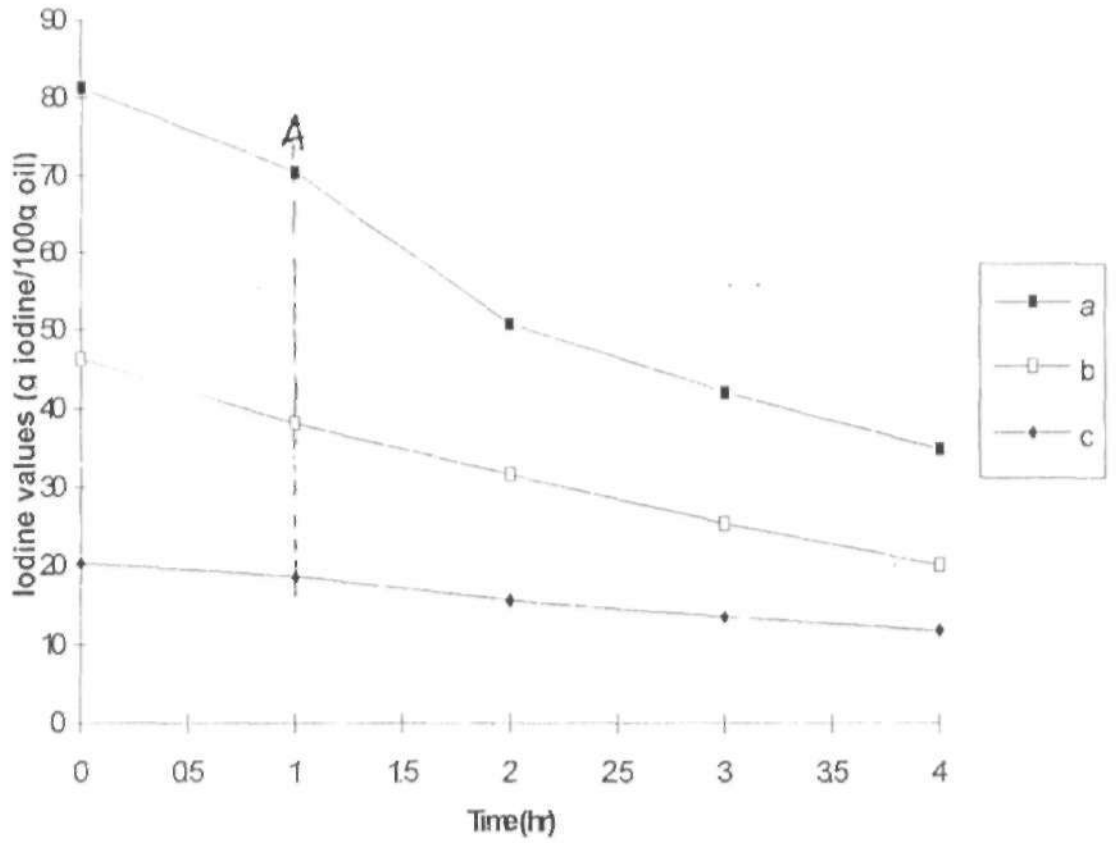


Fig. 4.1: Graph of variations of iodine values with time of dimerisation (a) = castor oil unsaturated fatty acids; (b) = palm oil unsaturated fatty acids; (c) = palm kernel oil unsaturated fatty acids. Slopes at point A (a) = 11; (b) = 8.5; (c) = 2.3.

The above reactions lead to decreases in iodine values and corresponding increases in relative viscosities and therefore shifts in absorbances of -C=C- infra-red bands with time of dimerisation in the series; $p_1 \rightarrow P_2 \rightarrow P_3 \rightarrow P_4$; $C_1 \rightarrow C_2 \rightarrow C_3 \rightarrow C_4$ and $PK_1 \rightarrow PK_2 \rightarrow PK_3 \rightarrow PK_4$ (Gunstones, 1967; Pecsok et. al., 1976) as defined in Table 4.6; Appendices 1 - 12 and the spectra in Appendices $P_1 \rightarrow P_4$; $C_1 \rightarrow C_4$; $PK_1 \rightarrow PK_4$. The absorbances are calculated from Beer-Lambert law which relates absorbance to concentration and transmittance (Pecsok et. al., 1976).

A summary of the shifts in absorbances of the IR spectral bands of the main functional groups involved are shown in Table 4.6 which allows for comparisons of the dimerisation reactions with time as the unsaturated centres are being consumed leading to the formation of saturated units (equations a - c above; Gunstone, 1967). However, contrasting the results in Table 4.6 for each series, indicate the effects of dimerisation reaction on band intensities (absorbances) as well as time dependence of dimerisation on the band intensities of the main functional group; -CH=CH-. Details of the spectral analyses are presented in Appendices 1 - 12.

4.6.1 Contrasting P_1 and P_2

Contrasting P_1 and P_2 in Table 4.6 indicates that there is increase in band intensity (absorbance) from $P_1 \rightarrow P_2$ for the -CH=CH- group. This confirms that there is separation of unsaturated fatty acids from the palm oil whole fatty acids by urea fractionation (Hilditch, 1964; section 2.12.3; Table 4.5).

Table 4.6:- Summary of variations of IR band intensities (absorbances) with time of dimerisation

	Absorbances											
Sample code	P_1	P_2	P_3	P_4	C_1	C_2	C_3	C_4	PK_1	PK_2	PK_3	PK_4
Functional group												
-CH=CH- (V)	0.8254	2.1805	2.0836	0.7690	2.1805	2.1805	0.4405	0.5726	2.1549	2.5376	0.4543	0.4938
-CH (V)	0.5485	1.2774	1.4776	0.9031	1.2262	1.3675	1.1198	0.5892	2.2798	1.0462	0.6749	0.7173
	1.7825	2.4815	2.4815	2.3010	2.4815	2.5272	2.7825	0.8097	2.1805	2.5436	0.5837	0.6282
	1.3054	2.5376	2.4815	1.6989	2.4815	2.5272	2.7825	0.7213		2.5436		

Key
(V) = Stretching vibration

P_1 = palm whole (mixed) fatty acids
P_2 = palm oil unsaturated fatty acids
P_3 = palm oil dimers at 2 hrs
P_4 = palm oil dimers at 4 hrs

C_1 = castor oil whole fatty acids
C_2 = castor oil unsaturated fatty acids
C_3 = castor oil dimers at 2 hrs
C_4 = castor oil dimers at 4 hrs

PK_1 = palm kernel oil whole fatty acids
PK_2 = palm kernel oil unsaturated fatty acids
PK_3 = palm kernel oil dimers at 2 hrs
PK_4 = palm kernel oil dimers at 4 hrs

4.6.2 Contrasting P_3 and P_2: effects of dimerisation on band intensity (absorbance)

There is decrease in band intensity from $P_2 \rightarrow P_3$, suggestive that unsaturated centres -CH=CH- are being consumed. This indicates the effect of dimerisation on band intensity which decreases at P_3 as the concentration of the unsaturated centres is being reduced (Simpson et. al., 1977).

Furthermore, C-H(V) band intensities at P_3 are largely below 3000 cm^{-1} and greater than at P_2, suggestive of the formation of saturated units from unsaturated centres (section 4.6; Szymaski, 1964).

4.6.3 Contrasting P_4 and P_3: time dependence of dimerisation on band intensity

Band intensity further decreases drastically from $P_3 \rightarrow P_4$ confirming the time dependence of dimerisation reaction (Ault, 1975). Furthermore, C-H(V) band intensities (absorbances) above 3000 cm^3 (frequency) decrease from $P_3 \rightarrow P_4$ and at the same time P_4 C-H(V) bands fall largely below 3000 cm^{-1}. The above statements suggest the formation of saturated units from unsaturated ones (Appendix I; Pecsok et. al., 1976).

4.6.4 Contrasting C_1 and C_2

The -CH=CH- band intensities remain the same at C_1 and C_2. This indicates the nearly 98% unsaturation in castor oil (triglycerides); Appendices I and J.

4.6.5 Contrasting C_3 and C_2: effects of dimerisation on band intensity

Here band intensity for -CH=CH- group decreases from $C_2 \rightarrow C_3$ suggestive that reaction occurs at the double bands (section 4.6.2). Similarly, band intensities below 3000 cm^{-1}

frequency increase from $C_2 \rightarrow C_3$ indicating formation of saturated units (Pecsok et. al., 1976).

4.6.6 Contrasting C_4 and C_3: time dependence of dimerisation on band intensity

The -CH=CH- band intensity slightly increases from $C_3 \rightarrow C_4$. This may be attributed to the isomerisation of two double bonds in linoleic acid to a conjugated system followed by a Diels-Alder addition to an isolated double bond of a second fatty acid molecule to produce a cyclic dimer (Cowan, 1962; Nelson et. al., 1975; Bellamy, 1974) as follows;

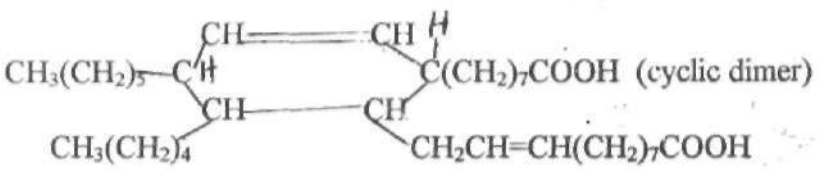
$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$ (linoleic acid)

↓ isomerisation

$CH_3(CH_2)_5CH$ $CH(CH_2)_7COOH$ (conjugated system)

\+ Diels-Alder addition

$CH_3(CH2)_4\ CH=CHCH_2CH=CH(CH_2)_7COOH$



The above reaction would have led to an increase in iodine value or iodine value remaining constant from $C_3 \rightarrow C_4$. However, this route was not dictated by measurements of iodine values (Fig. 4.1), instead iodine value decreases from $C_3 \rightarrow C_4$ (Appendix K). Moreover, C-H(V) bands fall below 3000 cm^{-1} frequency at C_4 indicating formation of saturated units as mentioned in section 4.6.3.

4.6.7 Contrasting PK_1 and PK_2

The -CH=CH- band intensity increases from $PK_1 \rightarrow PK_2$ indicating presence of higher level of unsaturated unit as in section 4.6.1.

4.6.8 Contrasting PK_3 and PK_2: effects of dimerisation on band intensity

There is a drastic drop in band intensity from $PK_2 \rightarrow PK_3$ as explained in section 4.6.2, with C-H(V) bands largely below 3000 cm^{-1} indicating formation of saturated units (Appendix I).

4.6.9 Contrasting PK_4 and PK_3: time dependence of dimerisation on band intensity

The -CH=CH- band intensity slightly increases from $PK_3 \rightarrow PK_4$ suggesting dimerisation reaction occurring by Diels-Alder route mentioned in section 4.6.8, however similar observations were made. In any case C-H(V) bands occur largely below 3000 cm^{-1} frequency suggesting formation of saturated units (Appendix I).

In summary, considering the results of urea fractionation (Table 4.5), variations of iodine values and relative viscosities with time of dimerisation (Appendix K) and the infra-red spectral analyses in terms of shifts in band intensities (Table 4.6), the following claims can be made:

i) Urea fractionation of mixed (whole) fatty acids has been achieved appreciably;

ii) dimerisation reactions through the double bonds of the unsaturated fatty acids has been achieved through mode (ii) - (iv) discussed in sections 2.14.1 and 4.6, since the Diels-Alder addition route via isomerisation has little or no possibility because the linoleic acid required occurs very little in the oils considered (Appendix H).

Furthermore, evidences from infra-red spectral analyses measured by shifts in absorbances of main functional groups (Table 4.6; Appendices 1 - 12) lay claims to dimerisation reactions occurring at the unsaturated centres (Gunstone, 1967; Syed, 1976).

4.7 Synthesis of fatty acid polyamides

The results indicate that condensation polymerisation is characterised by stepwise conversion of monomer (dimer acid) with two reactive end groups to higher molecular weight homologues which themselves retain two reactive ends (Mccafery, 1970). End-group analysis by titrimetry has been used to characterise polymers by measurement of molecular weight, monitoring the stoichiometry of two difunctional monomers in condensation polymerisation and in routine control of molecular weights in industrial and research polymerisation processes (Billmeyer, 1984).

Taking slopes between points C and A of the plots of variations of acid numbers with time of polymerisation (Fig. 4.2 below) give average rates of 0.80, 0.20 and 0.11 mg KOH/g/min for palm kernel, palm and castor oil dimer acids in that order. The differences in the average rates indicate the differences in the initial acid numbers at zero time (Appendices 13 - 15). Furthermore, a general survey of the progress of the reactions indicates that at 10 minutes of the reaction time, about half of the dimer acid concentrations have reacted (Appendices 13 - 15). Thereafter, the reactions proceed slower with time. This phenomenon agrees with the principle of step-growth polymerisatiopn in which monomer disappears early in the reaction and at degree of polymerisation ten, less than 1% monomer remains (Cowie, 1973; Sunmonu; 1994).

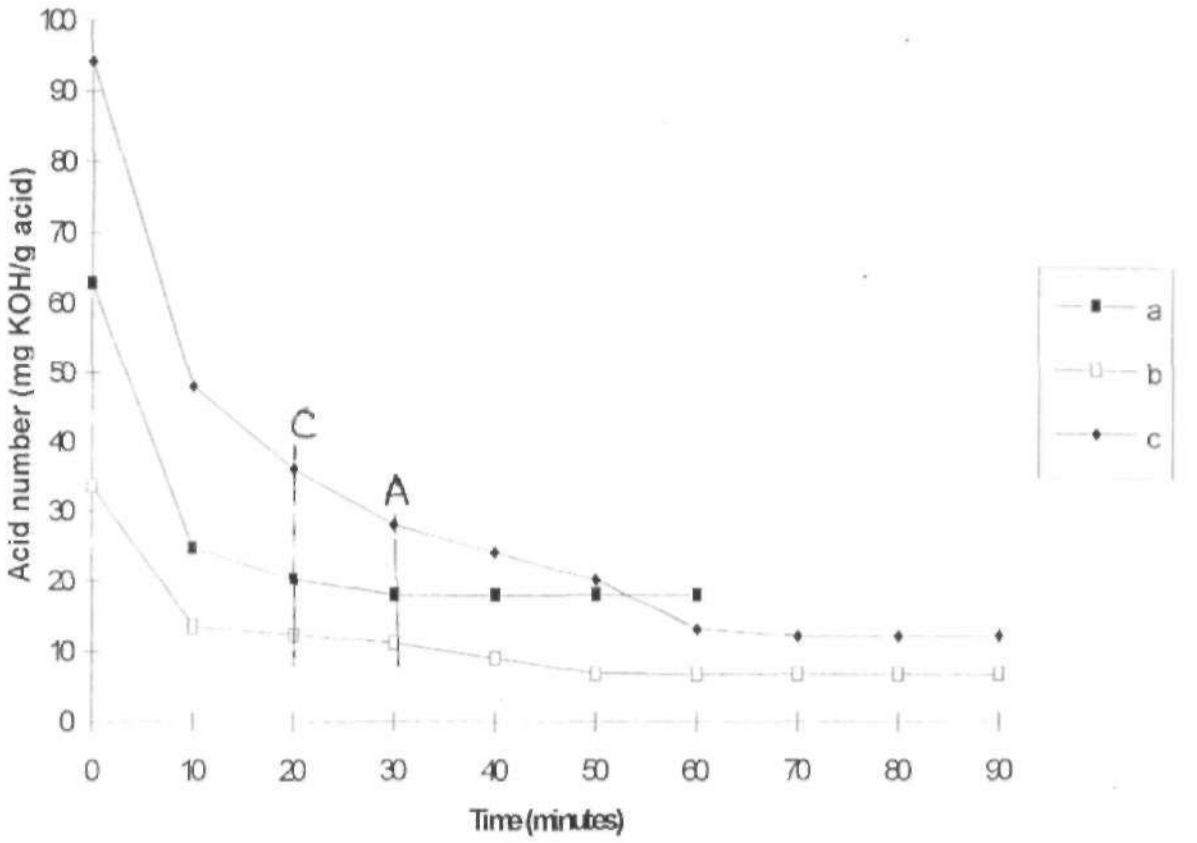


Fig. 4.2: Graph of variation of acid numbers with time of polymerisation: (a) = palm oil dimer; (b) = castor oil dimer; (c) = palm kernel oil dimer. Slopes at point A: (a) = 0.2; (b) = 0.11; (c) = 0.8.

The initial low acid number for castor oil dimer acid compared to those of palm oil and palm kernel oil, is due to a reaction between the OH-group on C-12 of ricinoleic with the -COOH group of adjacent ricinoleic molecule to form estolide (Naughton, 1974; equation 2-0) during the dimerisation reaction (section 2.14.1). Furthermore, the steady release of water by castor oil dimer acid reaction up to the 75th minute can be attributed to the above reaction (Appendix 14).

A survey of the data on Appendices 13 - 15, indicate that polymerisation reactions terminate at 30, 60 and 70 minutes for palm, castor and palm kernel oils in that order. Factors that may be responsible for these differences are; initial differences in acid numbers, the presence of mono-unsaturated and saturated fatty acids as "impurities" (Nelson et. al., 1975; Selke et. al., 1977).

Furthermore, a kinetic treatment of the data in Appendices 13 - 15 using the Carothers equation (section 2.16) give parameters such as percentage conversion (p), degree of polymerisation and number average molecular weight (Mn) (Appendix 16). From Appendix 16, a maximum %P, DP and Mn are in the order;

i) Palm kernel oil dimer acid at 70 minutes; p = 87.14%, DP = 7.77, Mn = 4,752.29

ii) Castor oil dimer acid at 60 minutes; p = 80.00%, DP = 5.00, Mn = 2,940.00

iii) Palm oil dimer acid at 30 minutes; p = 71.43%, DP = 3.5, Mn = 2,058.00.

The Mn values fall short of what have been reported in the region of 6000 - 9000 for this group of polyamides as low molecular weight film forming thermoplastics (Billmeyer, 1984). The reason for this observation may be attributed to the presence of mono-

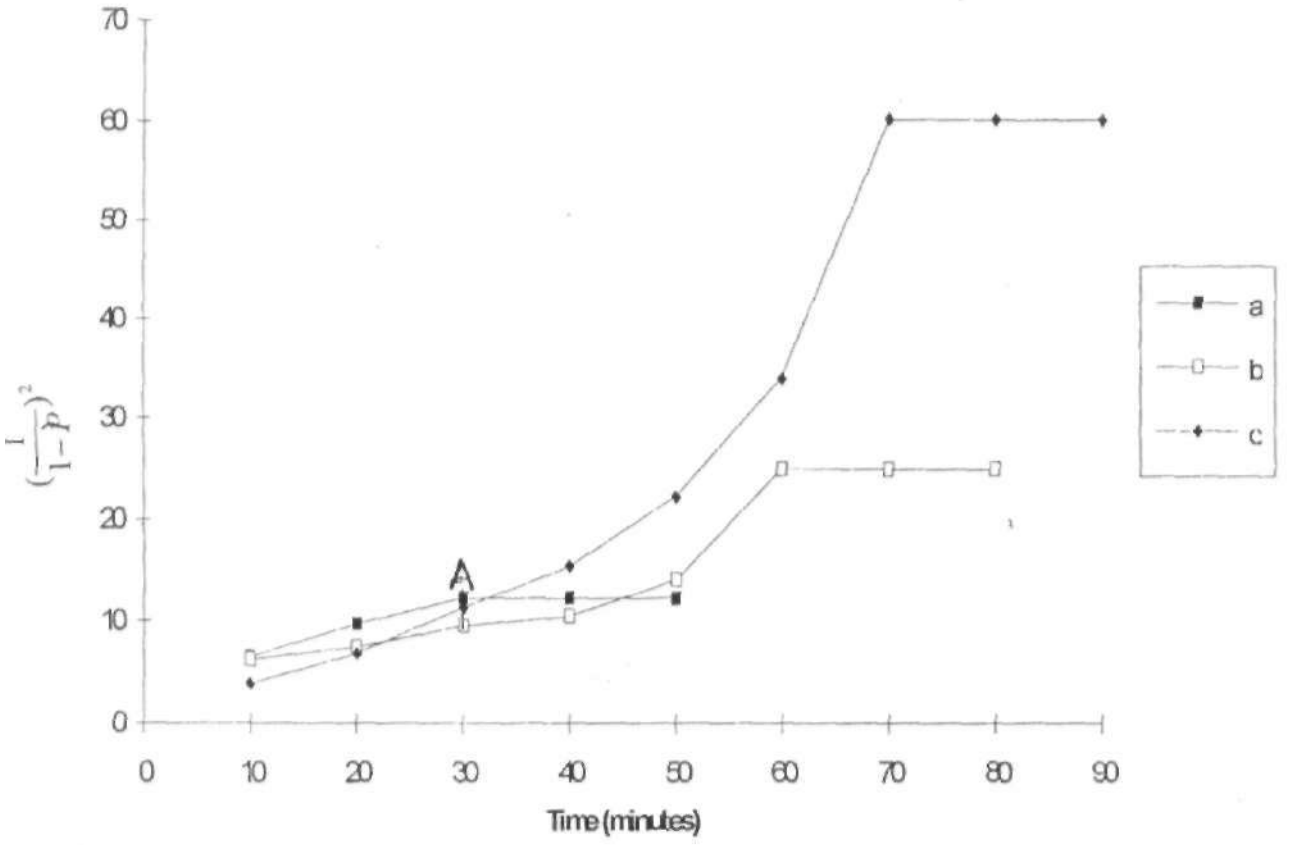


Fig. 4.3: Variation of $(\frac{1}{1-p})^2$ with time of polymerisation (Carothers equation)

(a) = palm oil; (b) = castor oil; (c) = palm kernel oil. Intercepts (a) = 4.0; (b) = 5.0; (c) 1.0. Slopes at point A (a) = 0.23; (b) = 0.15; (c) = 0.43.

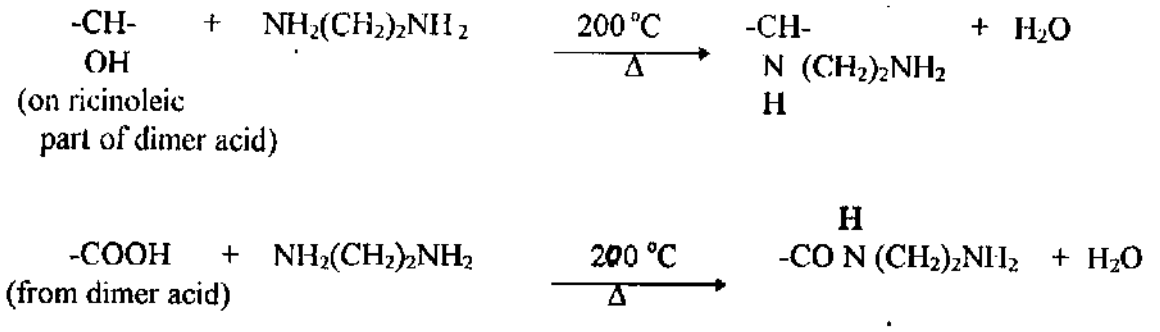
unsaturated and saturated acids as "impurities" in the dimer acids (Nelson et. al., 1975; Raie, 1976) which limit the chain-lengths of the polymers (Jenkins, 1972). Furthermore, plots of $(\frac{1}{1-p})^2$ against time from the Carothers equation (Fig. 4.3) yield the following data on Table 4.7

Table 4.7:- Data from the Carothers equation; $(\frac{1}{1-p})^2 = 2C_o^2kt + 1$

Dimer type	$C_o = AV_{to}$ mgKOH/g oil	$2C_o^2 = 2(AV_{to})^2$	Intercept	Slope	Rate constant(k) = slope/$2C_o^2$ (mgKOH/g oil/min) x 10^{-5}
P.K.O	94.248	17765.37	1.0	0.43	2.4204
P.O	62.832	7895.72	4.0	0.23	2.9129
C.O	33.660	2265.99	5.0	0.15	6.6196

$C_o = AV_{to}$ = initial acid number at time zero

From the intercept of the plots of the Carothers equation (Fig. 4.3), it is only palm kernel oil dimer acid that fits the relationship (Table 4.7), while castor oil and palm oil dimer acids show positive deviations above unity. The reason(s) may be anchored on what has been explained (see page 79). However, the higher intercept and k value (Table 4.7) for castor oil dimer acid may be due to the reaction of the OH group on C12 of ricinoleic acid with the NH_2 group of the diamine in addition to the reaction of -COOH group of the dimer acid with the NH_2 group of the diamine (Naughton, 1974) ordinarily as reactions of alcohols and primary amines (Vogel, 1971).



From the above, castor oil dimer acid has three functional groups, however, assumption of difunctional dimer acid is made and that it is only dimer acids with two -COOH groups were present in the reaction mix.

Generally, in addition to the requirements of high conversion and equimolarity of functional groups, successful polycondensation demands that reactants be extremely pure as minute amount of mono-functional "impurities" will limit drastically the molecular weight of the polymer by producing chains which are incapable of further growth (Jenkins, 1972). In any case, in industrial practice, most resins (as in this case), the basic polymerisation is taken to low conversion at which gelation does not occur and therefore the resin is workable (Cowie, 1973; Bolker, 1974). Furthermore, most reactions used in condensation polymerisation are in equilibria and in order to obtain high conversion, it is essential to provide some means of removing the small molecules such as H_2O, CO_2, HCl, eliminated during the reactions (Fig. 3.3; Jenkins, 1972). The fatty acid dimers in this case contain mono-acid "impurities" which limit high molecular weights, however, they are workable as resins (Billmeyer, 1984).

4.8 Characterisation of the polymer prepared

4.8.1 Results of infra-red spectral analyses

The results indicate the formation of Amide *I* and Amide *II* bands (Appendix *J*) in which the character of the C=O band is highly modified (Pecsok et. al., 1976). Detail analyses presented in Tables 4.8, 4.8.1 and 4.8.2 below lay claims to the formation of polyamides.

4.8.2 Solubility tests

The results indicate that all the polymers are soluble in the following solvents; acetone, toluene, kerosene, chloroform, carbon tetrachloride, 1,1 1-trichloroethane and insoluble in ethanol, methanol and water. This shows the fatty acid-based property of the polymers which make them soluble in non-polar solvents and insoluble in polar, organic solvents (Peerman, 1969; Olabisi et. al., 1979).

4.8.3 Melting ranges

The three types of polymers show melting ranges between 70 and 100 °C as;

Palm kernel oil polymer = 80 - 100°C

Palm oil polymer = 80 - 100°C

Castor oil polymer = 70 - 80°C

From the above analyses and especially from IR spectra of the compounds synthesised (section 4.7), and analyses presented in Tables 4.8, 4.8.1, 4.8.2 below, it can be concluded that these polymers are polyamides.

Table 4.8:- Sample P_5 (palm oil polyamides) IR spectral analyses

Functional group	Frequency (cm^{-1})	%Transmittance	Absorbance	Shade	Remarks
O-H (δ)	944.78	23.06	0.6371	sharp	Bending vibrations of O-H of carboxylic group (-COOH) chain ends of polyamide
-N-H (V)	3302.81	6.432	1.1917	sharp	Strong band intensity due to -N-H(V) of secondary amide (Appendix I) which arises from symmetric stretching vibration (Pecsok et. al., 1976; Kemp, 1991)
C-H (V)	3083.34	8.58	1.0665	sharp	Bands are largely below 3000 cm^{-1} indicative of saturated compounds with methylene linkages (Appendix I)
	3009.23	9.66	1.0153	sharp	
	2900.00	5.45	1.2636	sharp	
	2840.00	6.79	1.1681	sharp	
C-H (δ)	1466.86	11.87	0.9256	sharp	
-C=O (V)	1737.83	19.25	0.7156	sharp	Amide I band, as the C=O character has been modified compared to the carbonyl stretch in P_4 (Appendix I), while the band at 1637 cm^{-1} is referred to as Amide II (ref Appendix J). The disappearance of C=C band suggests that dimerisation continues during polymerisation (Appendices 1 - 12)
C=C (V)	-	-	-	-	
$-CONH_2$ (δ)	1637	7.2	1.1427	sharp	

NB: (V) = Stretching vibration
(δ) = Bending vibration

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Table 4.8.1:- Sample C_5 (castor oil polyamides) IR spectral analyses

Functional group	Frequency (cm^{-1})	%Transmittance	Absorbance	Shade	Remarks
O-H (V)	-	-	-	-	Disappearance of band suggests most of the OH group
O-H (δ)	-	-	-	-	of the COOH groups and those on carbon-12 have reacted (equations 2-0 & 2-28) and therefore more N-H(V) character is obtained (Cowie, 1973)
-N-H (V)	3298	21.8	0.6615	sharp	-N-H(V) is from a secondary amide as explained for P_5 (palm oil polyamide) corresponding band
C-H (V)	3011.8	25.106	0.6002	sharp	Absorption bands are essentially below 3000 cm^{-1}
	2900	13.26	0.8775	sharp	suggestive that long chain saturated hydrocarbons are
	2854	17.14	0.7659	sharp	present as explained for P_5 corresponding bands
C-H (C	1463.0	30.4	0.5171	sharp	
-C=O (V)	1734	26.9	0.5703	sharp	Amides I and II bands respectively as explained for P_5
C=C (V)	-	-	-	-	corresponding bands (Appendix J). However, P_5
$-CONH_2$ (δ)	1650.18	26.4	0.5784	sharp	corresponding absorbances are higher indicative that lesser amount of amide groups in C_5 as some of the -COOH groups have reacted with OH group on carbon-12 of the acid dimers (C_4 and equation 2-0). C=C(V) disappearance is as explained for P_5

Table 4.8.2:- Sample PK_5 (palm kernel oil polyamides) IR spectral analyses

Functional group	Frequency (cm^{-1})	%Transmittance	Absorbance	Shade	Remarks
O-H (δ)	944.29	17.52	0.7565	sharp	*Bending vibration* of O-H group of -COOH group of polyamide chain-ends, as stated for P_5 corresponding band
-N-H (V)	3280	0.18	2.7447	sharp	N-H(V) of secondary amide as stated for P_5 and C_5 corresponding bands
C-H (V)	3095.8	3.96	1.4028	sharp	Bands are below 3000 cm^{-1} suggestive of saturated long chain hydrocarbon compounds as stated for P_5 and C_5 corresponding bands
	2960	1.08	1.9666	sharp	
	2920	0.18	2.7447	sharp	
	2820	0.18	2.7447	sharp	
C-H (δ)	1460	2.9	1.5376	sharp	
-C=O (V)	1738.5	7.9	1.1024	sharp	Amides I and II bands respectively as described for P_5,
C=C (V)	-	-	-	-	C_5 corresponding bands (P_5 and notes referred). C=C(V)
$-CONH_2$ (δ)	1640	0.18	2.7447	sharp	disappearance suggested that reaction at the double bonds did continue during polyamide synthesis (P_5 and C_5).

4.9 Spray-coat trials on wood and leather surfaces

The results of both dry and wet rubfastness ratings for palm oil and palm kernel oil polyamide coats indictae good ratings on leather surfaces as they compare favourably with the ratings for standard polyurethane coats (Table 4.9 below; Sharphouse, 1989; Sarkar, 1991). However, all the trial coats show very poor rating on wood surfaces as a result of poor adhesion (Sarkar, 1991). Furthermore, the comparable good adhesion for palm oil and palm kernel oil polyamide coats suggests favourable interactions and compartibilities of the resin groups with the leather groups (Collagen groups) (Olabisi et. al., 1979, that is, the -COOH, -CONH, $-NH_2$ groups of the polyamides do interact with $-CONH_2$, -COOH, $-NH_2$ groups of collagen (Olabisi et. al., 1979; Sharphouse, 1989).

On the other hand, castor oil polyamide coat appears tacky and non-film forming perhaps as a result of the peculiarities of the main fatty acid mentioned in section 4.7 (Naughton, 1974).

In summary, the wet rubfastness ratings of palm oil and palm kernel oil polyamide coats show higher values compared to those of corresponding dry rubfastness as a result of high water repellency of the resins (Peerman, 1969).

Table 4.9:- Results of dry and wet rubfastness

a) Dry rubfastness tests

Polyamide type	Surface	No. of circles	stain on felt	Change in shade of sample	Stain on std. felt	Change in shade of std. sample
Palm oil	Leather	30	4	5	5	5
	"	50	4/5	4	4	4
	"	100	3	3/4	3	3
	"	150	1/2	2	3/2	2
Palm kernel oil	Leather	30	4	5	5	5
		50	4/5	4	4	4
		100	3	3	3	3
		150	1/2	2	2/3	2
Palm oil	Wood	30	1	1		
	"	50	-	-		
Palm kernel oil	Wood	30	1	1		
	"	50	-	-		

b) Wet rubfastness

Polyamide type	Surface	No. of circles	stain on felt	Change in shade of sample	Stain on std. felt	Change in shade of std. sample
Palm oil	Leather	30	5	5	5	5
	"	50	5	5	5	5
	"	100	5	5	5	5
	"	150	4	4	4/5	4/5
Palm kernel oil	Leather	30	5	5	5	5
	"	50	5	5	5	5
	"	100	5	5	5	5
	"	150	4	4	4/5	4/5
Palm oil	Wood	30	1	1		
	"	50	-	-		
Palm kernel oil	Wood	30	1	1		
	"	50	-	-		

1 = very poor finish 2 = poor finish 3 = good finish
4 = very good finish 5 = excellent finish

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

Polyamides from castor, palm and palm kernel oils serve several purposes including coating applications. This follows from the hydrolysis of the purified oils to obtain mixed fatty acids in yields up to 90%.

Urea fractionations of the mixed fatty acids give, 65.37%, 36.89% and 9.65% castor, palm and palm kernel oil unsaturated fatty acids respectively as against the reported 94 - 98%, 52% and 18% in that order.

Furthermore, results of dimerisation reactions show that the double bonds of the unsaturated fatty acids are involved as indicated by decreases in iodine values with corresponding increases in relative viscosities. These are supported by infra-red spectral analyses of the neat samples which show progressive shifts in absorbances of the double bond (-C=C-) functional group as; $P_2 \rightarrow P_3 \rightarrow P_4$; $C_2 \rightarrow C_3 \rightarrow C_4$ and $PK_2 \rightarrow PK_3 \rightarrow PK_4$.

Condensation of the dimer acids with ethylenediamine follow the general principle and kinetics of non-catalysed polycondensation reactions. In addition, kinetics treatment of the data shows appreciable agreement with the Carothers relationship; $(\frac{1}{1-p})^2 = 2C_o^2kt + 1$, for a non-catalysed polycondensation. However castor and palm oil dimer acids show intercept values of 5.0 and 4.0 respectively as against unity for palm kernel oil dimer acid. The positive deviation above unity is suggestive of the presence of mono-acid "impurities" in the dimer acids. Similarly, k values calculated from the slopes of the plots indicate; PK < PO << CO for palm kernel, palm and castor oil dimer acids respectively.

Characterisation of the polyamides by infra-red analysis, solubility tests and melting range give encouraging results.

Finally, spray-coat trials on wood and leather sample surfaces show good results on leather surfaces for palm kernel and palm oil polyamide coats as measured by dry and wet rubfastness ratings. Castor oil polyamide coat appears tacky and therefore not useful for this purpose. However, further work is necessary to improve on the properties of raw materials, process and equipment design in order to optimise products and therefore better results.

5.1 Recommendations for further work

1). Further work should be carried out to determine the ratio of dimer acids to mono acids

2). Blending of the polyamides in appropriate concentrations and their synergisms or otherwise should be studied.

3). Blending of the various dimer acids and copolymerisation of the unsaturated fatty acid types before polycondensation should be carried out and their synergisms or otherwise studied.

4). Other catalyst systems other than bentonite, such as BF_3, HF, Al_2O_3, Al/Pd, be used to see their effects on the rates of dimerisation reactions.

5). These polyamides should be tried as lubricants/release agents; stabilisers and plasticisers in plastic processing and the behaviours studied.

6). Oils (vegetable) of higher iodine values (>100) should be employed in the synthesis of the polyamides.

References

Abrahart, E. N (1968). Dyes and their Intermediates, Pergamon Press, London, pp 55 - 60.

Ackman, R. G (1974). Fish Lipids; Part I, Advances in Fish Science and Tech, pp 86 - 103.

Alexander, J. M , Brewer, R. C and Rowe, G. N (1987). Manufacturing Technology Vol 2, Engineering Processes, Ellishorwood Ltd London, pp 2 - 9.

An NNPC Point of View (1995). Investment Opportunities in the Oil, Gas and Petrochemical Industries in Nigeria, pp 2 - 3.

Ault, W. C (1975). Polybasic acids, in Encyclopedia of Chem. Tech. 8, Wiley Interscience New York, pp 847 - 849.

Bastic, M (1977). Sterols in Pumkin Seed Oil, J. Amer. Oil Chem. Soc. 84 (11) pp 525 - 527.

Baum, J. S (1970). Introduction to Organic and Biological Chemistry, Macmillan Company Ltd New York, pp 246 - 270.

Bell, E. W (1976). Sperm Oil Replacements from Selectively Hydrogenated Soyabean and Linseed Esters: Special Lubricants, J. Amer. Oil Chem. Soc. 53 (7), pp 511 - 513.

Bellamy, J. A (1974). An Introduction to Conservation of Orbital Symmetry, Longman Group Ltd London, pp 37 - 38.

Bennet, A. N (1955). Introduction to Paint Technology, Waterlow and Sons Ltd London, pp 15, 138.

Berger, K. G (1977). Some Theoretical and Practical Aspects of Fractionation of Palm Oil, Oil Palm News, No. 22, pp 10 - 18.

Bodor, G (1991). Structural Investigation of Polymers, Ellis Horwood Ltd, London, pp 11 - 113, 355 - 364, 372 - 391.

Bolker, H. I (1974). An Introduction to Natural and Synthetic Polymers, Marce Dekker New York, pp 50 - 58.

Boxall, J; Fraunhofer, J (1977).Concise Paint Technology, Elek Scientific Books Ltd London, Vol 53, 3, pp 30 - 60.

Brace, B (1976). Detergent Fraction of Fatty Oils in Palm Oil, J. Amer. Oil Chem. Soc., p 1042.

Brandrup, J and Imergut, E. H (1975). Polymer Handbook, 2nd Ed, Wiely Interscience New York, IV, 131 - 267.

Brian, A. F and Allan, G. C (1977). Food Science: A Chemical Approach to Food and Nutrition, Hoddler and Strongton Educational Press London, pp 92 - 130.

British Pharmaceutical Codex (1975). General Monographs, p 733.

Burger, A (1970). Medicinal Chemistry Part II. Edited, 3rd Ed, Wiley Interscience New York, pp 809 - 810.

Burges, D (1994). General Aspects of Fatliquoring. An Introduction to the Application and Chemistry of Fatliquoring, JSLTC, 78 pp 39 -49.

Burkill, H. M (1985). The Useful Plants of West Tropical Africa, Royal Botanical Gardens, Vol 1, pp 15 - 20.

Carter, D and Pike, M (May, 1975). The Effects of Antioxidants in Improving Palm Oil Quality and Keepability, Oilpalm News No. 19 pp 1 - 11.

Chang Shirpei, et.a l. (1975). Oligomeric Plasticizers from Cramble Oil-derived Dicarboxylic Acids for PVC. J. Amer. Oil Chem. Soc., Vol 52, 2, pp 102 - 105.

Clegg, A. J (1973). Production of Hydrolytically Stable Palm Kernels, Oilpalm News No. 15, pp 2 - 9.

Cocks, L. V and Rede, V. C (1973). Laboratory Handbook for Oil and Fat Analysis, Academic Press London, pp 58 - 85, 88 - 89, 99 - 101, 101 - 106, 107 - 125.

Collins, A. E, Bares, J and Billmeyer, W. F (1973). Experiments in Polymer Science; John Wiley and Sons Inc New York, pp 3 - 17, 38 - 47, 52 - 62, 82 -89, 113, 124 - 154 - 153, 362 - 366, 394 - 398.

Corley, V. H. R (1977). Vegetable Propagation of Oil-Palm via Tissue Culture, Oil Palm News No. 22, pp 26.

Cornelius, J. A (1975). Palm Oil from Hybrid Oil Palms, Oilpalm News, No. 19, pp 12 -13.

Cornelius, J. A (1977). Palm Oil and Palm Kernel Oil, Progress in the Chemistry of Fats and Other Lipids, 15, pp 5 - 27.

Cornelius, J. A and Southwell, K. H (1980). Component Fatty Acids of Palm Oil Samples, Oil Palm News No. 24 pp 2 - 3.

Cowan, J. C (1967). Condensation Monomers, J. Amer. Oil Chem. Soc., 39 pp 534 - 545.

Cowie, G. M .J (1973). Polymers, Chemistry and Physics of Modern Materials, International Textbook Co. Ltd, Bucks, pp 25 - 71.

Cowie, G. M. J (1973). Polymers: Chemistry and Physics of Modern Materials, International Textbook Company Ltd, Bucks, pp 10 - 20, 30 - 50, 80 - 120.

Deokar, F. B (1977). Response of Castor Oil Application to Nitrogen and Phosphorus in Black Soils of Maharashba, Oilseeds Journal, Vol VII Jan - June, p 57.

Dollear, G. F (1978). Fats and Oils, Edible In: Encyclopedia of Science and Technology, Vol 10, pp 199 - 203.

Dyson, R. W (1992). Specialty Polymers, Blackie Academic and Professional London, pp 1 - 14, 17 - 30.

Eckhart, H (1993). Fundamentals of Leather Manufacture, Edward Roether K G , Druckered and Verlag Darmstandt, pp 75 - 137, 570 - 582, 612.

Edoziem, J (1979). Management and Optimum Utilization of Resources, In : Amoda, M, "Technological Development in Nigeria (edited) Third Press International Lagos, pp 617 - 642.

Egon Stahl (1990). Thin Layer Chromatography: A Laboratory Handbook, Pergamon Press London, pp 6 - 7.

Ekpa, O. D and Ekpe, U. J (1996). Comparison of the Characteristic Parameters and Deterioration Properties of Oils from the Tevera and Dura Varieties of the Oil Palm; Nigerian Journal of Chemical Research, Vol 1, pp 26 - 33.

Ekpa, O. D; Epke, U. J (1996). Effects of Coconut Oil Concentration on the Melting Point Profile and Free Fatty Acid formation of Palm Oil, Nig. Journal of Chem. Research, Vol 1, pp 8 - 12.

Ekpenyong, K. I (1989). Para-toluene Sulphonic Acid Catalysed Methanol Esterification of cis-13-Docosenoic Acid, Bulletin of Chemical Society of Nigeria, 12, pp 26 - 36.

Etete, D (1995). World Energy Perspectives for Oil and Gas, an Address presented at the First Plenary Session of Fourth International energy Conference Puerto La Cruz, Venezuela, pp 5 - 15.

Fasina, A. K (1983). Food Analysis-Industrial Implications, Nigerian Food Journal, NIFST 1(1), pp25 - 30.

Fasman, G. D (1975). Handbook of Biochemistry and Biology, Chaucer Press London, pp 175 - 191.

Fasman, G. D (1975). Handbook of Biochemistry and Molecular Biology, Chaucer Press London, pp 175 - 189.

Fasman, G. D (1992). Handbook of Practical Biochemistry, 3rd edition, Lipids, Carbohydrates Steroids, Chaucer press London, pp 105 - 120.

Finar I. L (1975). Organic Chemistry Vol 2, Fifth edition, ELBS, Longman Press Ltd London, pp 517 -525.

Finar, I. L (1974). Organic Chemistry Vol 2, Longman Group Ltd London, pp 395 - 400.

Flory, P. J (1953). Principles of Polymer Chemistry, Cornell University Press, Ithaca, pp 20 - 120.

Gallagher, T; Kline, D. E (1977). Viscosity of Linseed Oil as a Function of Mineral Spirit and Temperature; J. Amer. Oil Chem. Soc., 54 (2), pp 68 - 69.

Gardner, K. H; Roberti, P. H (1960). Journal of American Oil Chemist Society, 37, pp 142 - 148.

George, T. A (1984). Shrives Chemical Process Industries, McGraw-Hill Inc, New York, pp 136 - 140.

Gunstavson, K. II (1956). The Chemistry of Tanning Processes, Academic Press Inc New York, pp 202 - 295.

Gunstone, F. D (1967). An Introduction to the Chemistry and Biochemistry of Fatty Acids and Their Glycerides, Chaucer Press London, pp 1 - 11, 15 - 30.

Gupta, S. K and Stallon, A. P (1985). Estimation of Oil Content of Side-line NMR, Oilcrops Newsletter No. 2, pp 17 - 21.

Hamilton, R. J, Bhati, A (1980). Fats and Oils, Chemistry and Technology, Edited, Applied Science Pub. Ltd, London, pp 1 - 25.

Hase, A; Darva, O; Pakkanen, T (April, 1974). Origin of Bicyclic Fatty Acids in Tall Oil, J. Amer. Oil Chem. Soc., 51 (4), pp 181 - 183.

Hase, A; Hase T; Anderegg, R (1978). Identification of Minor Cyclic Fatty Acids in Fractionated Tall Oil, J. Amer. Oil Chem. Soc., 55 (4), pp 407 - 411.

Hatch, F. L; Matar, S (1977). From Hydrocarbons to Petrochemical; Hydrocarbon Processing Part 2, pp 154 - 163.

Hilditch, T. P (1964). The Chemical constitution of Natural Fats, Spothwoode Baldantyne Co Ltd Essex, pp 5 - 50, 375 - 400.

Hill, W. John (1992). Chemistry for Changing Times, Sixth Edition, Macmillan Pub., Comp. New York, pp 541 - 551, 615 - 625.

Hubbard, W. D; Frankel, E. N; Hase, T (1977). Comparison of Various Methods for the Extraction of Total Lipids, Fatty Acids, Cholesterols and Other Sterols from Food Products; J. Amer. Oil Chem. Soc., 54 (2), pp 81 - 83.

IUP/20, Society of Leather Technologists and Chemists (1996). Rubfastness Testing. J. SLTC, Vol. 3, pp 6 - 10.

Jack, E. W; Hamilton, H. S; King, D. E. M; Blum, K (1975). Thin Layer Chromatographic Separation of Chloramphenicol and Thiangphenicol and Their Monochloro Analogue, Journal of Chromatography, 114 (1) pp 266 - 269.

Jamieson, R; Baughman, M (1926). Journal of Oil/Fats Ind. 3, pp 347 - 355.

Jenkins, A. D (1972). Polymer Science, North-Holland Pub. Company, London, pp 84 - 117.

Kates, M (1970). Plant Phospholipids and Glycolipids. Advances in Lipid Research 8, pp 225 - 265.

Kemp William (1991). Organic Spectroscopy, Macmillan Education Ltd, London, pp 29 - 72.

Khan, S. A; Qureshi, M. I; Bhalty, M. K (1972). The Fatty Acids of Indigenous Resources for Possible Industrial Applications, Pakistan Journal of Scientific and Industrial Research 15 (6), pp 402 - 404.

Khor, H. T and Koslawsky, L. H. S (1980). Glycolipids of Malaysian Palm Oil, Oilpalm News No. 24, pp 12 - 15.

Kohlhase, W. L; Frankel, E. N; Pryde, E. H (1977). Polyamides from Carboxy Stearic Acid, J. Amer. Oil Chem. Soc., 54 (11) 506 - 508.

Kohlhase, W. L; Neff, W. E; Pryde, E. H (1977). Isolation of the 9-and 10- Isomers of Carboxy Stearic Acids and Their Polyamidation with Hexamethylenediamine, J. Amer. Oil Chem. Soc., 54 (11), p 523.

Koslowsky, L. H. S; Taylor, A. M and Carter, D (1975). Chemical Fractionation of Palm Oil by Transesterification; Oilpalm News, No. 19, pp 14 - 16.

Lanteri, A (1978). Sulphonation and Sulphation Technology, J. Amer. Oil Chem. Soc., 55 (1), pp 128 - 133.

Lawson, N. E; Chang, T. T (1977). The Preparation of C19 Dicarboxylic Acid by Koch Reaction, J. Amer. Oil Chem. Soc., 54 (6), 225 - 227.

List, G. R; Hase, A; Hase, T (1978). Removal of Phosphorus and Iron by Commercial Degumming of Soyabean Oil, J. Amer. Oil Chem. Soc., 55 (2), pp 275 - 276.

Ibid- Steam-refined Soyabean Oil I: Effects of Refining and Degumming on Oil Quality; pp 177 - 179.

Ibid- Steam-refined Soyabean Oil II: Effects of degumming on Removal of Pro Oxidants and Phospholipids, pp 280 - 284.

Mast, C. R (1978). Fats and Oils, Soaps and Detergents, In: Encyclopedia of Science and Technology, Vol 10, Wiley Interscience London pp 443 - 445.

Medsen, E (1976). NMR as a Quick Method of Oil Content in Rapseed, J. Amer. Oil Chem. Soc., 53, pp 467 - 469.

Meier, G. M (1976). Leading Issues in Economic Development, Pergamon Press Ltd London, pp 629 - 635.

Meijboom, P. W; Jongenother, G. A (1979). Qualitative Determination of Tocotrienols and Tocopherols in Palm Oil by TLC - GLC, J. Amer. Oil Chem. Soc., 56 (1), pp 33 - 35.

Mileez, M. A (1974). The Adsorption Isotherms and the Heat of Adsorption of Methyl Acetate on Carbon Black. Pakistan Journal of Scientific and Industrial Research 17 (1), pp 1 - 4.

Mohammad, R and Salim, K. M (1977). Studies on the Fixed Oil of *Juniperus macropodabosis* Seeds; Pakistan Journal of Scientific and Industrial Research 20 (6), pp 377 - 378.

Mohammed Salim (1981). Fatty Acids as Indigenous Resources for Possible Industrial Applications, Pakistan Journal of Scientific and Industrial Research, 24 (1) pp 25 - 30.

Monts, L. T and Kohlkase, W. L (1978). Selective Hydrogenation of Soyabean Oil: Effect of Pressure on Copper Catalysis, J. Amer. Oil Chem. Soc., 55 (4), pp 402 - 403.

Morgan, W. M (1982). Outlines of Paint Technology, Charles Griffin and Co Ltd, London, pp 171 - 183.

Nakanishi, Koji (1964). IR Absorption Spectroscopy (Practical), Nankodo Co. Ltd Tokyo, pp 44 - 451.

Naughton, C. F (1974). Production, Chemistry and Commercial Applications of Various Chemicals from Castor Oil, J. Amer. Oil Chem. Soc., 51 (3) pp 65 -71.

Nelson, J. P; Millun, A. J (1975). Dimer Acids, Gas Chromatographic Analysis, J. Amer. Oil Chem. Soc., 52 (3), pp 81 - 83.

Ngnokam, D (April - June, 1994). Steroids and Terpenoids from the Bark and the Wood of *Entandrophragma cylindricum*, Bulletin of Chemical Society of Ethiopia pp 15 - 20.

Nkeonye, O. P (1990). Fundamental Principles of Textile Dyeing, Printing and Finishing. ABU Press Zaria, pp 163 - 164.

NNPC Pub (1995). History of Crude Oil Marketing in Nigeria.

Oilpalm News No. 14 (1972). Vegetable Fat Products Based on Palm Oil, pp 12 - 18.

Oilpalm News No. 22 (1977). Oilpalm Market Review, pp 19 -24.

Oilpalm News No. 24 (1980), Oil Palm Market Review, pp 14 - 17.

Oilpalm News No. 19 (1975). Oilpalm Products, Review of National Policies and Plans for Nigeria, pp 18 - 20.

Oils and Oilseeds Journal (1976). Import ans Export Data on Oils and Oil Seeds of India 1975 - 1976Vol XXVIII, pp 15 - 25.

Oilseeds Journal (Jan - June, 1974). Export Data of Oilseeds, Oil and Oilcakes from India During 1973 - 1974, pp 103 - 204.

Oilseeds Journal (March 1974). Weekly Wholesale Prices of Oilseeds, Oils and Oilcakes at Selected Centres in India, Castor Seed Production, pp 40 -41.

Olabisi, O; Lloyd, M. R; Montogmery, T. S (1979). Polymer - Polymer Miscibility, Academic Press New York, pp 1 - 25.

Olayiwola, A. F (1994). Preparation og Fatty Acids from some Vegetable Oils. B.Sc. Project, Chemistry Department, A.B.U. Zaria.

Paqurt, C (1979). IUPAC; Standard Methods for Analysis of Oil, Fats and Derivatives. Pergamon Press New York, pp 52 - 66.

Parker, H. R (1978). An Introduction to Chemical Metallurgy, 2nd edition, Pergamon Press New York, pp 263 - 320.

Paulose, M. M and Chang, S. S (1978). Chemical Reactions Involved in the Deep-fat Frying of Foods VIII,, Characterisation of Non Volatile Decomposition Products of Triolein, J. Amer. Oil Chem. Soc., 55 (4), pp 375 - 380.

Pecsok, L. R; Shields, D. L; Cairns, T; McWilliam, G. T (1976). Modern Methods of Chemical Analysis, 2nd Edition, John Wiley and Sons New York, pp 180 - 191, 210 - 240.

Peerman, (1969). Fatty-acid-based Polyamides, In: Encyclopedia of Polymer Science and Technology Vol 10, John Wiley and Sons New York, pp 520 - 702.

Philips, J. R; Singleton, B (1978). The Determination of Specific Free Fatty Acids in Peanut Oil by Gas Chromatography, J. Amer. Oil Chem. Soc., 55 (2), pp 225 - 227.

Pine, H. S (1987). Organic Chemistry. Mcgraw-Hill International Edition New York, pp 858 - 861, 900.

Pritchard, L J (1975). Refining Palm Oil, Oilpalm News, No. 20, pp 5 - 13.

Pryme, R. H (1975). Dimer Acids, In: Encyclopedia of Chemical Technology Vol 8, John Wiley and Sons New York, pp 820 - 847.

Purseglore, J (1972). Tropical Crops, Monocotyledons, Longman Press London, p 5454.

Rabeks, F. J (1980). Experimental Methods in Polymer Chemistry - Physical Principles and Applications, John Wiley and Sons New York, pp 755 - 780.

Rackis, J. J (1974). Biological and Physiological Factors in Soyabeans, J. Amer. Oil Chem. Soc., 54 (1), p 168A.

Raghunath, R; Ramaswammy (1986). Aqueous Top Coat Based on Cellulose Acetate Phthallate, Leather Science 33 (3), pp 67 - 70.

Raie, M. Y (1976). Location of Ethlenic Bonds in Fatty Alkene Compounds, Pakistan Journal of Scientific and Industrial Research 19 (2), pp 55 - 601.

Ramanamurthy (1975). An Action Plan for Castor in Andhrapradesh, Oilseeds Journal, V (2), pp 1 - 4.

Raw Materials Research and Development Council Pub. 2nd Edition (1990). Raw Materials Sourcing for Manufacturing in Nigeria, a Synthesis of Reports of Ten Techno-Economic Surveys of ten Industrial Sectors in Nigeria. pp 21 - 30.

Reid, B. E (1978). Fats and Oils, Non-edible In: Encyclopedia of Science and Technology, Vol 10, John Wiley Interscience London, pp 203 - 205.

Richardson, E. W; Smith C. J (1974). Synthesis of Novel Alkyl-aryl Polyamides, J. Amer. Oil Chem. Soc., 51 (11), p 500.

Robert, L. R; Lewis, B. S (1974). Fats in Today's Food Supply - Level of Use and Sources, J. Amer. Oil Chem. Soc., 52(11) pp 244 - 250.

Roger, E. R (1975). Fatty Acid Ester Lubricants. J. Amer. Oil Chem. Soc., 52 (12) pp 620 - 625.

Rogers, G. E (1964). The Permeability and Chemical Resistance of Polymers, In: E. Baer Ed; Engineering Design of Plastics, Reinhold Publishing Corp. New York, pp 102 - 130.

Sarkar, K. T (1991). Theory and Practice of Leather Manufacture; The Author, Mondras pp 600 - 628.

Scott, A (1985).Natural Resources Economics, Edited, Clarendon Press Oxford, pp 15 - 20, 173 -195.

Selke, E; Rohwedder, w. K; Dulton, H. J (1977). Volatile Components from Triolein Heated in Air, J. Amer. Oil Chem. Soc., 54 (2), pp 62 - 65.

Sharphouse, J. H (1989). Leather Technician Handbook, Leather Producers Association, London, pp 373 - 424.

Simpson, T. D; Hagemann, J. W (1975). Crystallographic Study of Tritetracosanoin, J. Amer. Oil Chem. Soc., 52 (8), pp 423 - 425.

Simpson, T. D; Miwa, T. K (1977). X-ray Study of Hydrogenated Jojoba Wax, J. Amer. Oil Chem. Soc., 54 (2), pp 54 - 57.

Sindagi, S. S (1974). Perfo. mance of Some Selections in Castor (Ricinus communis), Oilseeds Journal IV, p31.

Skipski, V. P and Barclay, M (1969). TLC of Lipids. In: Methods in Enzymology Vol 14, Lipids ed. J. M. Lowenstein, Academic Press New York, pp 531 - 598.

Slade, E Philip Jr (1973). Polymer Molecular Weights Part I, Marcel Dekker Inc New York, pp 1 - 7, 9 - 12, 161 - 163.

Sparnanij, L. D; Vander-Vossen, H. M (1980). Developments in Oilpalm Breeding: A Re-appraisal of Present and Future Breeding Procedures in the Light of Results from the Nigerian Institute for Oil Palm Research Breeding Programme, Oilpalm News No. 24, pp 4 - 10.

Stepek, J. Peerman A (1987). Polymer as Materials for Packaging, Ellis Horwood Ltd London, pp 192 - 195, 270 - 276, 312 - 315.

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Stocchi, E (1990). Industrial Chemistry Vol I, Market Cross House London, pp 23 - 38, 234 - 280, 438 - 490.

Sumrell, G; Mod, R. R; Magne (1978). Anti Microbial Activity of Some Fatty Acid Derivatives, J. Amer. Oil Chem. Soc., 55 (4), pp 395 - 397.

Sunmonu, O. K (1994). An Introduction to Polymer Science and Technology, Vol I, ABU Press Ltd Zaria, pp 10 -14.

Sutherland, J. P; Varnam, A. H; Evans, M. G (1986). Food Quality Control; Wolfe Pub. Ltd London, pp 126 - 130.

Swamy, M. P; Bangaruswammy, S; Rao, J. B (1984). Studies on the Fixation of Acid Dye in Leathers Tanned with (a) Straight Ti, Cr, Al and Syntan and (b) Combination of them, Part III, Leather Science 13 (12) p 343.

Swern, D; Mattil, F. K; Norris, A. F and Stirton, J. A (1964).Barley's Industrial Oil and Fat Products. 3rd Edition Interscience Publishers New York, pp 637 - 972.

Syed, M A (1976). Determination of Fat Content in Ghee Hydrogenated Oils, Butter and Powdered Milk by IR Spectra, Pakistan Journal of Scientific and Industrial Research 19 (1), pp 29 - 31.

Szymanski, A. H (1964) Interpreted IR Spectra Vol I; Plenum Press New York, pp 12 - 37.

Szymanski, A. H (1964). Interpreted IR Spectra Vol II, Plenum Press New York, pp 27 - 34, 31, 47.

Taylor, A. M; Jurgen Ltd (1973). Palm Oil Crystallisation and Fractionation, Oilpalm News No. 15, pp 18 - 22.

Tedder, J. M; Nechvatal, A; Jubb, A. H (1975). Basic Organic Chemistry Part 5, Industrial Products; John Wiley and Sons New York, pp 11 - 40.

Terill, R. L, Ault, W. C (1975) Castor Oil, In: Encyclopedia of Chemical Technology, Speneer Kellog and sons Inc New York, Vol 4, pp 529 - 533.

The Nigerian Palm produce Board, Calabar Information Sheet (1982) pp.2 - 7.

Thompson, T. M (1983). Dye House Laboratory Practice, Society of Dyers and Colorists, Bradford, pp 64 - 66.

Thorpe's Dictionary of Applied Chemistry, Fourth Edition, (1975), Vol IX, Oils and Fats John Wiley and Sons New York, pp 59 - 64.

Thorstensen C. T (1993). Practical Leather Technology, Krieger Pub. Comp Ithaca, pp 150 - 175.

Twitchell, John; Weir Tony (1990). Renewable Energy Resources, E and F.N, Spon Bonn, pp 3 - 151.

Vogel, A. J (1971). Elementary Practical Organic Chemistry, Part III Quantitative Organic Analysis, Seventh edition, Longman Ltd London, pp 657 -768.

Walker, S; Straw, H (1964). Spectroscopy Vol 2, Chapman and Hall London, pp 125 - 127.

Warner, K (1978). Flavour, Score Correlation with Pentanal and Hexanal Contents of Vegetable Oil, J. Amer. Oil Chem. Soc., 55 (2), pp 252 - 256.

Wells, F. A (1970). Studies in Industrialisation, Pergamon Press New York, pp 26 - 54, 77 - 91.

Wood, D. E, Taylor, A. J (April, 1958). The Preparation of Aluminum Soaps by continuous Process 1. Aluminum Laurate, J. App. Chem. B, pp 237 - 251.

Appendix 1: Sample P_1 IR spectral analysis (palm oil whole (mixed) fatty acids).

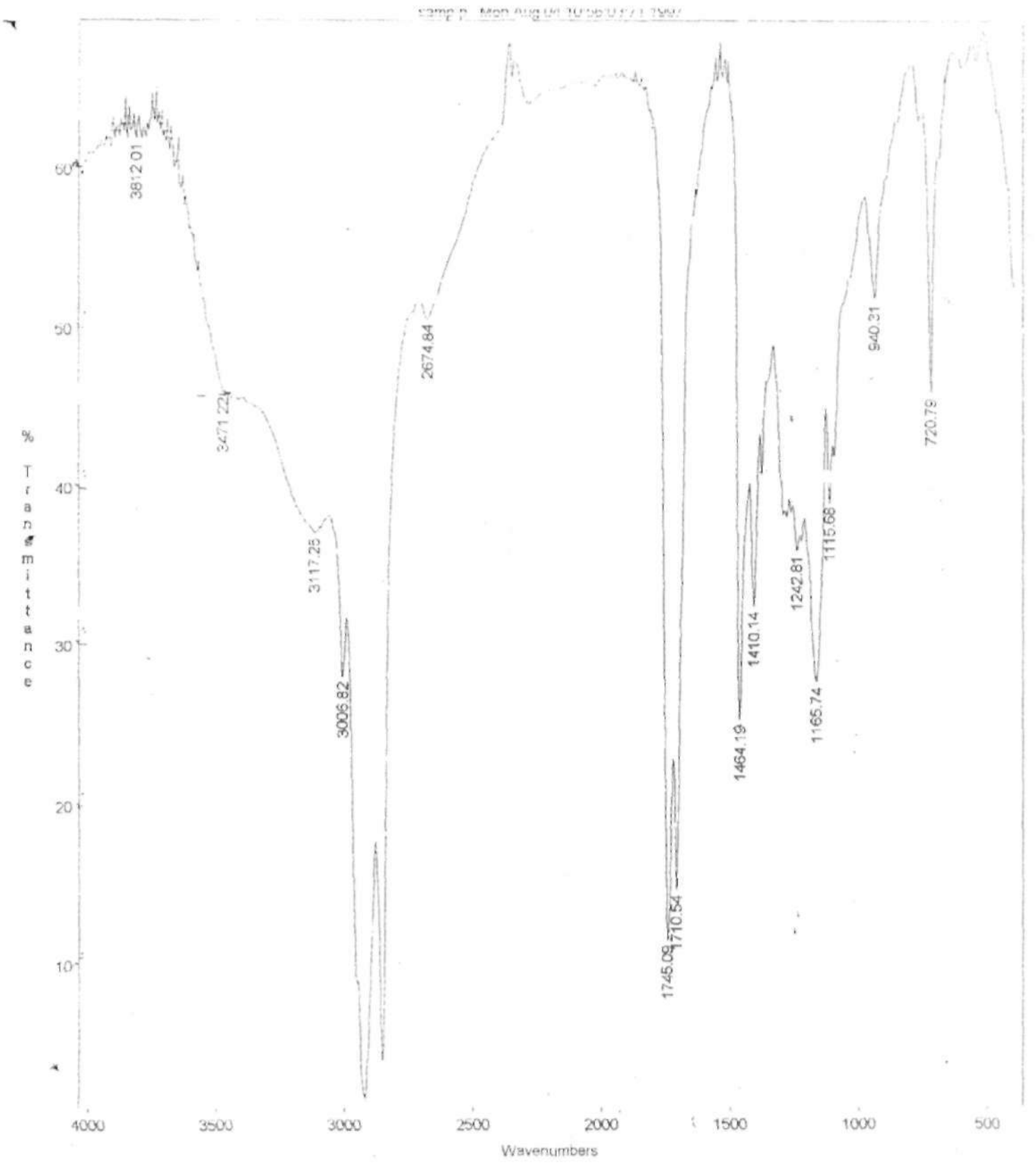
Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3471.2	45.94	0.3378	Broad	OH group is bonded through H-bonding (section 2.3.1) as for carboxylic
	3117.25	36.60	0.4362	Broad	acids (Appendix I). This lowers the absorption frequencies from the
-O-H (δ)	940.31	51.65	0.2869	Sharp	normal 3600 - 3560 cm^{-1}. The band at 940.31 cm^{-1} confirms the presence of carboxylic acids (Walker, 1964; Kemp, 1991)
C-H (V)	3006	28.3	0.5482	Sharp	C-H (V) above 3000^{-1} indicates presence of olefinic hydrocarbons and
	2900	1.65	1.7825	Sharp	below this frequency shows the presence of saturated hydrocarbons
	2844.39	4.95	1.3054	Sharp	(Appendix I) which means both saturated and unsaturated fatty acids are
C-H (δ)	1464	25.94	0.5860	Sharp	present (Szymanski, 1964).
-C=O (V)	1745.09	11.65	0.9337	Sharp	Presence of the normal carbonyl absorption frequency of the -COOH
-C-O (V)	1320	41.65	0.3804	Narrow	group of the fatty acids (Appendix I; Pecsok et. al., 1976).
-C=C- (V)	1710.5	14.95	0.8254	Sharp	The strongly intense band is due to (-C=C) olefinic unsaturation, a little above the normal 1650 - 1670 cm^{-1} as a result of antisymmetric stretching vibration (Szymanski, 1964).

From the above analysis, both saturated and unsaturated fatty acids are present in the mixed fatty acids

Key/note: IR = Infra-red
(V) = Stretching vibration
(δ) = Bending vibration
Absorbance = log 1/transmittance.

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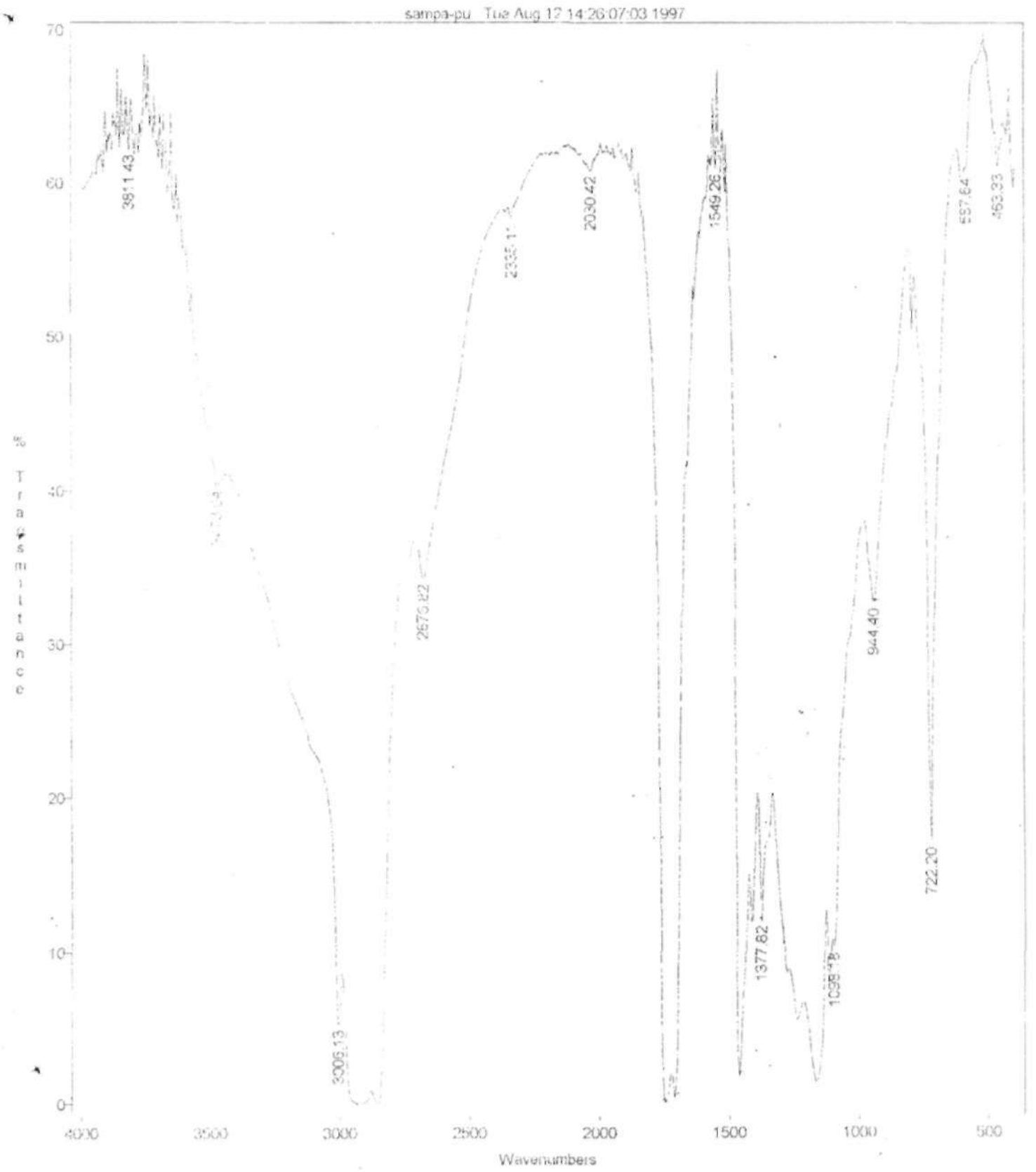
SAMPLE P1


3812.01
3471.22
3117.25
3006.82
2674.84
1745.09
1710.54
1464.19
1410.14
1242.81
1165.74
1115.68
940.31
720.79
%Transmittance
60
50
40
30
20
10
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

Appendix 2: Sample P_2 (palm oil unsaturated fatty acids) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3473.64	40.33	0.3944	Sharp	H-bonding is present as in P_1. However, the bond at 3117.25 in P_1 is
-O-H (δ)	9414.4	33.3	0.7776	Sharp	absent here suggesting lesser H-bonding in P_2 than in P_1 (Pecsok et. al., 1976).
C-H (V)	3006	5.28	1.2774	Broad	Absorbances here are higher than the corresponding ones in P_1
	2900	0.33	2.4815	Broad	suggesting presence of unsaturated centres meaning that separation of
	2844.39	0.29	2.5784	Broad	unsaturated fatty acids from the mixed fatty acids has been effected
C-H (δ)	1460	2.64	1.5784	Sharp	(section 2.12.3).
-C=O (V)	1745	0.33	2.4815	Sharp	Absorbances are higher than corresponding ones in P_1 suggesting higher
-C-O (V)	1377.8	10.33	0.9859	Sharp	presence of long chain unsaturated fatty acids (Nakanishi, 1964).
-C=C- (V)	1710.5	0.66	2.1805	Sharp	Absorbance here is almost triply higher than corresponding one in P_1,
					confirming that the separation of unsaturated fatty acids from the mixed fatty acids (P_1) has been reasonably achieved by urea fractionation (section 2.13.1; Table 4.5; Appendix I).

SAMPLE P2


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70
60
50
40
30
20
10
0
T r a n s m i t t a n c e
3911.43
2930.42
2675.22
1549.26
1377.82
1098.18
944.40
722.20
497.64
463.93
3306.13
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

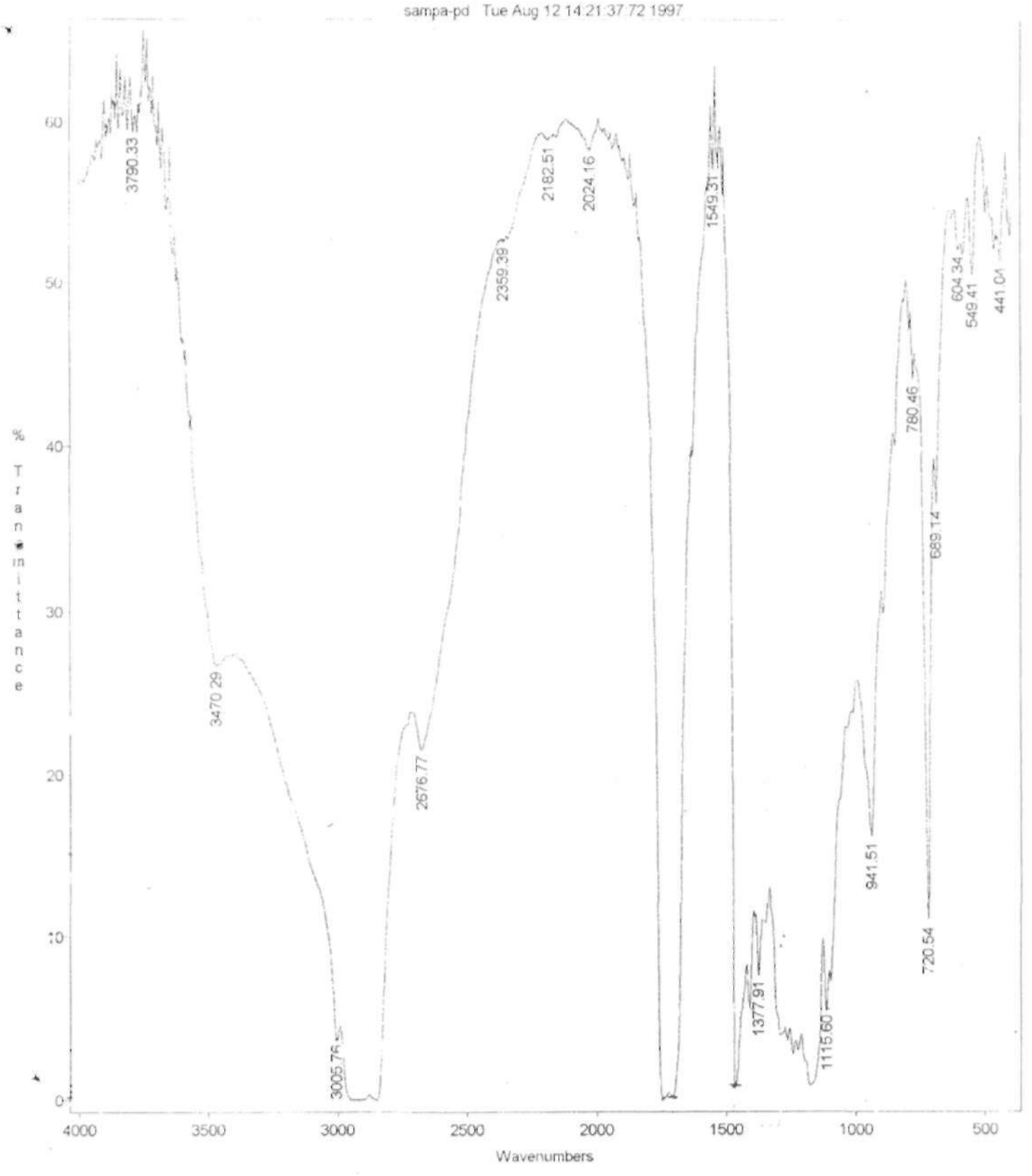
Appendix 3: Sample P_3 (palm oil dimers at 2 hrs) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3470.29	26.6	0.5775	Narrow	The absorbances are higher than corresponding ones in P_1 and P_2
-O-H (δ)	941.51	15.25	0.8167	Sharp	indicating loss of H-bonding and intermolecular associations, as dimerisation proceeds (Syed, 1976).
C-H (V)	3005.76	3.33	1.4776	Sharp	Absorbances are slightly higher than the corresponding ones in P_2 and
	3000	0.33	2.4815	Broad	largely fall between 2900 - 3000 cm^{-1} suggesting the formation of
	2900	0.33	2.4815	Broad	saturated linkages (Appendix I). Furthermore, the band area above 3000
C-H (δ)	1497.9	1.65	1.7825	Sharp	cm^{-1} has similarly reduced from $P_2 \rightarrow P_3$ indicating a reduction in the amount of unsaturation (Gunstone, 1964).
-C=O (V)	1720	0.297	2.5272	Sharp	Absorbances have increased from $P_2 \rightarrow P_3$ correspondingly, however, the
-C-O (V)	1377.91	8.250	1.0836	Sharp	absorption frequency of C=O (V) has shifted from 1745 cm^{-1} for P_2 to 1720 for P_3. This shift may be due to the positive inductive effects of OH group on C=O as H-bonding has been loss as mentioned above (Kemp, 1991).
-C=C- (V)	1700	0.825	2.0836	Sharp	Decrease in absorbance from $P_2 \rightarrow P_3$. This suggests that dimerisation is occurring at the double bonds, hence the -HC=CH- group has been reduced as the reaction progresses (Pecsok et. al., 1976).



SAMPLE P3

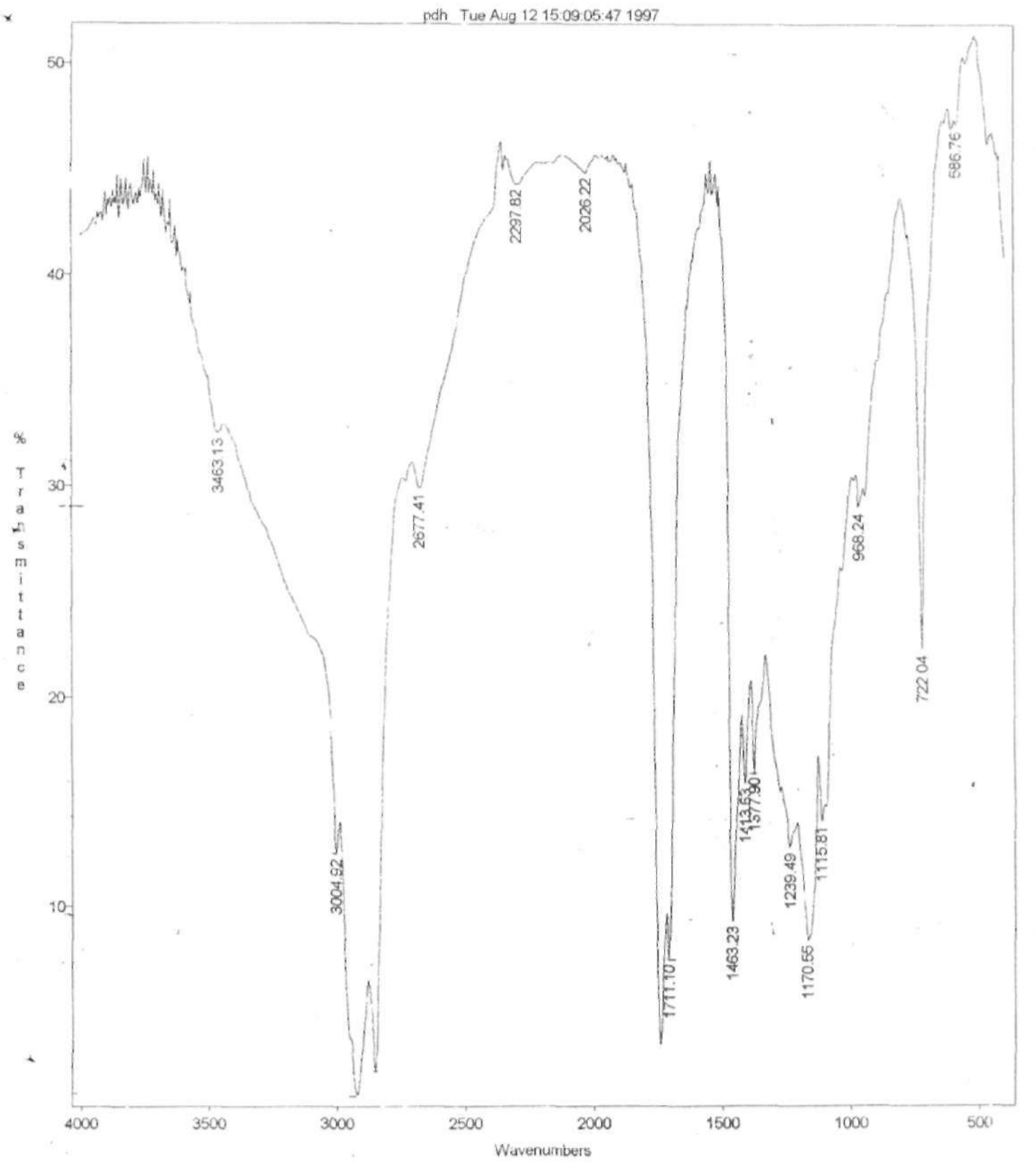
sampa-pd Tue Aug 12 14:21:37.72 1997



Appendix 4: Sample P_4 (palm oil dimers at 4 hrs) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3463	32.50	0.4882	Narrow	Absorbance has dropped slightly from $P_3 \rightarrow P_4$, especially for the OH (V) band due to vibrational couplings as dimerisation progressed from $P_3 \rightarrow P_4$. This led to drop in frequency for C-H (V) band from $P_3 \rightarrow P_4$ and an increase for OH (δ) band from $P_3 \rightarrow P_4$ (Reger, 1974).
-O-H (δ)	968.24	29.0	0.5376	Narrow	
C-H (V)	3004 92	12.5	0.9031	Sharp	Absorbances which decreased from $P_3 \rightarrow P_4$ are largely below 3000 cm^{-1} frequency (Appendix I) which suggests that saturated units have been formed (Pecsok et. al., 1976).
	2990.00	0.5	2.3010	Sharp	
	2800	2.0	1.6989	Sharp	
C-H (δ)	1463.25	9.25	1.0339	Broad	
-C=O (V)	1720.00	3.0	1.5229	Sharp	Absorbance for C=O (V) decreased from $P_3 \rightarrow P_4$ suggesting a minor loss or decrease in the positive inductive effects of the OH group on C=O, however, the frequencies remain the same.
-C-O (V)	1377.9	16.0	0.7959	Sharp	
-C=C- (V)	1711.10	17.0	0.7696	Sharp	Absorbance has drastically dropped from $P_3 \rightarrow P_4$. This supports dimerisaton reaction occurring at the unsaturated centres, which are being loss (Kemp, 1991).

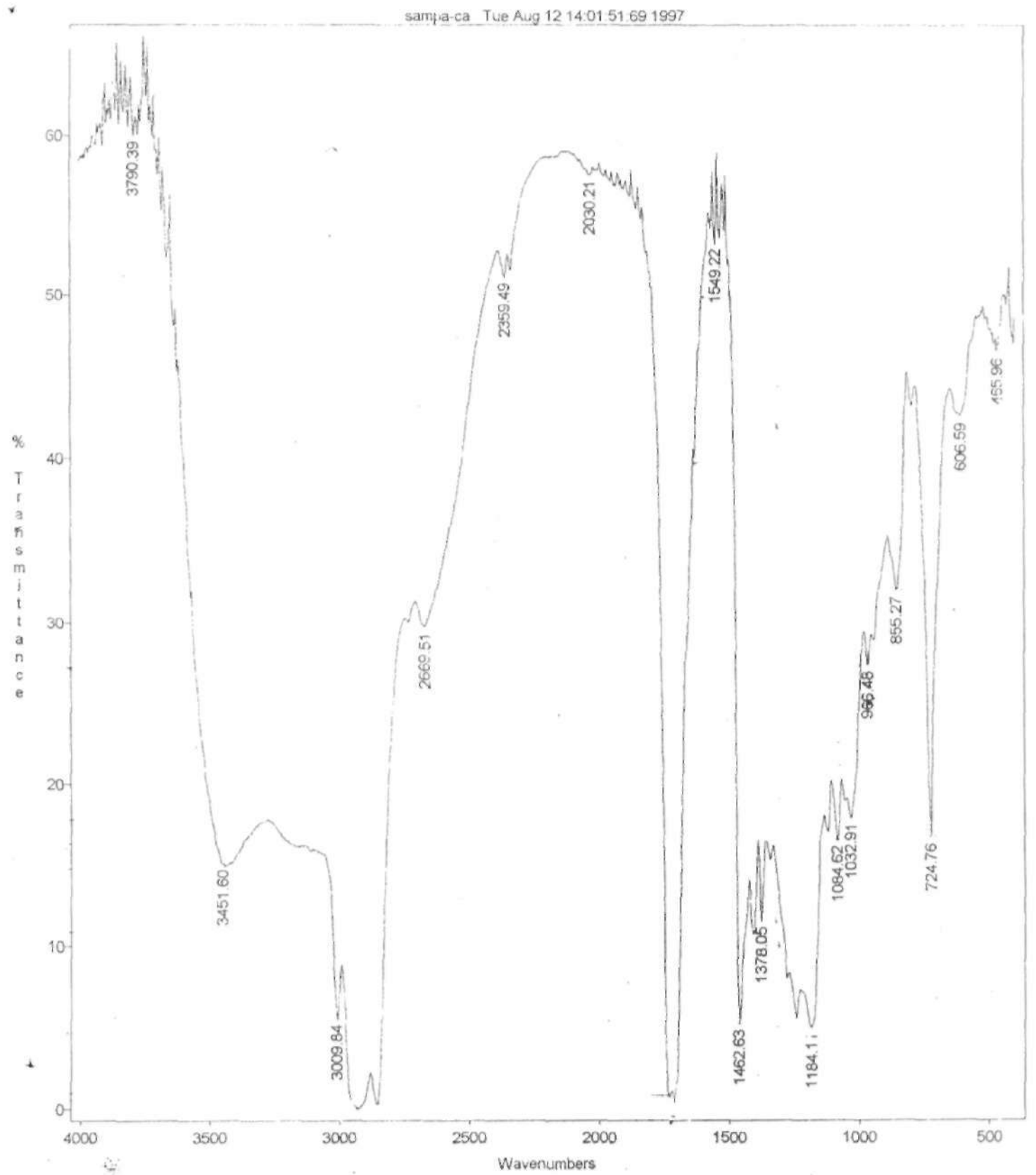
SAMPLE P4


pdh Tue Aug 12 15:09:05:47 1997
%Transmittance
50
40
30
20
10
3463.13
3004.92
2677.41
2297.82
2026.22
1711.10
1463.23
1413.63
1377.90
1239.49
1170.55
1115.81
968.24
722.04
586.76
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

Appendix 5: Sample C_1 (Castor oil mixed fatty acids) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	*Remarks*
-O-H (V)	3451.60	14.95	0.8254	Broad	OH group is bonded through H-bonding and vibrational couplings and
-O-H (δ)	966.27	27.26	0.5645	Sharp	molecular associations existed thereby lowering the vibrational frequencies a bit compared to P_1. However, the band areas are higher than the corresponding ones in P_1 suggestive that there are more OH groups in this sample, that is, OH groups due to COOH groups and that on carbon-12 of ricinoleic acid the principle acid of castor oil (Appendices I and J).
C-H (V)	3009.84	5.94	1.2262	Sharp	Presence of olefinic double bonds (Szymanski, 1964)
	3000 - 2840	0.33	2.4815	Sharp	Presence of long chain hydrocarbon of methylene linkages.
C-H (δ)	1462.63	5.28	1.2774	Sharp	
-C=O (V)	1710.0	0.99	2.0044	Sharp	Carbonyl absorption frequency reduced due to the positive inductive effects
-C-O (V)	1378.1	11.98	0.9215	Sharp	of OH groups and other vibrational couplings as explained for P_3 and P_4 samples, earlier.
-C=C- (V)	1700	0.66	2.1805	Sharp	Antisymmetric stretching of C=O. However, high absorbance indicates presence of high unsaturation (Appendix I).
Other complementary	1410.86	10.99	0.9590	Sharp	
bands	1184.11	4.95	1.3054	Sharp	

SAMPLE C1


sample-ca Tue Aug 12 14:01:51.69 1997
% Transmittance
Wavenumbers
4000
3500
3000
2500
2000
1500
1000
500
0
10
20
30
40
50
60
3790.39
3451.60
3009.84
2669.51
2359.49
2030.21
1549.22
1462.63
1378.05
1184.1
1084.62
1032.91
966.48
855.27
724.76
606.59
465.96

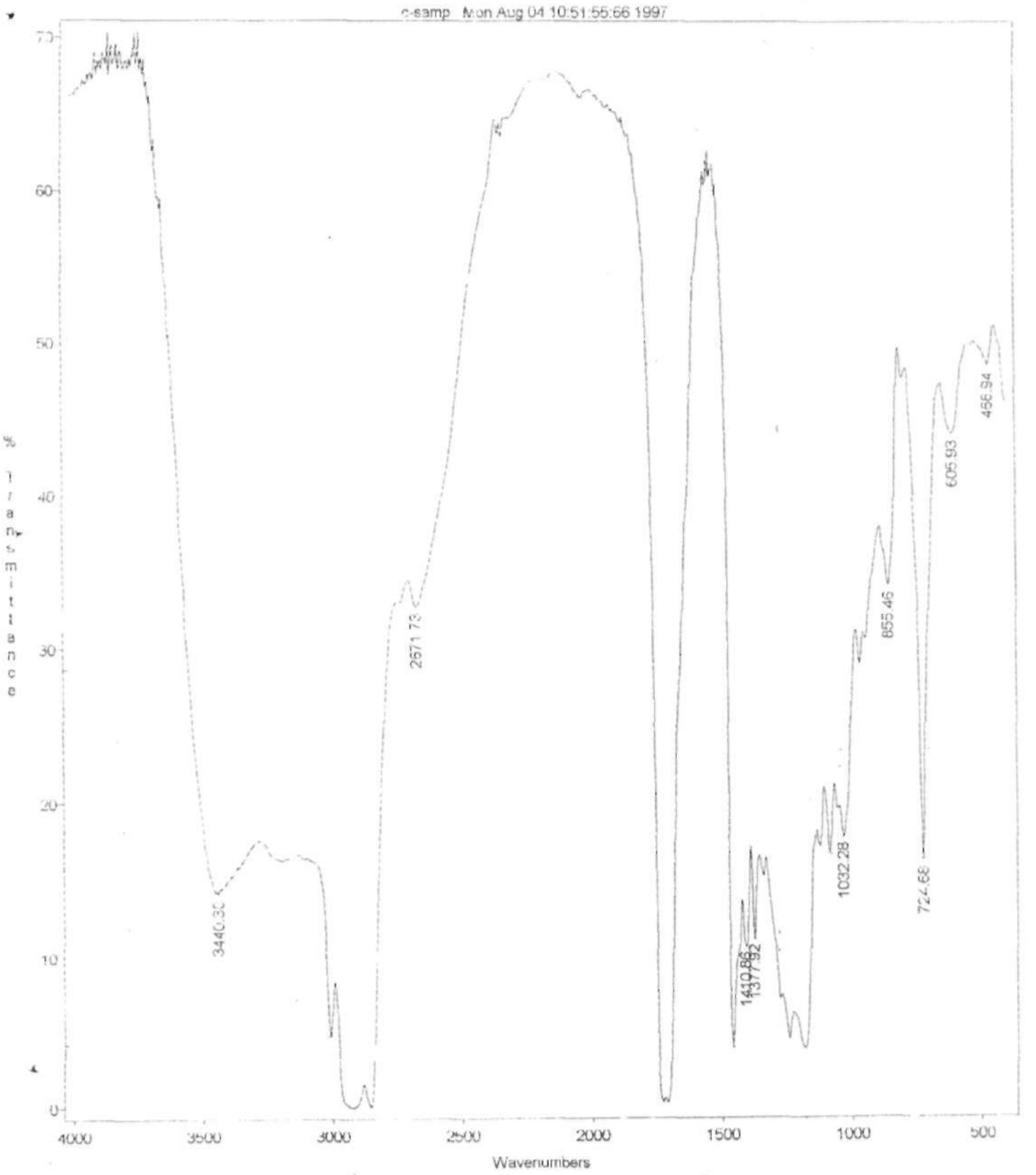
Appendix 6: Sample C_2 (Castor oil unsaturated fatty acids) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3440.3	13.96	0.8551	Sharp	As explained for C_1, however, absorbances remain essentially constant
-O-H (δ)	966.48	28.25	0.5489	Sharp	due to the near monomeric nature of the oil (Appendix H).
C-H (V)	3009.8	4.29	1.3675	Sharp	Absorbances increase slightly over those of corresponding bands in C_1
	2900 - 2840	0.297	2.5272	Sharp	suggestive of higher unsaturation.
C-H (δ)	1497	3.90	1.4023	Sharp	
-C=O (V)	1720	0.99	2.0044	Sharp	Same as for C_1 corresponding bands.
-C-O (V)	1377.92	11.32	0.9462	Sharp	
-C=C- (V)	1700	0.66	2.1805	Sharp	Same as for C_1 corresponding band as castor oil contains about 98% unsaturation (Appendix H).
Other complementary	1410.86	10.33	0.9859	Sharp	Absorbances here have slightly increased compared to corresponding ones
bands	1184.11	3.63	1.4401	Sharp	in C_1.

Note: As castor oil contains a very high level of unsaturation, urea fractionation removed only about 2% being amount of saturation in the mixed fatty acids (Appendix H)

University of Nairobi

SAMPLE C2


c-samp Mon Aug 04 10:51:55:66 1997
%Transmittance
70
60
50
40
30
20
10
0
3440.30
2671.73
1410.86
1377.92
1032.28
855.46
724.68
605.93
456.94
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

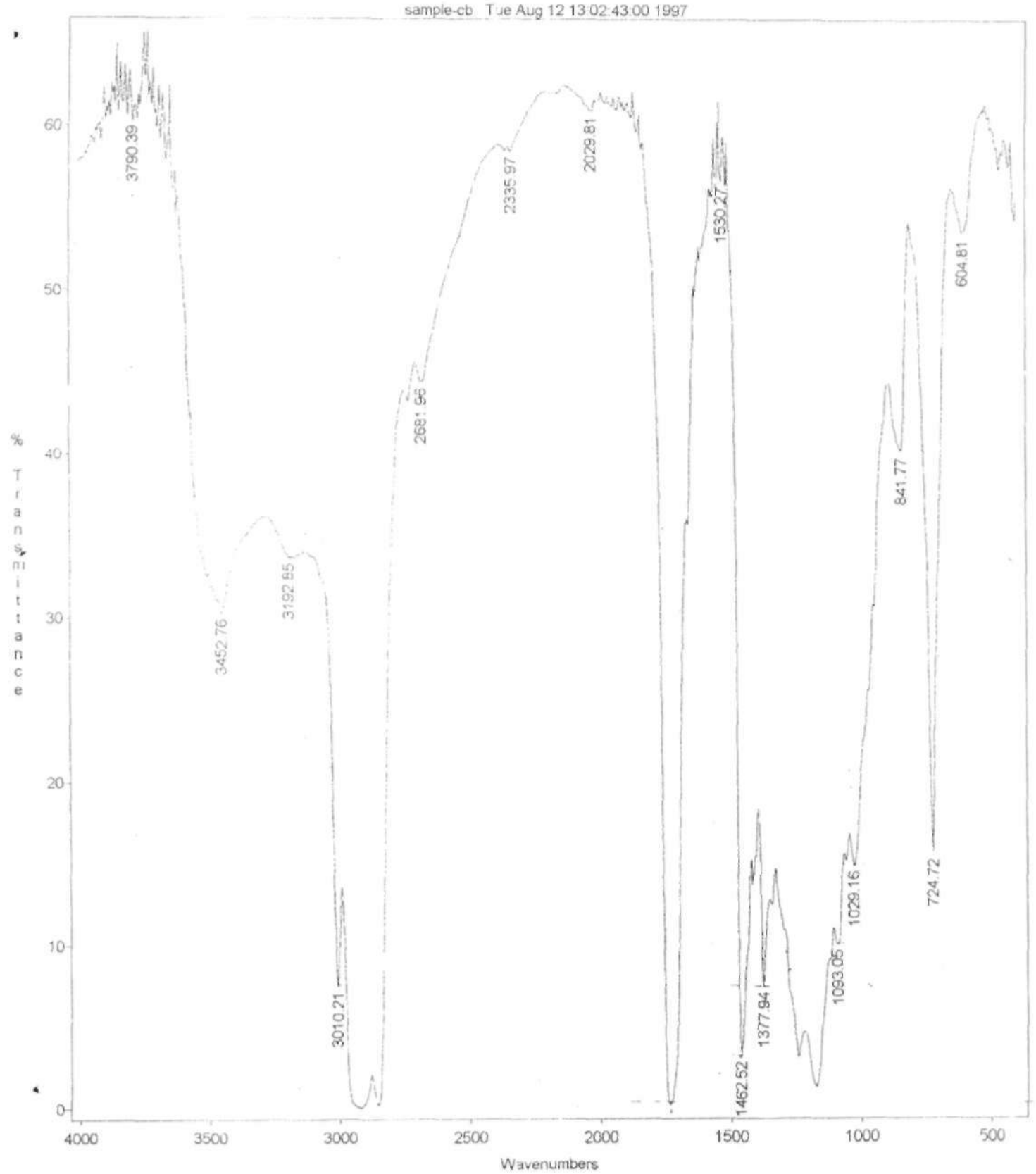
Appendix 7: Sample C_3 (Castor oil dimers at 2 hrs) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3452.76	30.26	0.5191	Sharp	Absorbances have dropped due to molecular association and vibrational couplings, as explained for P_3 samples corresponding bands.
	3192.85	33.64	0.4733	Broad	
-O-H (δ)	-	-	-	-	Furthermore, the amount of OH character has reduced as a result of formation of estolides (equation 2-0; Naughton, 1974).
C-H (V)	3010.25	7.59	1.1198	Sharp	Generally absorbances have increased when compared to corresponding ones in C_2 which indicates that more saturated compounds have been formed, evidenced by higher number of bands occurring below 3000 cm^{-1} (saturated alkane bands as explained for P_3: Appendix I).
	2900.00	0.165	2.7825	Broad	
	2840.00	0.165	2.7825	Sharp	
C-H (δ)	1462.52	3.33	1.4776	Sharp	
-C=O (V)	1720	0.66	2.1805	Sharp	Again absorbances have increased correspondingly from C2 → C_3 and the positive inductive effects further increased as explained for P_3 corresponding sample bands
-C-O (V)	1377.94	8.58	1.0665	Sharp	
-C=C- (V)	1640	36.27	0.4405	Weak	Absorbances have decreased more than the corresponding one in C_2. suggestive that reactions have occurred at the double bonds, supporting evidence for dimerisation as mentioned earlier.
Others	1410.8	13.8	0.8601	Sharp	
	1184.11	1.32	1.8794	Sharp	



SAMPLE C 3

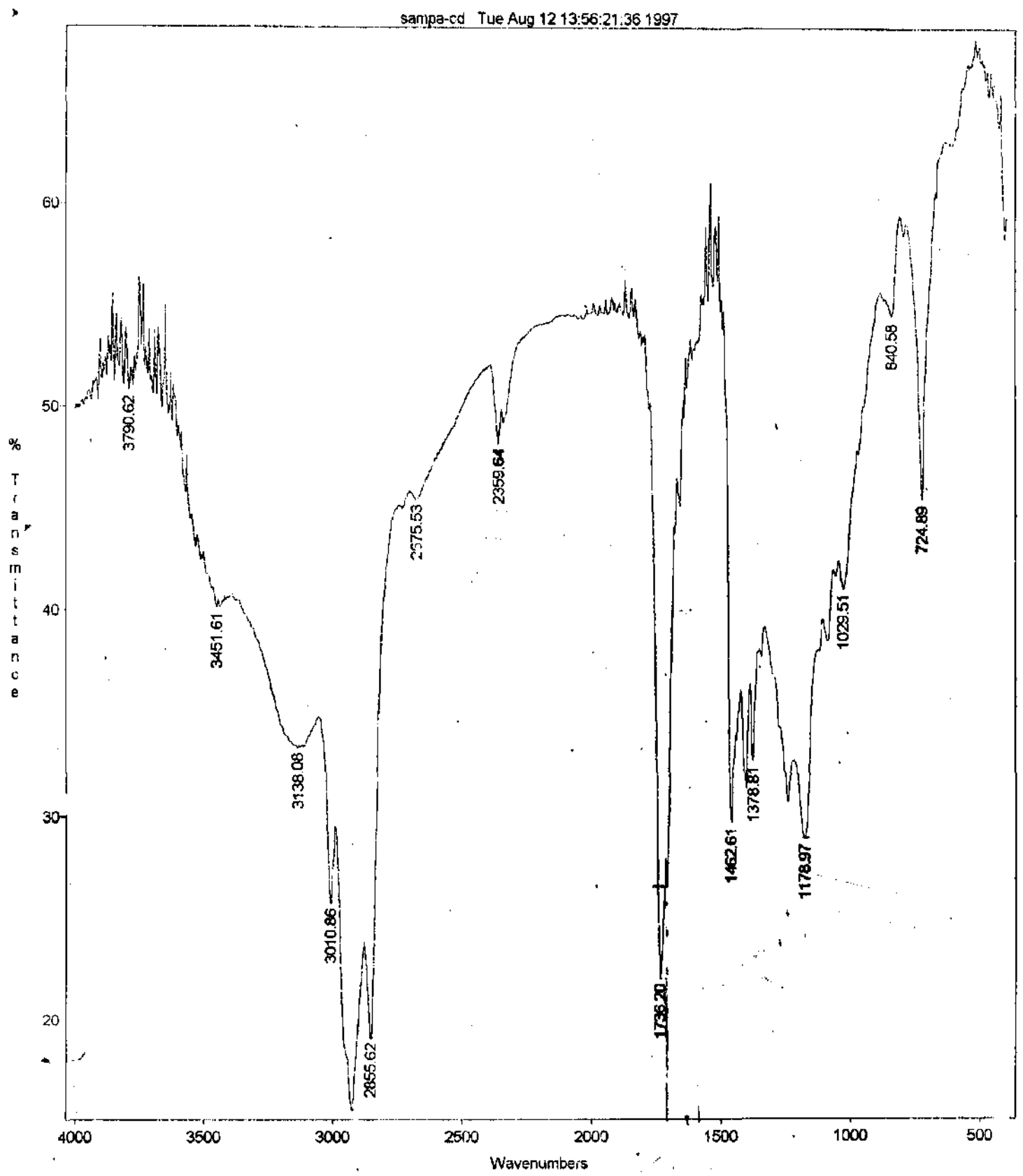
sample-cb Tue Aug 12 13:02:43:00 1997



Appendix 8: Sample C_4 (Castor oil dimers at 4 hrs) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3451.61	40.0	0.3979	Narrow	Absorbances generally dropped from $C_3 \rightarrow C_4$ as the OH- character of the
	3138.08	33.25	0.4782	Broad	acid has been reduced due to formation of estolides mentioned for C_3.
-O-H (δ)	-	-	-	-	
C-H (V)	3010.84	25.75	0.5892	Sharp	Absorbances have dropped appreciably compared to corresponding ones
	2900.00	15.5	0.8097	Sharp	in C_3 suggestive of higher amount of saturation (alkane type), supporting
	2855.6	19.0	0.7213	Sharp	dimerisation reaction at the double bonds, since most bands are below
C-H (δ)	1462.52	30.0	0.52213	Sharp	3000 cm^{-1} (Appendix I).
-C=O (V)	1736.52	22.50	0.6478	Sharp	Absorbances here have decreased compared to corresponding ones in C_3,
-C-O (V)	1378.81	31.75	0.4983	Sharp	suggesting that the estolides formed have increased in amount and
-C=C- (V)	1700	26.75	0.5726	Sharp	therefore OH group positive inductive effects have been lost appreciably. Absorbance for this frequency has correspondingly increased slightly over that of C_3. This could be attributed to dimerisation occurring by isomerisation and Diels-Alder addition, and or by the polar reaction (equations 2-9, 2-12 respectively; section 2.14.1). However, this was not confirmed by measurement of iodine values (Appendix K)

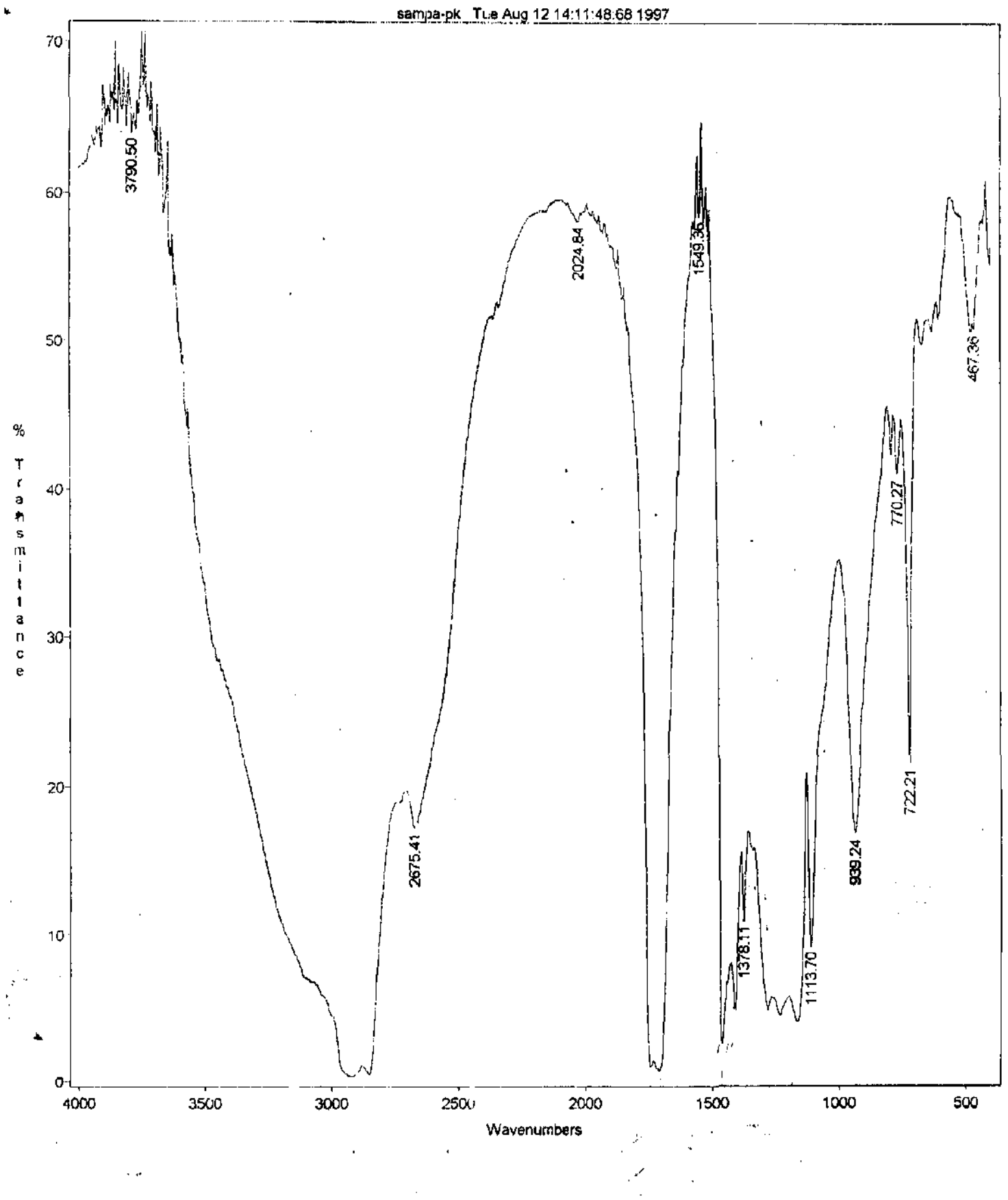
SAMPLE C4


sampa-cd Tue Aug 12 13:56:21.36 1997
% Transmittance
60
50
40
30
20
3790.62
3451.61
3138.08
3010.86
2855.62
2575.53
2359.64
1736.20
1462.61
1378.81
1178.97
1029.51
840.58
724.89
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

Appendix 9: Sample PK_1 (Palm kernel oil mixed fatty acids) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3100	7.0	1.1549	Blunt	OH group is bonded as explained for P_1 and C_1 bands
-O-H (δ)	939.2	17.35	0.7601	Sharp	
C-H (V)	3010	0.525	2.2798	Broad	Saturated and unsaturated fatty acids are present as explained for P_2, C_2
	2840	0.56	2.1805	Sharp	corresponding bands.
C-H (δ)	1460	2.45	1.6108	Sharp	
				Sharp	
-C=O (V)	1740	1.05	1.9788	Sharp	Normal carbonyl (C=O) absorption band of the -COOH group of fatty
-C-O (V)	1373	11.05	0.9566	Sharp	acids.
-C=C- (V)	1700	0.70	2.1549	Sharp	Antiymmetric stretching frequency for -C=C- as explained for P_1 and C_1
					corresponding bands.

SAMPLE PK1

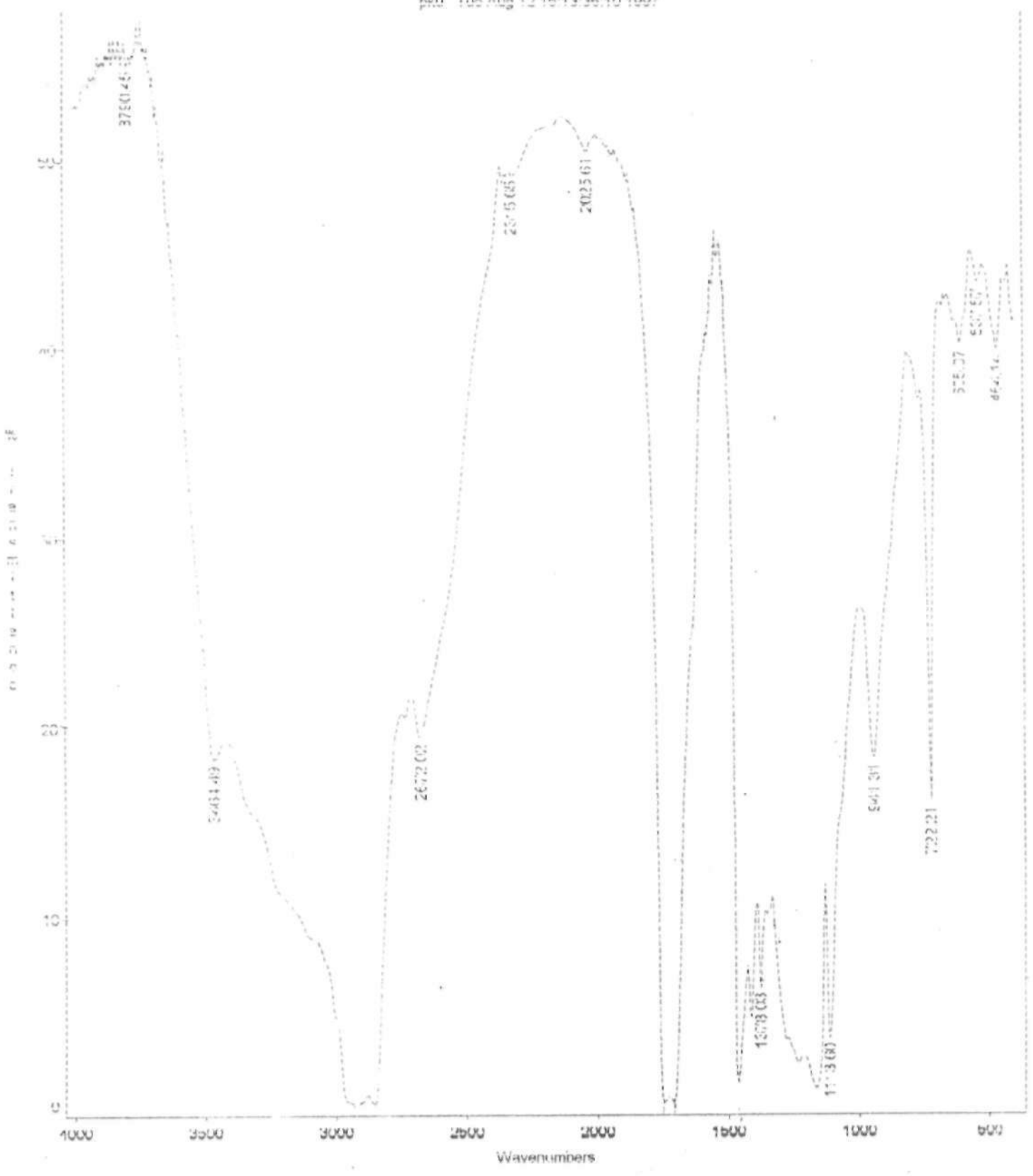

sampa-pk Tue Aug 12 14:11:48.68 1997
% Transmittance
70
60
50
40
30
20
10
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
3790.50
2675.41
2024.84
1549.36
1378.11
1113.70
939.24
770.27
722.21
467.36

Appendix 10: Sample PK_2 (Palm kernel oil unsaturated fatty acids) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3464.5	18.70	0.7282	Sharp	Absorbances here have dropped correspondingly from $PK_1 \rightarrow PK_2$ suggestive
-O-H (δ)	941.3	18.99	0.7215	Sharp	of more H-bonding.
C-H (V)	3100 - 3010	8.99	1.0462	Narrow	A significant portion of the band area lies above 3000 cm^{-1} suggesting C-H
	2900	0.286	2.5436	Sharp	(V) of olefins when compared to PK_1 corresponding bands (Appendix I;
	2840	0.286	2.5436	Sharp	Pecsok et. al., 1976).
C-H (δ)	1460	1.16	0.9356	Sharp	
-C=O (V)	1740	0.29	2.5376	Sharp	Slight increases in absorbances than corresponding PK_1 bands, resulting
-C-O (V)	1378.1	6.67	1.1759	Sharp	from positive inductive effects of OH group of -COOH group, on the carbonyl carbon as explained for P_2 corresponding sample bands.
-C=C- (V)	1700	0.29	2.5376	Sharp	Much higher absorbance than that of corresponding band in PK_1, indicating higher amount (presence) of unsaturated centres. Therefore supporting the fact that urea fractionation has been appreciably achieved (section 2.12.3; Table 4.5).

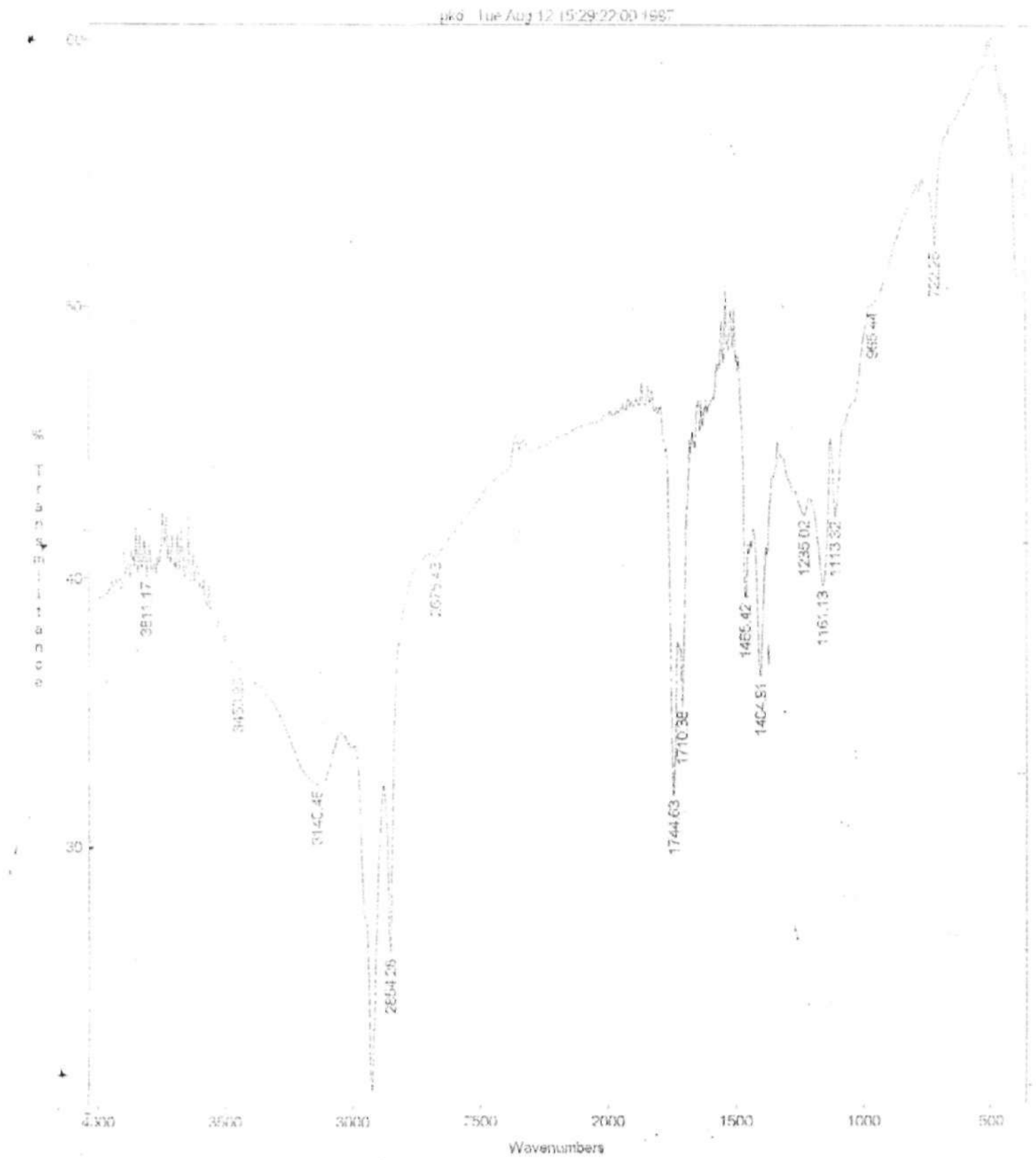
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SAMPLE PK2


3750.148
2925.685
2025.161
2672.002
1378.003
941.391
732.221
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

WebIR/ST Report :
Name :
Date :
Sample :
Comments :

SAMPLE PK3

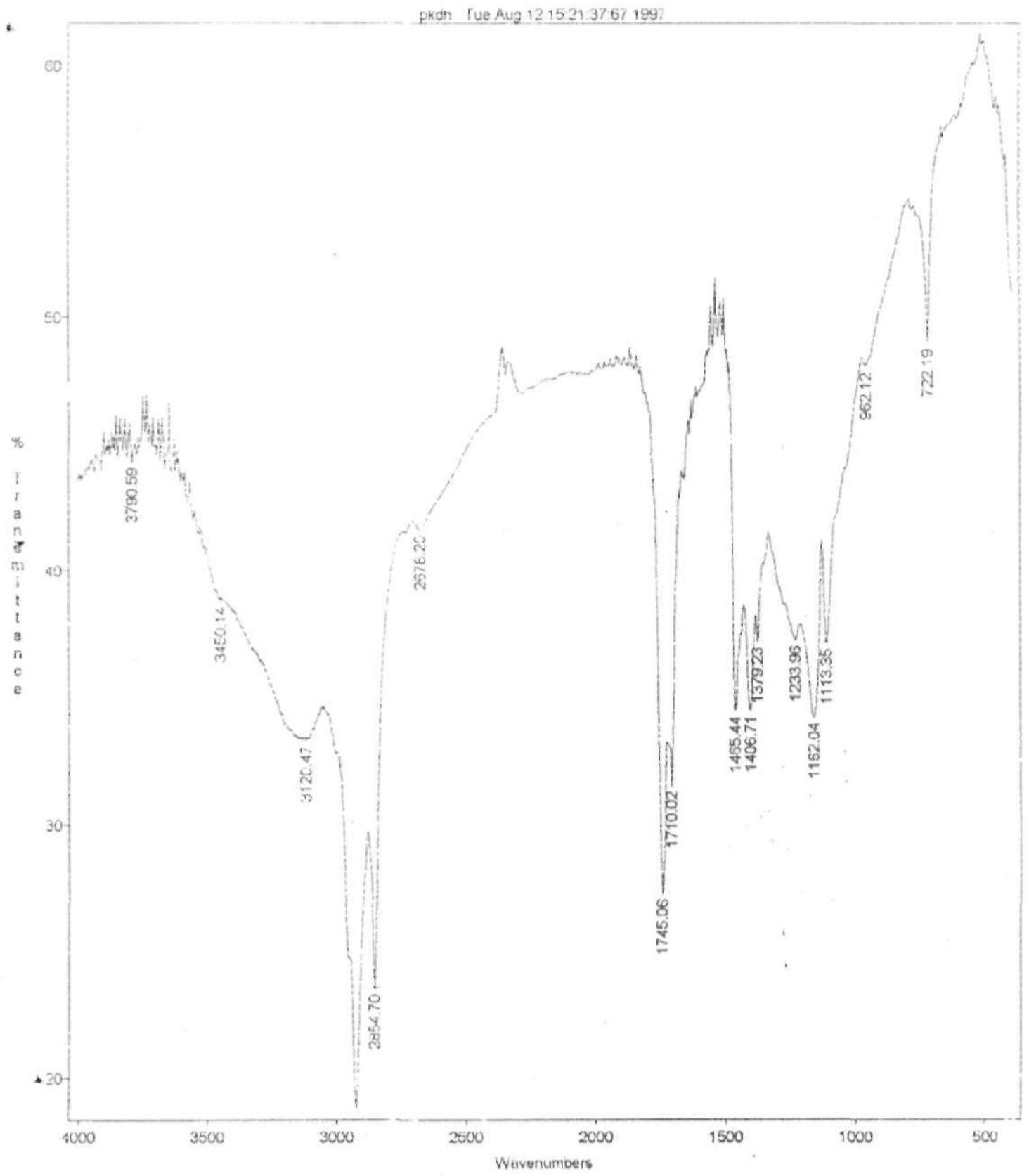


Appendix 12: Sample PK_4 (Palm kernel oil dimers at 4 hrs) IR spectral analysis

Functional group	Frequency (cm^{-1})	% Transmittance	Absorbance	Shape	Remarks
-O-H (V)	3120.5	33.3	0.4776	Broad	Absorbances remain significantly constant as in PK_3; reasons as
-O-H (δ)	962.12	47.1	0.3269	Narrow	explained for the corresponding bands in PK_3.
		19.17			
C-H (V)	2920	19.17	0.7173	Sharp	Slight increases in absorbances compared to corresponding bands in PK_3,
	2854.7	23.54	0.6282	Sharp	hence more linkages have have formed or more saturated compounds
C-H (δ)	1465.4	34.8	0.4584	Sharp	have been formed; reasons, as explained for PK_3 bands.
				Sharp	
-C=O (V)	1745.1	27.3	0.5638	Sharp	Slight increases in absorbances suggestive of slight positive inductive
-C-O (V)	1379.2	36.9	0.4329	Sharp	effects of OH group as explained for P_4. C_e corresponding bands or less vibrational couplings.
-C=C- (V)	1710.02	32.08	0.4938	Sharp	The absorbance here has slightly increased compared to corresponding PK_3 band. This could be attributed to dimerisation occurring by the polar reaction or isomerisation and Diels-Alder addition (equations 2-9 and 2-12 respectively; section 2.14.1). However, this was not confirmed by measurement of iodine values (Appendix K).

Name:
Date:
Sample:
Comments:

SAMPLE PK 4



Appendix 13: Variations of acid values of palm oil dimer acid with time of polymerisation

Time (min)	Vol(cm^3) of water released	Vol (cm^3) 0.8 M KOH	Acid values mg KOH/g acid dimer
0	0	2.80	62.83
5	2.40		
10	2.50	1.10	24.68
15	2.60		
20	2.60	0.90	20.20
25	2.60		
30	2.60	0.80	18.00
35	2.60		
40	2.60	0.80	18.00
45	2.60		
50	2.60	0.80	18.00
55	2.60		
60	2.60	0.80	18.00

Appendix 14: Variations of acid values of castor oil dimer acid with time of polymerisation

Time (min)	Vol(cm^3) of water released	Vol(cm^3) 0.8 M KOH	Acid values mg KOH/g acid dimer
0	0	1.50	33.660
5	0.40		
10	0.40	0.6	13.464
15	0.50		
20	0.60	0.55	12.342
25	0.70		
30	1.00	0.52	11 22
35	1.10		
40	1.20	0.50	8.976
45	1.25		
50	1.30	0.40	6.7632
55	1.30		
60	1.30	0.30	6.732
65	1.30		
70	1.40	0.30	6.732
75	1.50		
80	1.50	0.30	6.732
85	1.50		
90	1.50	0.30	6.732

Appendix 15: Variations of acid values of palm kernel oil dimer acid with time of polymerisation

Time (min)	Vol(cm^3) of water released	Vol(cm^3) 0.8 M KOH	Acid values mg KOH/g acid dimer
0	0	4.2	94.248
5	0.18		
10	0.36	2.14	48.022
15	0.54		
20	0.72	1.61	36.128
25	0.89		
30	1.07	1.25	28.050
35	1.25		
40	1.43	1.07	24.011
45	1.61		
50	1.79	0.89	19.972
55	1.97		
60	2.14	0.72	16.157
65	2.32		
70	2.32	0.54	12.118
75	2.32		
80	2.32	0.54	12.118
85	2.32		
90	2.32	0.54	12.118

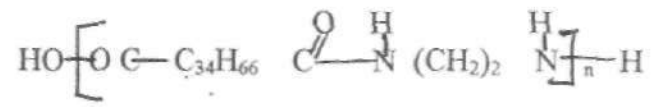
Appendix 16: Results of kinetic treatments of polymerisation data

Dimer type	Time (minutes)	Acid values mg KOH/ g acid	Amount reacted after time t $(AV_{to} - AV_t)$	% extent of reaction $P = \frac{AV_{to} - AV_t}{AV_{to}}$	% fraction unreacted (1 - P) x 100	Number average degree of polymerisation $\bar{Xn}(DP) = \frac{1}{(1-P)}$	Number average molecular weight $(\bar{Mn})$ = M_o x DP	$\frac{1}{(1-P)^2}$
Palm oil	0	62.832	-	-	-	-	Mo = 588	-
dimers	10	24.684	38.148	60.71	39.29	2.545	1496.46	6.478
	20	20.196	42.636	67.86	32.14	3.111	1829.27	9.681
	30	17.952	44.880	71.43	28.57	3.500	2058.00	12.251
	40	17.952	44.880	71.43	28.57	3.500	2058.00	12.251
	50	17.952	44.880	71.43	28.57	3.500	2058.00	12.251
	0	33.660	-	-	-	-	-	-
Castor oil	10	13.464	20.196	60.00	40.00	2.500	1470.00	6.250
dimers	20	12.342	21.318	63.33	36.67	2.727	1603.48	7.437
	30	11.669	21.991	65.33	34.67	2.884	1695.79	9.528
	40	11.220	22.440	66.67	33.33	3.000	1764.00	10.462
	50	8.976	24.684	73.33	26.67	3.750	2205.00	14.059
	60	6.732	26.928	80.00	20.00	5.000	2940.00	25.000
	70	6.732	26.928	80.00	20.00	5.000	2940.00	25.000
	80	6.732	26.928	80.00	20.00	5.000	2940.00	25.000

Appendix 16 continued:

Dimer type	Time (minutes)	Acid values mg KOH/ g acid	Amount reacted after time t ($AV_{to} - AV_t$)	% extent of reaction $P = \frac{AV_{to} - AV_t}{AV_{to}}$	% fraction unreacted (1 - P) x 100	Number average degree of polymerisation $\bar{X}n(DP) = \frac{1}{(1-P)}$	Number average molecular weight ($\bar{M}n$) = M_o x DP	$\frac{1}{(1-P)^2}$
Palm	0	94.248	-	-	-	-	-	-
kernel oil	10	48.022	46.226	49.05	50.95	1.963	1154.24	3.852
dimers	20	36.128	58.120	61.67	38.33	2.609	1534.10	6.807
	30	28.050	66.198	70.23	29.76	3.360	1975.68	11.291
	40	24.011	70.237	74.52	25.48	3.925	2307.90	15.403
	50	19.972	74.276	78.81	21.19	4.719	2774.72	22.271
	60	16.157	78.091	82.86	17.14	5.834	3430.39	34.039
	70	12.118	82.130	87.14	12.86	7.776	4572.29	60.467
	80	12.188	82.130	87.14	12.86	7.776	4572.29	60.467
	90	12.118	82.130	87.14	12.86	7.776	4572.29	60.467

Note: M_o = molecular weight of repeat unit calculated based on diolein residues as polyamide repeat unit



∴ For n = 1; DP = 1; M_o = 588 g; Av_{to} = Acid value at time = 0; Av_t = Acid value at time = t

Appendix A: Hydrolysis products of lipids

Lipid class	Hydrolysis products										
	Fatty acids	Aldehydes	Phosphoric acid	Glycerol	Other alcohols	Sphing-4-ethene and related bases	Choline	Ethanolamine	Serine	Inositol	Carbohydrates
1. Esters											
a) Glycerides	+	(+)		+	(+)						
b) Waxes	+				+						
c) Glycoglycerides	+			+							+
d) Phosphoglycerides											
i Phosphatidic acids	+		+	+							
ii.Phosphatidylglycerols	+		+	+			+	+	+		
iii Phosphatidic esters	+	(+)	+	+	(+)					+	
iv Phoshatidic inositides	+	(+)	+	+	(+)						
2. Amides											
e) Sphingolipids											
i) Cerebrosides	+	(+)				+					+
ii) Gangliosides	+					+					+
f) Sphingomyelins	+		+			+	+				
g) Plant phosphosphingolipids	+		+			+				+	+

\+ = Indicates that these constituents are always present
(+) = Indicates that these constituents are sometimes present

Source:- (Gunstone, J.D (1967); Robert, L.R (1974); Hamilton, R. J and Bhati, A (1980).

Appendix B:- Fatty acid compositions of some vegetable oils

		% saturated fatty acids						% unsaturated fatty acids				
Plant oil	Source	*Lauric* C_{12}	*Myristic* C_{14}	*Palmitic* C_{16}	*Stearic* C_{18}	*Arachide* C_{20}	*Others*	*Palmitoleic*	*Oleic* C_{18}	*Linoleic* C_{18}	*Linolenic* C_{18}	*Others*
Castor oil	Ricinus communis	←		2.4	→	-	a,b,c	-	7.4	3.1	-	87.92
Cocoa butter oil	*Theobroma* cocoa	-	-	24.4	35.4	-	-	-	38.1	2.1	-	-
Coconut oil	Cocas nucifera	45.4	18.0	10.5	2.3	0.4	0.8[a] 5.4[b] 8.4[c]	0.4	7.5	trace	-	
Cotton seed oil	Gossypium hirsutum	-	1.4	23.4	1.1	1.3	-	2.0	22.9	47.8	-	-
Olvie oil	Olea earopae savita	-	trace	6.9	2.3	0.1	-	-	84.4	4.6	-	-
Palm oil	Elaeis guinensis	-	1.4	40.1	5.5	-	-	-	42.7	10.3	-	-
Palm kernel oil	Elaeis guinensis	46.9	14.1	8.8	1.3	-	2.7[b] 7.0[c]	-	18.5	0 7	-	-
G/nut oil	Arachis hypogea .	-	-	8.3	3.1	2.4	-	-	56.0	26.0	-	3.1 1.1
Soya bean oil	Glycine soja	0.2	0.1	9.8	2.4	0.9	-	0.4	28.9	50.7	6.5	0.1

KEY:- a = caproic acid; b = caprylic (C_8) acid; u = lignoceric (C_{24}); n = Behenic axcid; r = Ricinoleic acid; g = C_{14} monoethenic ac

Source:- Fasman, G. D 1975; Encyclopadia of Food Science and Technology, Vol. 3, 1978: Oils and oil seeds journal, June, 1976.

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Appendix C: Established oil-palm plantations (hectares) in Nigeria (Pre-1980 era)

S/No	States	Government	Private	Total
1	Anambra/Enugu	1977.50	8664.06	10641.81
2	Edo/Delta	9100.90	14252.33	23354.23
3	Benue	444.40	285.85	730.25
4	Cross River/Akwa Ibom	14423.43	31610.01	46033.44
5	Adamawa/Taraba	73.50	50.00	123.50
6	Imo/Abia	6015.70	20657.80	28673.50
7	Kaduna	N/A	N/A	N/A
8	Kwara/Kogi	-	111.77	111.77
9	Lagos	231.40	-	231.40
10	Niger	-	59.00	59.00
11	Ogun	6134.00	599.70	6733.70
12	Ondo/Ekiti	11521.40	1847.51	13368.91
13	Oyo/Osun	139.00	290.40	429.40
14	Plateau	N/A	N/A	N/A
15	Rivers/Bayelsa	5989.32	6851.70	12841.02
	Total	56051.80	82280.13	141331.93

N/A = Data not available

Source: Nigerian Palm Produce Board, 1982.

Appendix D: World production of castor beans in tonnes

Country \ Year	1950- 54	1954 - 59	1959	1960	1961	1962
Brazil	187414	185977	160000	248000	200000	210000
India	120960	127008	125440	118720	99680	113120
Thailand	11280	29665	37530	47350	36120	41335
Ecuador	7182	17431	19500	21800	22815	24250
Rumania	2226	12434	18300	29000	22375	
U.S.A	13449	9293	12165	15635	19000	
Tanzania	9985	14746	15898	20560	12039	22000
Ethiopia	10730	15650	17000	19000	11000	
Argentina	3229	4785	9500	12870	8000	
World total	366455	544785	557590	668410	583815	609155

Source: Terill et. al., 1975, in Encyclopedia of Chemical Technology Vol. 4 pp 529 - 533.

Note: Figures for 1962 for some countries are not indicated.

Appendix E: Lyes for alkaline refining

Degree Baume' at 15 °C	% NaOH W/V content
10°	6.57
12°	8.00
14°	11.06
16°	12.68
18°	14.36
20°	16.09
22°	17.87
24°	19.70
28°	21.58
30°	23.50

Source:- Swern et. al., (1964), Bailey,s Industrial Oil and Fat Products, 3rd edition, pp 735 - 739.

Appendix F: Some physical and chemical characteristics of some vegetable oils

Name	Specific gravity 15/15°C	Solidification point °C	Acid value mg/g	Saponification mg/g	Iodine value g/100g
Castor oil	0.960 - 0.967	-17 to -18	0.12 - 0.8	175 - 183	84
Cocoa butter	0.764 - 0.974	21.5 to 23	1.1 - 1.9	192.8 - 195	32.8 - 42
Cottonseed oil	0.917 - 0.918	+12 to -13	0.6 - 0.9	194 - 196	103 - 111.3
Linseed oil	0.930 - 0.938	-19 to -27	1 - 3.5	188 - 195	175 - 202
Olive oil	0.914 - 0.918	+2 to -6	0.3 - 1.0	185 - 196	79 - 88
Palm oil	0.924	35 50 42	10	200 - 205	49.2 - 58.9
Palm kernel oil	0.866 - 0.874			243 - 255	10.5 - 17.5
Rapeseed oil	0.913 - 0.917	-10	0.36 - 1.0	168 - 179	94 - 105
Soyabean oil	0.924 - 0.927	-10 to -16	0.3 - 1.8	189 - 193	122 - 134
Sperm oil	0.878 - 0.884	15.5	13.2	120 - 137	80 - 84
Tung oil	0.939 - 0.949	Below 17	2	190 - 197	163 - 171

Source:- Dollear (1978) Encyclopedia of Science and Technology Vol. 10 pp 199 - 203.

Appendix G: Physical properties of some fatty acids

Common name	Systematic name	Chemical formula	Molecular weight	Melting point °C	Boiling point °C/mm[a]	Specific gravity	Refractive index N_D°C	Solubility
Lauric	Dodecanoic	$C_{11}H_{23}COOH$	200.3	44.3	225/100	0.8690 (60°)	1.4261 [6]	s. acet. al. eth, pet. ether
Myristic	Tetradecanoic	$C_{13}H_{27}COOH$	228.4	54.9	250/100	0.8662 (54°)	1.4273 [29]	s. acet. al. eth. pet. ether
Palmitic	Octadecanoic	$C_{15}H_{31}COOH$	256.4	63.1	268/100	0.8487 (70°)	1.4309 [29]	s. acet. h.al. eth, pet.ether
Stearic	Octadecanoic	$C_{17}H_{35}COOH$	284.5	69.6	213/5	0.8390 (60°)	1.4337 [29]	s.acet, hal. eth. pet. ether
Oleic	cis-9-octadecenoic	$C_{17}H_{33}COOH$	282.5	13.4	234/15	0.8905 (20°)	1.4582 [29]	s. acet. eth. me. al.
Linoleic	cis-9-cis-12-octa decadienoic	$C_{17}H_{31}COOH$	280.5	-5.2	202/1.4	0.9038 (18°)	1.4699 [29]	s. acet. al. eth, pet. ether
Linolenic	cis-6, cis-9, cis-12-octadecatrienoic	$C_{17}H_{29}COOH$	278.4	-	-	-	-	s. acet. al. eth, pet. ether
Ricinoleic	d-12-hydroxy-cis-9-octadenoic	$C_{17}(OH)H_{33}COOH$	298.5	5	225/10	0.940 (27°)	1.4716 [29]	s. acet. al. eth.

Key: acet = acetone, al = ethanol, eth = ether, h = hot, me = methyl, pet = petroleum, s = soluble, mm[a] = millimetre mercury

Sources:- Encyclopadia of Polymer Science and Technology Vol I (1975).

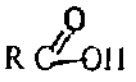
Appendix H: Fatty acid composition of castor, palm and palm kernel oils

Fatty acid	% composition	Number of double bonds	% total unsaturation
i) Castor oil fatty acids			
Lauric acid	2.4	Nil	
Myristic acid	2.4	Nil	
Palmitic acid	2.4	Nil	
Stearic acid	2.4	Nil	
Oleic acid	7.4	one	≈ 98
Linoleic acid	3.1	two	
Ricinoleic acid	89 - 90	one	
ii) Palm oil fatty acids			
Myristic acid	1.4	Nil	
Palmitic acid	40.1	Nil	
Stearic acid	5.5	Nil	
Oleic acid	42.7	one	≈ 53
Linoleic acid	10.3	two	
Palm kernel oil fatty acids			
Lauric acid	46.9	Nil	
Myristic acid	14.1	Nil	
Palmitic acid	8.8	Nil	
Stearic acid	1.3 - 2.0	Nil	
Capric acid	7.0	Nil	
Oleic acid	18.5	one	≈ 19
Linoleic acid	0.7	two	

Source: Gerald. D. Fasman, 1975.

Appendix I: Absorption characteristics of carboxylic acid, alkanes and alkenes (cm^{-1})

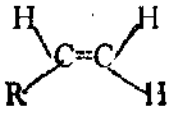
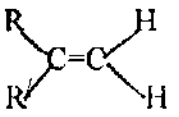
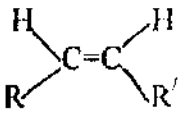
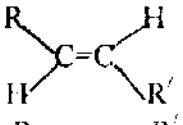
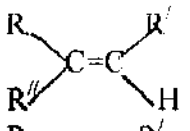
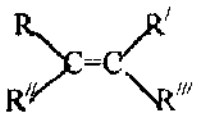
(a) Carboxylic acid

Type	V(OH) free	V(OH) bonded	V(C=O)	V(C-O)
	3560 - 3500	3000 - 2500	1740 - 1650	1320 - 1210

(b) Alkanes

Type		V(CH)	δ(CH)
Group			
Methine	-C-H	2890	1340
Methylene	$-CH_2$	2853 - 2926	1465
Methyl	$-CH_3$	2872 - 2962	1365

(c) Alkenes

Group	Structure	V(CH)	V(C=C)	δ(CH)
Vinyl		3085	1642	1415
Vinylidene		3080	1652	1415
cis-disubstituted		3020	1657	1300
trans-disubstituted		3020	1672	1410
Trisubstituted		3030	1670	1345
Tetrasubsituted		-	1670	-

Source: Pecsok et. al., 1976, pp 201-213.

Appendix J: Absorption characteristics of amines and amides (cm^{-1})

Group \ Type		V(N-H)	δ(N-H	γ(C=O)
1° amine	RNH_2	3500 - 3400	1600	-
2° amine	R_2NH	3350	1600	-
1° amide	$-CONH_2$	3500	1600	1690
2° amide	-CONH-	3430	1600	1680

Notes: Amides I and II bands are not pure C=O(V) and N-H(δ) respectively. Amide I may be as high as 80% -C=O(V) in character, but Amide II is strongly coupled interaction between -N-H(δ) and C-N(V) (Pecsok et. al., 1976). Amides readily condense as do carboxylic acids, but in amides, the situation is additionally complicated by considerable double bond character of the O C N and secondly the degree of vibrational couplings that take place, for instance N-H(V) may couple with N-H(δ) and moreover, N-H(δ) couples strongly with C=O(V) (Cowie, 1973). Therefore self association, cis-, trans- isomerism and vibrational couplings are some of the factors that influence absorption bands of amides (Kemp, 1991). Furthermore, H-bonding is less in amides and amines since nitrogen is less electronegative than oxygen, the consequent of is this that in amides, the positive inductive effects of NH_2 produce lengthening (weakening) of the C=O bond leading to lower frequency compared to the corresponding ketone (Pecsok et. al., 1976). In addition, the negative inductive effects of nitrogen atom is being dominated by the positive mesomeric effects of the pair of electrons on the nitrogen (Kemp, 1991).

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Appendix K: Variations of iodine values; relative viscosities with time of dimerisation

Oil type / Parameter	Castor oil compounds						Palm oil compounds						Palm kernel oil compounds					
	C_o	C_a 0 hr	C_b 1 hr	C_c 2 hr	C_d 3 hr	C_e 4 hr	P_o	P_a 0 hr	P_b 1 hr	P_c 2hr	P_d 3 hr	P_e 4 hr	PK_o	PK_a 0 hr	PK_b 1 hr	PK_c 2 hr	PK_d 3 hr	PK_e 4 hr
Iodine value	76.2	81.2	70.5	50.8	42.1	34.9	41.11	46.2	38.1	31.6	25.3	19.99	17.75	20.3	18.5	15.5	13.5	11.75
Relative viscosities (30°C)	1.38	1.33	1.37	1.41	1.43	1.45	1.13	1.10	1.11	1.25	1.30	1.34	1.06	1.05	1.06	1.07	1.09	1.10

KEY

Castor oil compounds

C_o = castor oil whole (mixed) fatty acids

C_a = castor oil unsaturated fatty acids at 0 hr

C_b = castor oil dimer at 1 hr

C_c = castor oil dimer at 2 hr

C_d = castor oil dimer at 3 hr

C_e = castor oil dimer at 4 hr

Palm oil compounds

P_o = palm oil whole (mixed) fatty acids

P_a = palm oil unsaturated fatty acids at 0 hr

P_b = palm oil dimer at 1 hr

P_c = palm oil dimer at 2 hr

P_d = palm oil dimer at 3hr

P_e = palm oil dimer at 4 hr

Palm kernel oil compounds

PK_o = palm kernel oil whole (mixed) fatty acids

PK_a = palm kernel oil unsaturated fatty acids at 0 hr

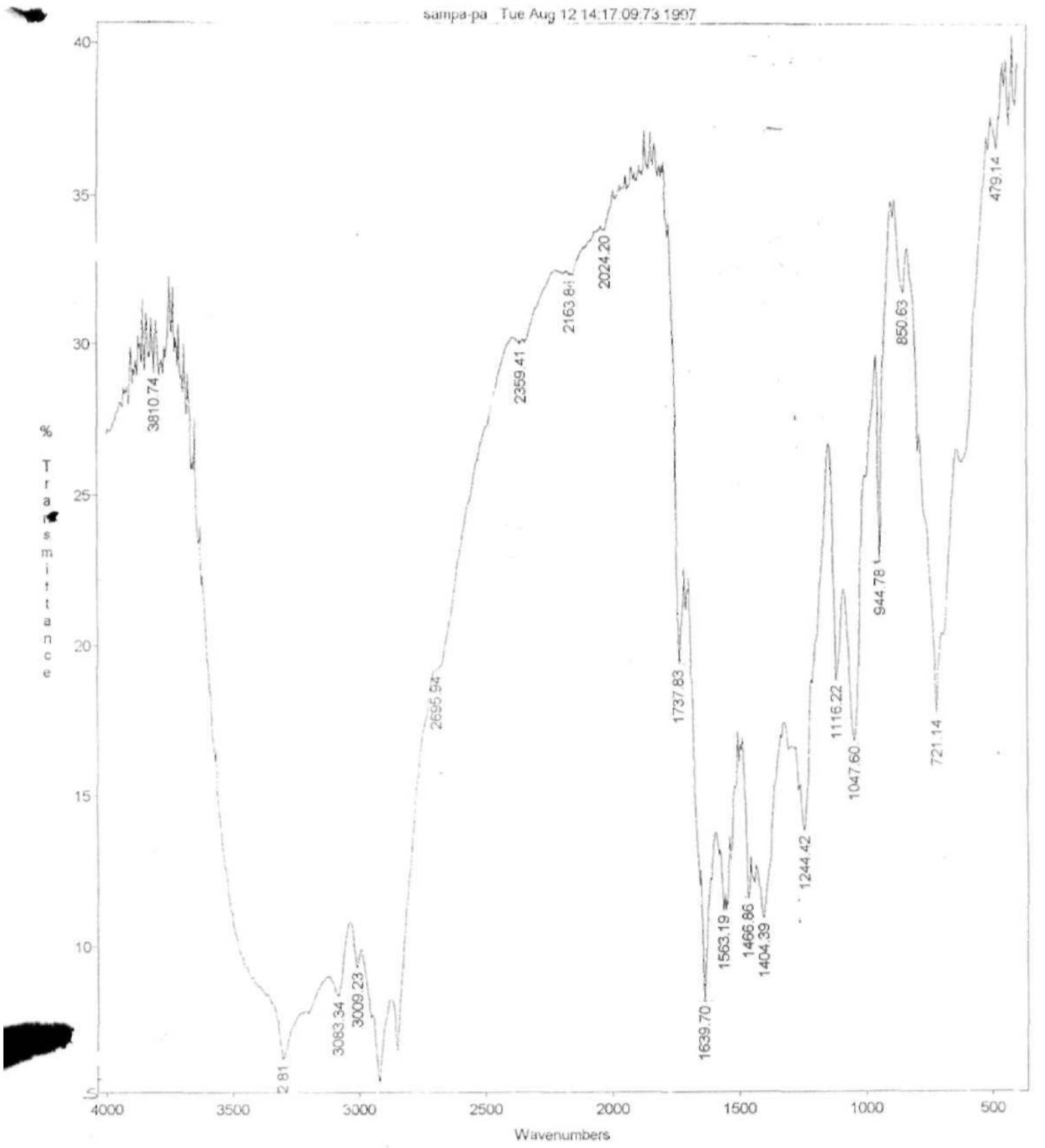
PK_b = palm kernel oil dimer at 1 hr

PK_c = palm kernel oil dimer at 2 hr

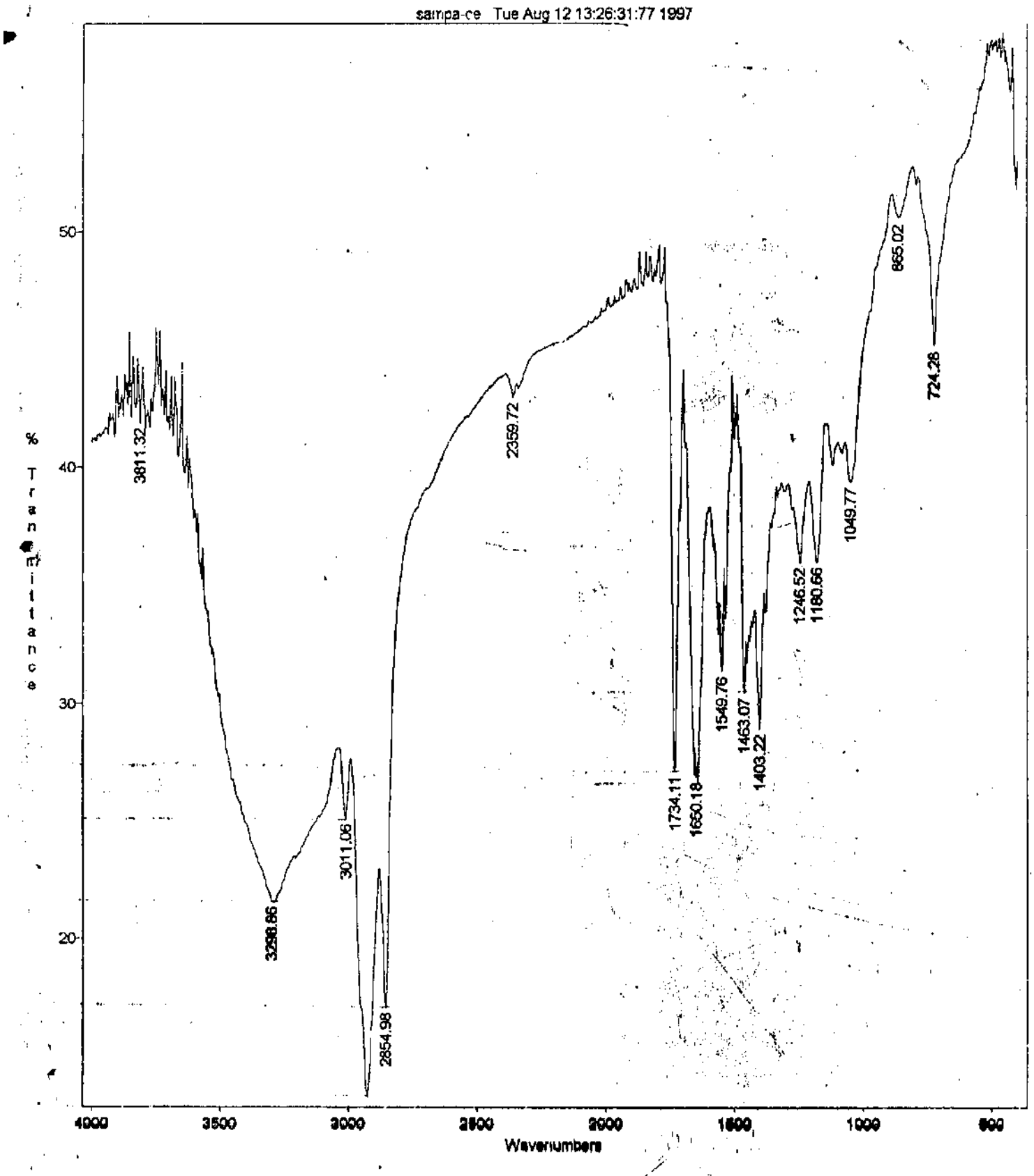
PK_d = palm kernel oil dimer at 3 hr

PK_e = palm kernel oil dimer at 4 hr

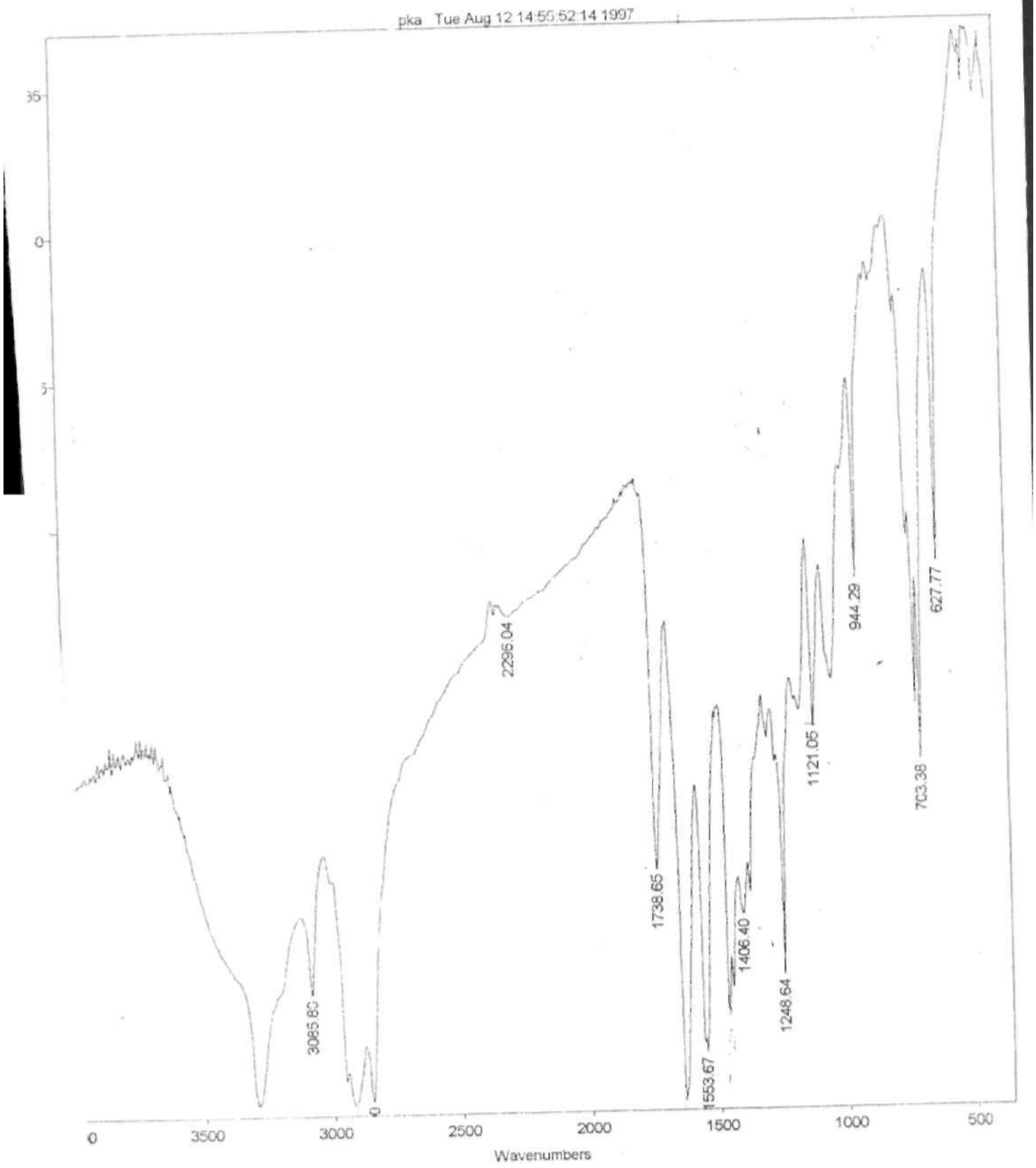
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30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
3810.74
2359.41
2163.81
2024.20
2695.94
2861
3083.34
3009.23
1737.83
1639.70
1563.19
1466.86
1404.39
1244.42
1116.22
1047.60
944.78
850.63
721.14
479.14

SAMPLE C5


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30
20
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2359.72
865.02
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1049.77
1246.52
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1734.11
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1549.76
1463.07
1403.22
3298.86
3011.06
2854.98
4000
3500
3000
2500
2000
1500
1000
Wavenumbers

SAMPLE PK5


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1000
500
Wavenumbers