

Dearomatization of Naphtha Cuts from Saudi Arabian Crudes Using Different Selective Solvents

by

Syed Halim Hamid

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DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

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using different selective solvents**

Hamid, Syed Halim, M.S.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1980

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DHAHRAN, SAUDI ARABIA


COLLEGE OF GRADUATE STUDIES

This thesis, written by Syed Halim Hamid under the direction of his Thesis Committee, and approved by all its members, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE IN CHEMICAL ENGINEERING.


Dean

College of Graduate Studies

Date: 8-4-77


Department Chairman

Thesis Committee


Chairman


Member


Member

dedicated to
MY DEAREST MOTHER

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ABSTRACT

An experimental investigation was carried out to evaluate the efficiencies of different selective solvents used for the extraction of aromatic hydrocarbons from Saudi Arabian crude oils light fraction (Boiling range 23-200 °C). The solvents used were 3-methoxypropionitrile, Dimethylsulfoxide, Phenol, Sulfolane, Nitrobenzene and Ethylene Glycol. Parameters studied are operating temperature (range 20-80°C), solvent-to-oil ratio (range 1:1 to 3:1), selectivity and solvent capacity.

One of the main objectives of this study is to determine quantitatively the potential of the recovery of aromatics from such fractions. Separated aromatics could then be used as a basic feedstock for the petrochemical industry in the Kingdom of Saudi Arabia.

The results indicate that sulfolane exhibits excellent extractive properties as compared to other solvents. The feasibility study provides justification for setting up aromatics production plant in the Kingdom of Saudi Arabia.

CHAPTER 1

INTRODUCTION

In the age we live in, crude oil has become a vital lymph; without it, the modern way of life on earth would be paralyzed in a very short time. The importance of crude oil in the various fields of modern life is so great that not only scientists, but politicians and economists all over the world focus their attention on it.

In the refineries crude oil is subjected to a greater number of processes, in order to obtain higher yields in valuable products having greater demand on the market. Topping, cracking and reforming processes, distillation under vacuum for lubricating oils, alkylation and polymerization processes, are all dressed to obtain the highest amount of valuable products from crude oil, i.e. gasoline, fuel oil, lubricants of different viscosities and related products.

Since the second World War, there has been a phenomenal increase in the utilization of raw materials of petroleum origin to provide the basic building blocks for the manufacture of these commodities which are now classified as "Petrochemicals". These raw materials are transformed by stages into the more familiar end-use product. First they are processed into "basic intermediates" and then, often,

through "secondary intermediates" into the end-use products. The raw materials used in petrochemical products are classified according to their stage of transformation through various technical processes toward the final products as follows :

Class (I) Basic raw materials:

Petroleum and natural gas.

Class(II) Basic intermediates:

These include the hydrocarbons of olefins, paraffins and aromatics, namely : ethylene, propylene, butylene, methane series, benzene, toluene, xylenes etc.

Class(III) Secondary intermediates

These include inter-alia, the basic intermediates which have been processed into the following : acetaldehyde, acetone, styrene, caprolactam, acetic anhydride, vinyl chloride, methanol, ammonia, glycol, polyisobutylene, alcohols, and polyolefins.

Class (IV) Final or end-use products:

These include plastics, synthetic fibres, detergents, nitrogenous fertilizers, synthetic rubbers, automotive chemicals, resins, insecticides etc.

Aromatics constitutes one of the main classes of hydrocarbons along with olefins and diolefins, on which the petrochemical industry rests. Refinery and chemical planning people are convinced that the demand for aromatic derivatives will continue its relatively rapid growth over the next ten years. The underlying force sparking this demand, in addition to the normal population growth, is the reason that B.T.X. (Benzene, Toluene, Xylene) aromatics enclose in their ring structure a potentially available pool which can meet the requirement created due to recent petrochemical proliferation.

During the past 15-20 years, the use of aromatics for chemical derivatives has grown steadily, and now this market represents a significant business interest to most petroleum and chemical companies. Most of the aromatics used today are derived from petroleum refining operations. The following tabulation of B.T.X. supply sources indicates the major role of catalytic reformat as well as the growing importance of pyrolysis gasoline. The yield of pyrolysis gasoline have been projected on the basis of the use of gas oils for steam cracking to make up the incremental feedstock required above that available from natural gas liquids. However, if naphtha is in abundance, it may be substituted for gas oil, and the yield of pyrolysis gasoline will be substantially less.

B.T.X. SOURCE IN THE U.S.A. [1]
(Percent of total B.T.X. Chemical Demand)

	1970	1975	1980
Catalytic Reformate	84	86	86
Pyrolysis Gasoline*	4	6	9
Coal-Tar	12	8	5

* 50 percent of B.T.X. in pyrolysis gasoline assumed for chemical use.

In the past, the refinery producing aromatics from reformat had to cope with the increasing disparity caused by the greater growth rate of aromatics for chemical use (9% per year) compared to aromatics for gasoline (3% per year). However, during the next decade, the requirement for unleaded gasoline are expected to increase aromatics output for gasoline by 7% per year or nearly one million barrels per calendar day. During this period the demand for aromatics for chemical use should grow at approximately the same rate or about 120 thousand barrels per calendar day. This synchronization of growth rates will be beneficial. However, to meet the requirements for stepped-up aromatic production, the refinery will face new problems [1].

The catalytic reforming process evolved from the necessity for producing high octane gasoline via greater aromatics concentrations [2]. Fundamentally the reactions taking place in a

catalytic reformer are :

- Dehydrogenation of cycloparaffins to aromatics
- Isomerization of normal paraffins to isoparaffins
- Dehydrocyclization of paraffins to aromatics
- Hydrocracking of paraffins to light hydrocarbons

Catalytic reforming is the heart of aromatic processing. In this operation, the aromatic precursors for subsequent operations are formed. Commercial experience along with persistent research has led to a series of recent improvements. The new methods are directed at obtaining greater individual control over the various reactions. Aromatic production in a catalytic reformer is maximized as the severity of the operation is increased. Substantial dehydrocyclization and concomitant hydrocracking occur at severe condition. The severity level then becomes an economic consideration that balances the increased aromatic production against the loss of liquid products.

The C₆ - C₉ fractions from catalytic reforming and steam cracking are relatively high in aromatic concentrations. Solvent extraction processes have been invented to extract aromatics from the feed with solvents which preferentially dissolve the aromatics. Some of the most popular solvents in major use today are sulfolane, 3-methoxy propionitrile, n-methylpyrrolidone, Dimethyl sulfoxide, morpholine and various glycols such as mono-di-tri and tetra-ethylene glycols etc. [3,4,5]. The cost of an aromatics extraction process is related directly to the quantity

of solvent required for a given feed stock. In recent years, process improvements have been aimed at reducing the solvent-to-feed ratio. The improvements were made primarily with catalytic reformat as feedstock that contains aromatics in about 50% concentration.

The choice to be made on the process presents itself in the choice of the solvent to be used. Through the years a host of selective solvents for the physical group separation in extraction and extractive distillation have been proposed and selected. Among the criteria for selection, such obvious and practical items are stability, chemical indifference, availability, toxicity and price have been featured, but it is the basic solvent properties, such as selectivity and solvency which make a solvent[6]. Since we are here considering the high boiling solvents (heavy solvents) and wide range feedstocks, the boiling point and the molecular weight selectivity also assume more importance.

Many contributors in the field of dearomatizing petroleum fractions mainly stressed on the improvement in the quality of fraction by dearomatization. This includes A.A. Farag et al, [7], A.G. Ismailau et al [8], A.S. Zhurba et al [9], and number of others, who worked on improving the quality of kerosine, jet fuel, lubricant base etc. Abdel-Al et al [10] have published the work concerning the dearomatization of Saudi Crude distillates for producing high viscosity index (VI) paraffinic lube oils. Obviously this work was confined to the heavier fractions of the

Saudi Crude (Boiling range 111°C - 355°C).

Literature cites deficiency in the field of dearomatizing light fractions of Saudi Crudes for the purpose of obtaining aromatics suitable for petrochemical feedstocks.

In view of this, it becomes imperative to carry out research work on the efficiencies of different selective solvents used in the extraction of aromatic hydrocarbons using the light fractions of Saudi Arabian Crudes - the major supplier of the Crude Oil to the world.

This research will report experimental findings on the solvent extraction of aromatics - using different selective solvents for Saudi Arabian light fractions. One of the main objectives of this work is to evaluate the quality of such fractions for the recovery of aromatics, which is used in the petrochemical industry. The investigation includes the effect of four different variables on the extraction of aromatics from low boiling fractions. These are, solvent to oil ratio, operating temperature, selectivity and solvent capacity.

CHAPTER 2

LITERATURE REVIEW

2.1 Historical Background

The demand for aromatics of the organic chemical industry was met over several decades by the production potential of the Coal-Coke industry. As the rate of coke necessary to provide one ton of raw steel was decreased by about 50 percent and the demand for aromatics was increasing constantly, the market could no longer be satisfied by the Coal-Coke industry [11]. Literature cites a search for a commercial route to petroleum-derived-benzene via thermal processing as far back as 1885. Later on, the field of aromatic recovery from petroleum was subjected to tremendous innovations. With the passage of time, the improvement and development in the pertinent field provides an impetus in the process development.

During World War I, the soaring demand for toluene as a raw material for T.N.T manufacture made its separation from petroleum necessary, even though expensive process had to be used. Between 1920 and 1940 small amount of mixed aromatics were obtained for solvent purposes by the extraction of petroleum fraction with sulphurdioxide.

After World War I Coal-tar and Coke oven light oil again satisfied virtually the entire light aromatic demand. The aromatics product, impure by today's standard were separated by fractional distillation, clay treatment and washing with concentrated H_2SO_4 to remove some of the remaining contaminants. Table (2.1) shows 1950 ASTM nitration grade specifications for Benzene, Toluene and Xylene [12].

Between World War I and II the aromatic demand for chemicals was small and coal supplied all that was required. While some research work on petroleum-derived aromatics continued during this period, the efforts were far from intense. Much of the work in late 20's and 30's concentrated on pyrolysis methods for increasing the aromatic content of hydrocarbon fractions. Eventually as a result of this program the original catalytic reforming process, hydroforming was developed by Standard Oil Company [4].

At the beginning of World War II, the first commercial hydroforming unit was converted from motor gasoline production to toluene production. Under the wartime stimulus seven other such units were placed in production and initiated the trend from coal to petroleum as a major source of aromatics. This trend was continued when benzene was produced commercially by dehydrogenation of cyclohexene in 1950 [5].

The advent of catalytic reforming process in about 1940 and the tremendous post war expansion of catalytic reforming

TABLE (2.1)

A.S.T.M. (1950) NITRATION GRADE
AROMATIC SPECIFICATIONS

	<i>Benzene</i>	<i>Toluene</i>	<i>Xylene</i>
Specific gravity	0.882 - 0.886	0.873 - 0.889	0.865 - 0.870
Acid Wash Color	2 Max	2 Max	6 Max
Dry Point, °C	--	--	--
Solidification point, °C (Anhydrous Basis)	4.85 Min	--	--
Paraffin Content, LV %	--	1.5 Max	4 Max
Color	Not darker than a soln. of 0.003g/l K ₂ Cr ₂ O ₇ in water		
Acidity	----- No free acid -----		
Sulfur Compounds	----- Free of H ₂ S and SO ₂ -----		
Copper Corrosion	No irridescence; no gray or black deposit or discoloration.		

revolutionized the production of aromatics from petroleum. The combination of post-war demand for high-octane gasoline rich in aromatics coupled with the development of new catalysts and of new methods for separating aromatics has resulted in huge output, and a much greater potential output of aromatics from petroleum. The reaction of benzene and alkyl benzenes with inorganic substances are well known. Indeed, sulfonation and nitration of benzene and toluene are among the foundation stones on which the present-day organic chemical industry was built.

Aromatics constitute one of the main classes of hydrocarbon-building-blocks, along with olefins and diolefins, on which the petroleum chemicals industry is based. Since World War I and the first "Coaltar" dyes, benzene has been one of the backbones of the synthetic organic industry. The dominance of benzene as a raw material remains, but more and more benzene is being made from petroleum rather than coal, and the end uses extend from mere dyes stuffs into fibers, plastics, detergents, and a host of other products [13].

Toluene, once thought of largely as the basis for (T.N.T) is now finding expanding use as a solvent and as a chemical intermediate. The Xylenes, once used almost exclusively in mixed forms as a solvent are now separated into pure ortho, meta, and para isomers and used as chemical starting materials. Oxidation of the various xylenes to phthalic,

isophthalic and terephthalic acids is typical of the new and growing uses for aromatics.

2.2 Conventional Processes in Aromatic Extraction

On technical scale, aromatics are almost exclusively separated from non aromatics of the same boiling range by liquid-liquid extraction. Figure (2.1) illustrates the process flow of liquid-liquid extraction using a high-boiling solvent. The solvent is fed to the top of a multi-stage extractor where it travels downwards and preferentially dissolves aromatics. The mixture to be separated is charged to the centre of the extraction tower. The solvent loaded with aromatics leaves the tower bottom while the non aromatics go overhead. The extract is distilled off from the extract phase and subsequently fractionated into pure products. The well known processes are :

(i) Udex Process

The above described principles underline the Udex process developed jointly by Dow Chemical Corporation and Universal Oil Products Company [14]. This process was the first aromatic recovery process to combine liquid-liquid extraction with extractive distillation as shown in Figure (2.2). With the commercialization of the first Udex Unit in 1952 the process was readily accepted by the industry [11,15,16].

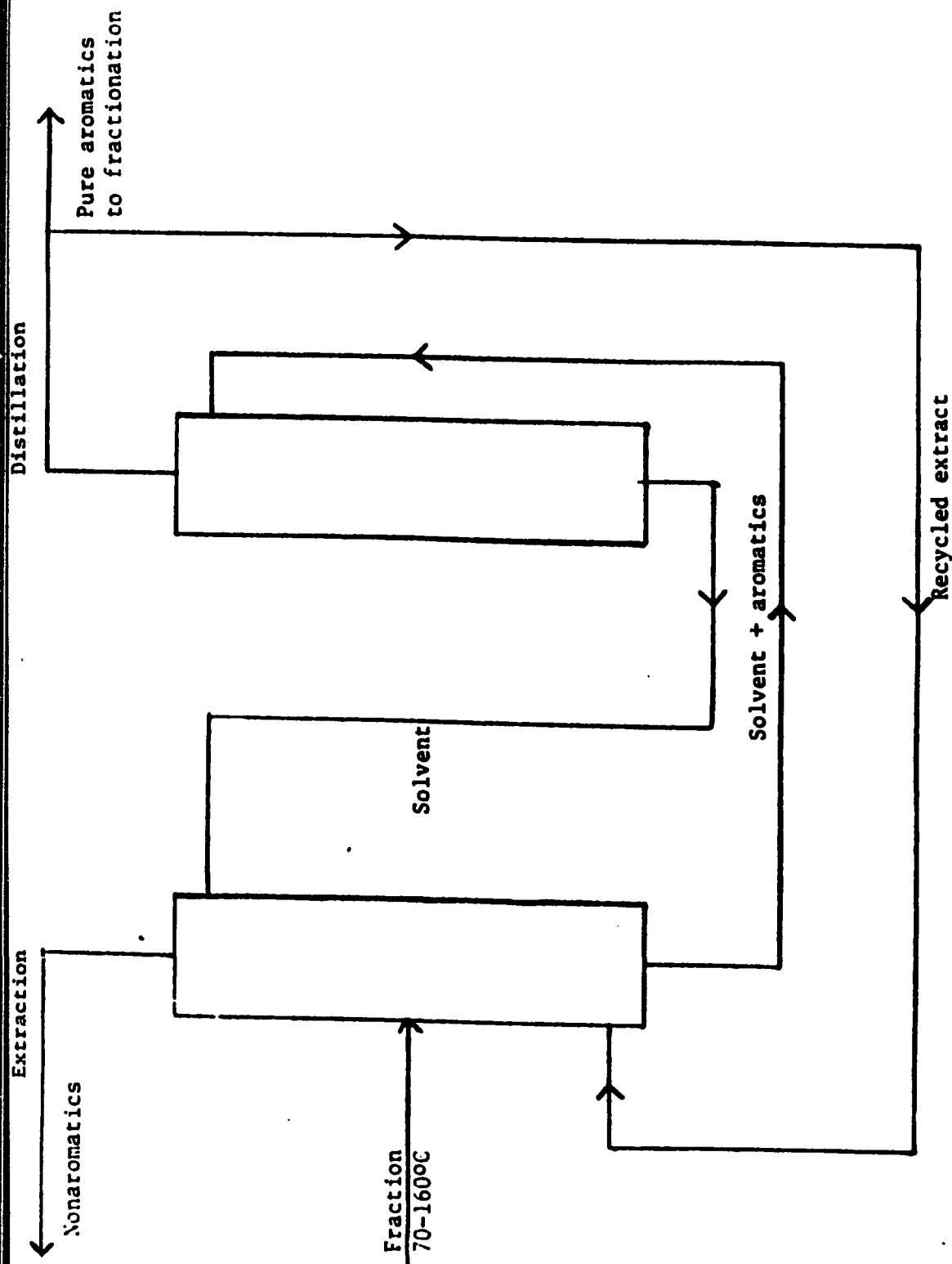


FIGURE (2.1) PRINCIPLE OF LIQUID-LIQUID EXTRACTION

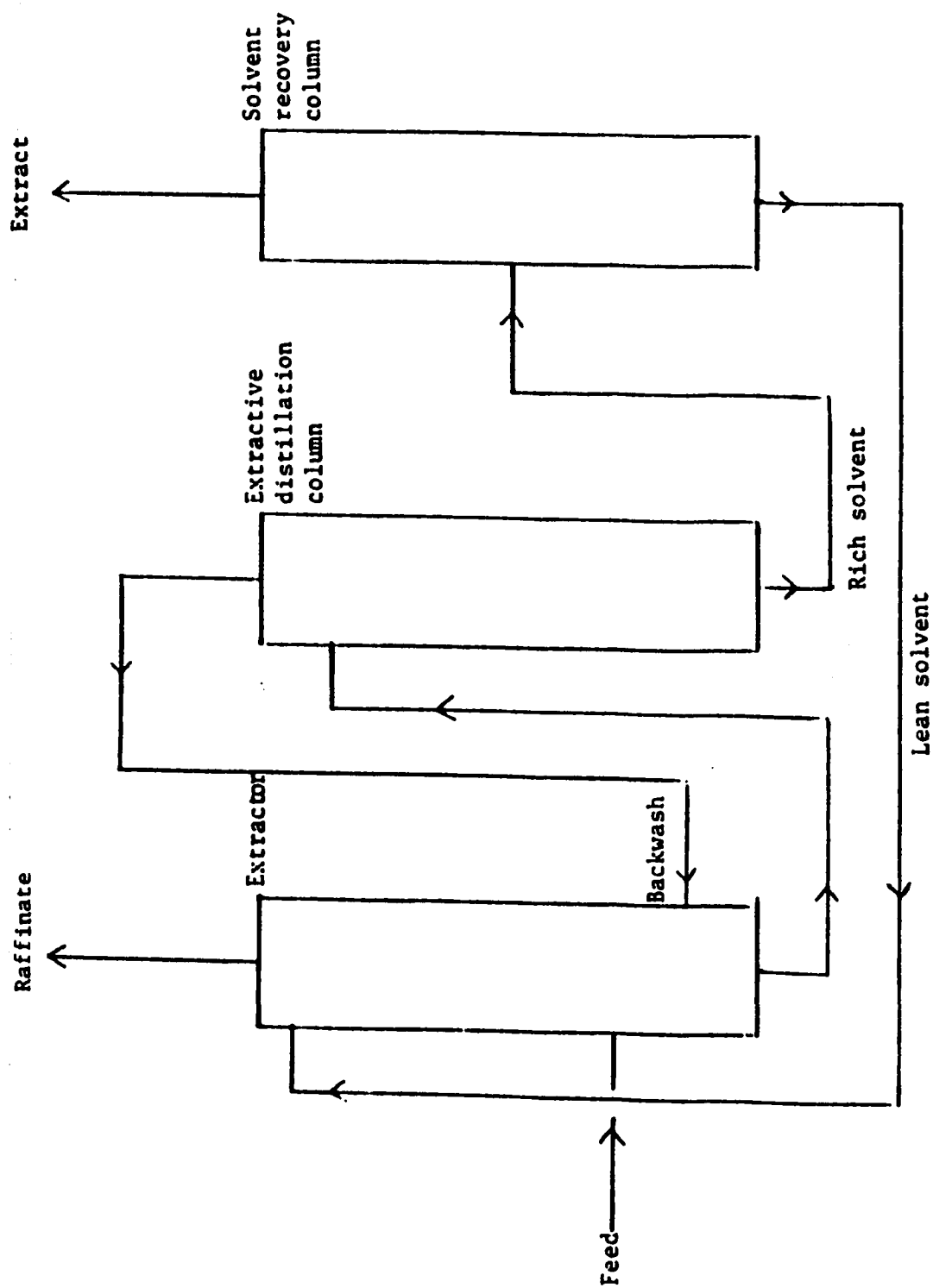


FIGURE (2.2) COMBINATION OF EXTRACTION WITH EXTRACTIVE DISTILLATION

The process has been applied in about forty plants to a variety of feedstocks of different origins, including hydrogenated Coke oven light-oil. The process uses diethylene glycol or mixtures with triethylene glycol as solvent. The extraction process is operated at temperature above 100 °C. The process furnishes high yields and the aromatics recovered are of optimum purity. The ability to handle a wide boiling range is an outstanding feature of the process as shown in Table (2.2) [13,17,18].

(ii) Shell Sulfolane Process

This process was developed by Shell in 1959. Sulfolane was first used commercially in 1962 at two Shell's own refineries. Sulfolane process is a combination of liquid-liquid extraction with extractive distillation as shown in Figure (2.3). Sulfolane is a five member heterocyclic compound. Some of the unique properties of sulfolane is given in Table (2.3) [21].

Fresh feed enters an extraction tower, e.g. a rotating disc contactor that operates at increased temperature (about 50-100 C), representing a compromise between solvent selectivity and solvent power. The extent of aromatic recovery depends jointly on the solvent to feed ratio and the number of extraction stages [23]. Solvent phase enters an extractive distillation tower

TABLE (2.2)

CHARGE AND PRODUCT PROPERTIES

(Miles Process)

<i>Product Properties</i>	<i>Udex Charge</i>	<i>Raf- finite</i>	<i>Benzene</i>	<i>Toluene</i>	<i>Mixed Xylenes</i>
Gravity, °API	51.9	76.4			
Specific gravity, 20/4	0.772	0.681	0.885	0.873	0.873
% aromatics	51.3	3.5	99.9	99.8	99.8+
Solid point, °C			5.49		
<i>Distillation</i>	°F.	°F.	°C.	°C.	°C.
1bp	150	145	79.7	110.2	(*)
50%	210	170	80.1	110.8	
Dry point	302	295	80.3	111.0	
<i>Acid Wash Color</i>					
Color acid phase			0	0+	0+
Color hydrocarbon phase			0	0	0+
<i>Acidity, mg</i>					
NaOH/100-ml sample	-----No free acid-----				
Copper-strip corrosion	-----Passed-----				
<hr/>					
* Ethylbenzene, 14.5 wt %; p-xylene, 19.0 wt %; m-xylene, 42.0 wt %; oxylene, 24.5 wt %.					

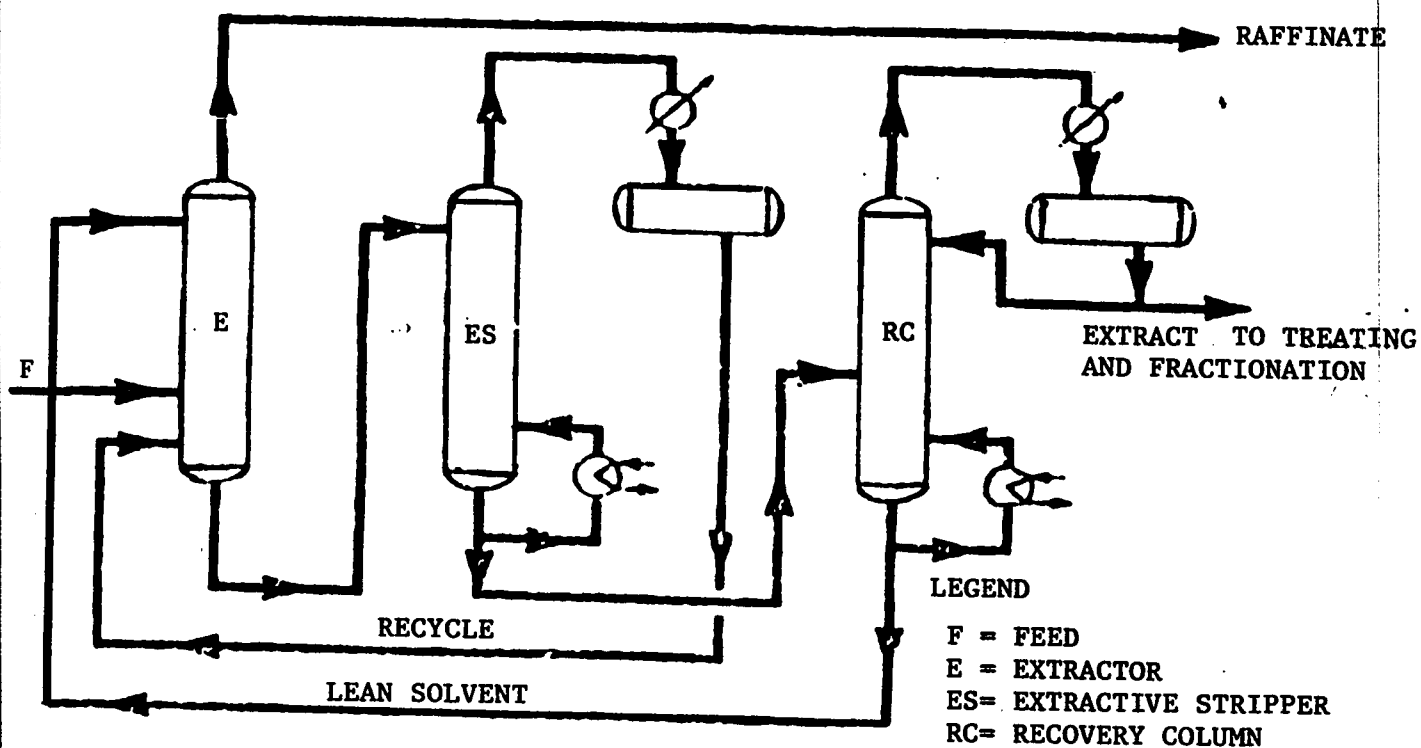


FIGURE (2.3) AROMATIC RECOVERY BY SHELL SULFOLANE PROCESS

TABLE (2,3)
SULFOLANE PROPERTIES

Boiling point, °F.	549
Freezing point, °F.	82
Specific gravity at 212 °F.	1.20
Viscosity at 212°F., cp	2.5
Heat capacity at 212°F., Btu/lb/°F.	0.40
Interfacial tension at 212°F., dynes/cm.	3.0

which yields aromatic-rich as a bottom and an overhead back-wash stream that returns to the extract. The raffinate from this arrangement leaves the top of the extractor [20].

One advantage claimed for this arrangement is its ability to reject both light and heavy aromatic from the extract. The non-aromatics leaving the extractor in the solvent phase are predominantly light, and can easily be stripped out overhead during subsequent extractive distillation. The heavy non aromatics are rejected directly from the extractor in the raffinate-phase [22,24]. Shell has successfully extracted aromatics with Sulfolane at its Rho Oil Refinery in Italy. The purities obtained are shown in Table (2.4) and the consumption figures of the Sulpholane extraction Unit at Rho Refinery are shown in Table (2.5) [11,25].

Many advantages are claimed for the substitution of Sulfolane for the Polyethylene glycols generally used for aromatic-paraffins separations.

Over most of the range of aromatic-paraffins concentration, the selectivity factors for Sulfolane are substantially higher than for diethylene glycol. The superior selectivity persists until the plait point occurs which is at about 80 mole % aromatics (diethylens glycol does not exhibit such a plait point).

TABLE (2.4)

PURITY OF AROMATICS (SULFOLANE PROCESS)

	<i>Benzene</i>	<i>Toluene</i>	<i>Xylene</i>
Spec.gravity 15/4°C	0.8842	0.872	0.8694
ASTM analysis :			
IBP°C	79.3	110.1	138.3
5 percent	79.8	110.3	139.0
95 percent	80.1	110.5	140.1
FBP °C	80.2	110.5	140.3
Non-aromatics	0.06	0.01	0.01
Benzene	99.93	--	--
Toluene	0.01	99.99	0.02
Xylenes + ethylbenzene	--	--	99.97
Freezing point °C	5.39	--	--

TABLE (2,5)

CONSUMPTION FIGURES (SULFOLANE PROCESS)

	<i>Units per ton feedstock</i>	<i>Units per ton of reco- vèred aromatics</i>
Utilities:^a		
Steam(t)	0.87	2.35
Cooling water (cu.m.)	36	98
Electric power (kWh)	6	16
Solvent ^b (kg.)	0.2	0.54 = 3.60 DM/t
Composition of feedstock :		
Non-aromatics(vol.per cent)	68.6	
Benzene (vol.per cent)	5.2	= 37 Wt. per cent
Toluene (vol.per cent)	16.1	
Xylene + ethylbenzene(vol. per cent)	10.1	
Yield :		
Benzene + toluene + xylenes + ethyl- benzene		96 wt. per cent
<hr/>		
a Distillation inclusive		
b Price of sulfolane : 6.70 DM/kg.		

The significant differences between Sulfolane and diethylene glycol in separating aromatics from paraffins are : [26]

- (1) Sulfolane is the more selective except near its plait point.
- (2) Sulfolane selectivity is less sensitive to molecular weight differences between aromatics and paraffins.
- (3) Sulfolane selectivity is less sensitive to water addition at the same time water addition does not reduce the solvency to the same extent.
- (4) Hydrocarbons are much soluble in Sulfolane.
- (5) Hydrocarbons have a higher partial pressure over diethylene glycols.
- (6) Sulfolane is more heat and oxidation stable than diethylene glycol and has a lower heat capacity (0.3) as against (0.65) Btu/(lb)(°F).
- (7) Sulfolane extraction are done at 248°F, those with diethylene glycol at 302°F.

The higher solubility and selectivity of Sulfolane leads to lower solvent to feed ratio.

(iii) Arosolvan Process

N-methyl pyrrolidene with a boiling point of 206°C is used by Lurgi on a technical scale as selective solvent

in the so-called Arosolvan process. Since 1968 the following capacity of plants based on the Arosolvan process has been installed [27].

1,050,000 tons per year B.T.X. in Western Europe
290,000 tons per year B.T.X. in U.S.A.
450,000 tons per year B.T.X. in Japan
490,000 tons per year B.T.X. in Eastern Countries
210,000 tons per year B.T.X. in Brazil

As shown in Figure (2.4), the solvent is charged to the top of a multi-stage extractor from which it travels downwards. The mixture to be separated is fed to the centre of the extractor. The non aromatics insoluble in the solvent pass upwards and leave the extractor at the top, while the solvent flows downwards and becomes loaded with aromatics. In a distillation tower, extract and solvent are separated, the latter being returned to the process. The distillate from extract distillation, consisting of aromatics and non aromatics, goes to the aromatics stripper where low boiling non-aromatics and part of the benzene are distilled off. The residue, the pure aromatics, is fractionated subsequently [11].

The high solvent capacity of N-methylpyrrolidone (N.M.P) can be easily adjusted over a wide range of

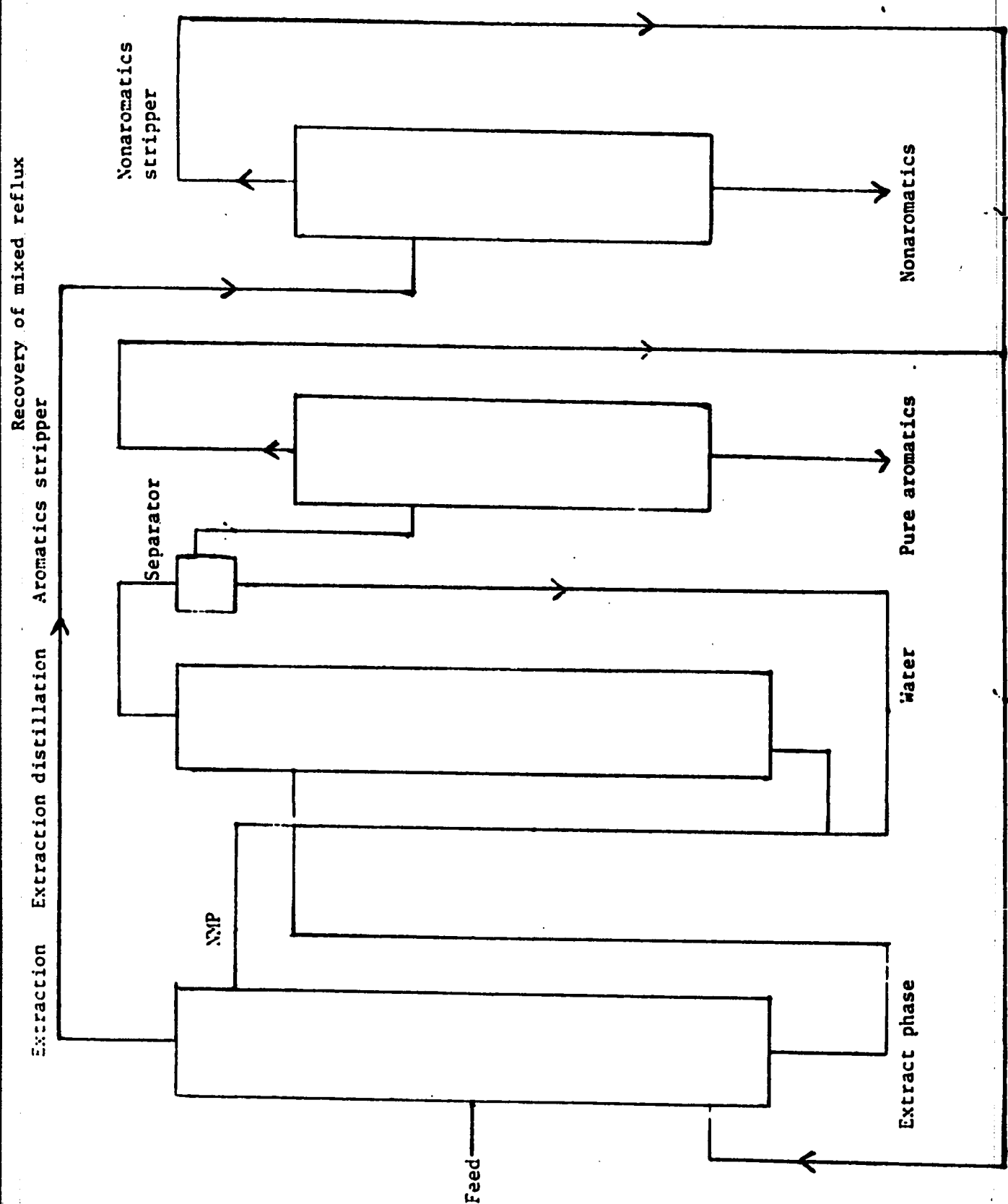


FIGURE (2.4) FLOW DIAGRAM OF NMP PROCESS

strength by addition of water. Owing to its physical properties, e.g. its low melting point - 24 °C and its low viscosity, extraction can be carried out at low temperatures, contrary to other processes. Figure (2.5) shows the selectivity of some solvent mixtures of N-methylpyrrolidone and water contents [4,5,26].

(iv) Union Carbide Process

Union Carbide Corporation claims that the conventional processes for aromatic extraction which includes Arosolvan, Udex and Sulfolane etc. are similar to each other and each produces a liquid solution of the aromatic as feed to the fractionation train. Such processing schemes involve the distillation of a substantial amount of extractor reflux, water and polar solvent, as well as the revaporization of the aromatics.

Therefore, Union Carbide proposed a process in which a gasoline fraction is first treated in a primary extraction with a polar, selective solvent (Tetraethylene glycol). Aromatics are then transferred into a high boiling aliphatic fraction in a secondary extraction (Dodecane).

Finally, aromatics are fractionally distilled from the second extract. In this process no water is distilled, no extractor reflux is distilled, and the aromatics are

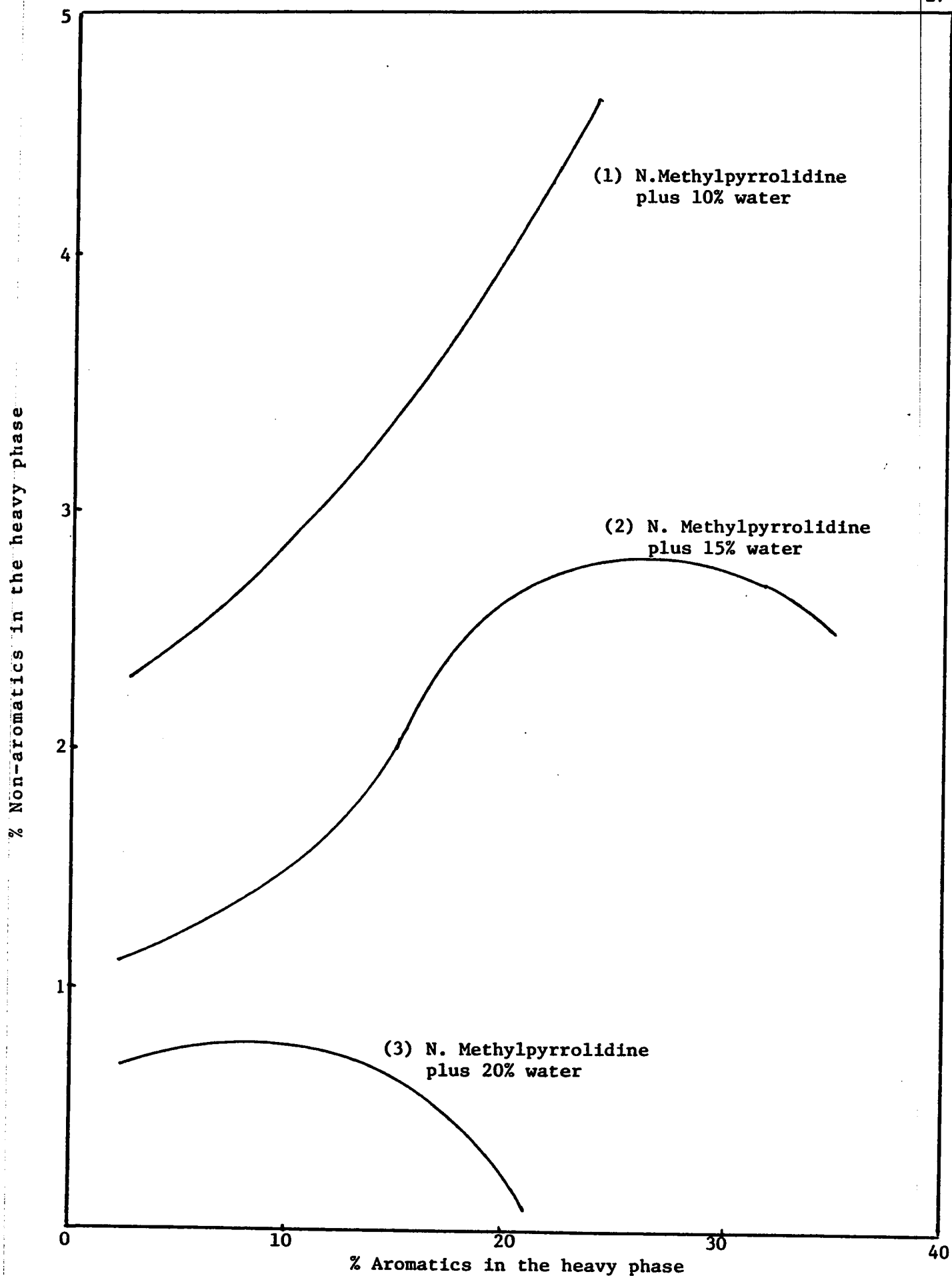


FIGURE (2.5) SELECTIVITY OF SOLVENT MIXTURES OF NMP

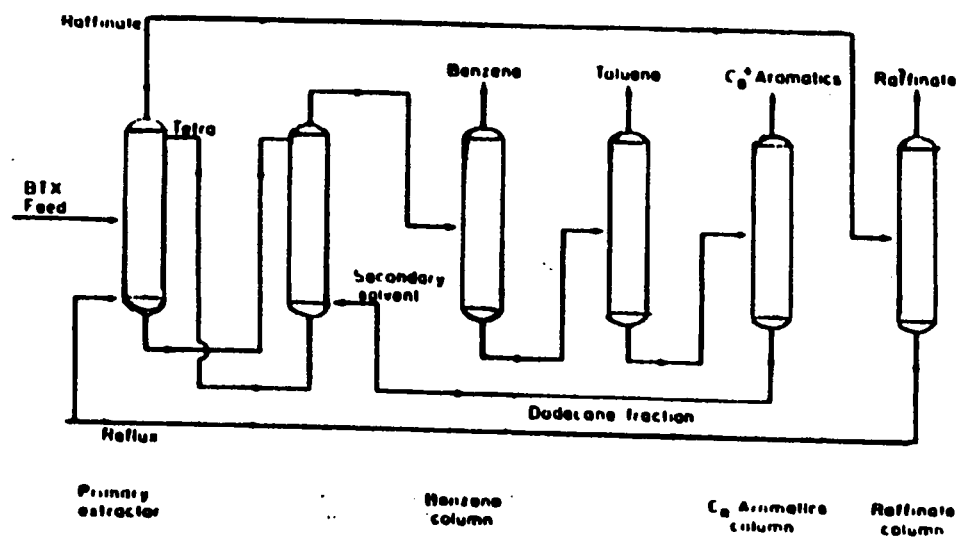


FIGURE (2.6) SCHEMATIC FLOW DIAGRAM OF UNION CARBIDE PROCESS

vaporized only once. Thus, the process has significantly better economic advantage compared with conventional process as shown in Figure (2.6) [17].

(v) I.F.P. Process

The process developed by the "Institute Francais du petrole" uses dimethyl Sulphoxide (DMSO). The process is complicated by the fact that the separation of DMSO from the aromatics is carried out by means of re-extraction with a secondary solvent made up of hydrocarbons. Moreover DMSO is a product which requires certain precautions in its use [13].

(vi) MOFEX Process

The process developed by "Leuna-Werke" of East Germany uses monoethyle formamide in a 90% aqueous solution. The solvent is somewhat unstable under heating conditions and has to be recovered by vacuum distillation [13].

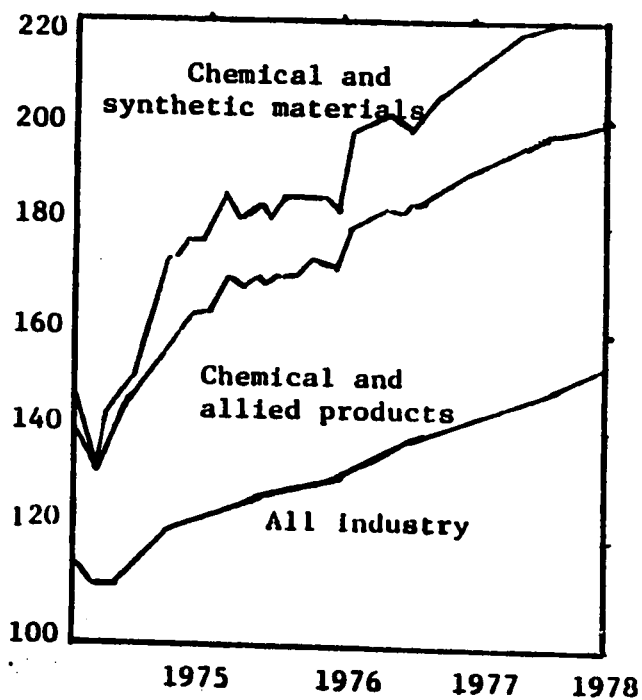
(vii) Morphylene Process

The process developed by Snam-Progetti using a morpholine derivative (such as N-formylmorpholine, a reaction product of formic acid with morpholine). This is commonly a combination of liquid-liquid extraction and extractive distillation. This has been commercialized in Germany. It has been quoted as particularly applicable

to the extraction of aromatics from hydrogenated pyrolysis gasoline [13] .

2.3 Modern Trends for Increasing Aromatics Output

Refinery and chemical planning people are convinced that the demand for aromatic derivatives will continue its relatively rapid growth over the next ten years. In the past, the refineries producing aromatics from gasoline had to cope with the increasing disparity caused by the greater growth rate of aromatics for chemical use (9% per year) compared to aromatics gasoline (3% per year). Despite politico-economic reaction to the OPEC cartel, overall gasoline demand is still increasing and reached all-time high in 1978 [29]. Furthermore, the U.S. Government objectives for reducing domestic demand beyond 1980 may prove to be unattainable [30]. Even more significant for B.T.X. however, is the projected future growth of market for petrochemicals, as shown in Figure (2.7) and Table (2.6). The indicated world wide growth of the B.T.X. market is at a compounded annual rate of 4-6 percent over the 1978-81 period and probably through 1985. Similar projected growth in U.S. use of feedstock for primary olefins and aromatic production is shown in Table (2.7). The shortfall in B.T.X. can be made up by hydrocracking heavy stocks to B.T.X. boiling range materials, proprietary hydrocracking process, Unicracking [28].



Demand, MM metric tons/year

	1976	1980	1990
Primary olefins	18.6	25.7	42.1
Benzene + P/O xylenes	6.8	8.7	13.7

Average annual percent growth

	1954-1964	1964-1974	1976-1980	1980-1990
Olefins and aromatics	15.0	9.7	7.8	5.0
Real GNP	3.6	3.3	4.5	3.3
Growth ratio	4.2	2.9	1.7	1.6

FIGURE (2.7) U.S. CHEMICAL AND PETROCHEMICAL
MARKET GROWTH

TABLE (2.6)**PREDICTED GROWTH RATES FOR BTX(%)**

	<i>Benzene</i>	<i>Toluene</i>	<i>Xylene</i>
U.S.A.			
1978 - 1981	5.6	2.3	4
1981 - 1985	4.5	2.4	2.5
Western Europe			
1978 - 1981	4	4.5	5
Japan			
1978 - 1981	4	3	3

TABLE (2.7)**FEEDSTOCKS FOR U.S. PRIMARY OLEFINS
AND AROMATICS, 1,000 bpd**

	<i>1976</i>	<i>1980</i>	<i>1990</i>
N.C.L.	620	650	510
Naphthas (net)	190	260	450
Gas oil	140	300	820
TOTAL	950	1210	1780
Percent of U.S. petroleum consumption	5.4	5.8	7.6

Source : D.L.Fridley, ACS, Chicago, Aug.29,1977.

(i) The Unicracking Process

This established process can increase basic petrochemical stocks, produce good quantity of fuel distillates and yields more useful products, from petrochemical naphtha and gasoline to high yield of top quality turbine fuels and diesels. Prime quality naphtha can be obtained at the same time high yields of middle distillate products are made.

Figure (2.8) shows typical unicracker process configurations, consisting of a hydrotreating reactor containing a high activity, proprietary catalyst for hydrogenation of nitrogen, sulphur, and oxygen compounds followed by one or two hydrocracking reactors. The hydrotreating reactor effluent flows directly into the first hydrocracking reactor. In single stage units unconverted oil recovered in the fractionation section is recycled to the single hydro cracking reactor (R-2 reactor in Figure (2.8))

The two stage may employ the same or different unicracking catalysts depending on process objectives. Unicracking technology embraces a family of noble and non-noble metal catalysts designed for efficient operation with a wide range of feedstocks and under diverse conditions.

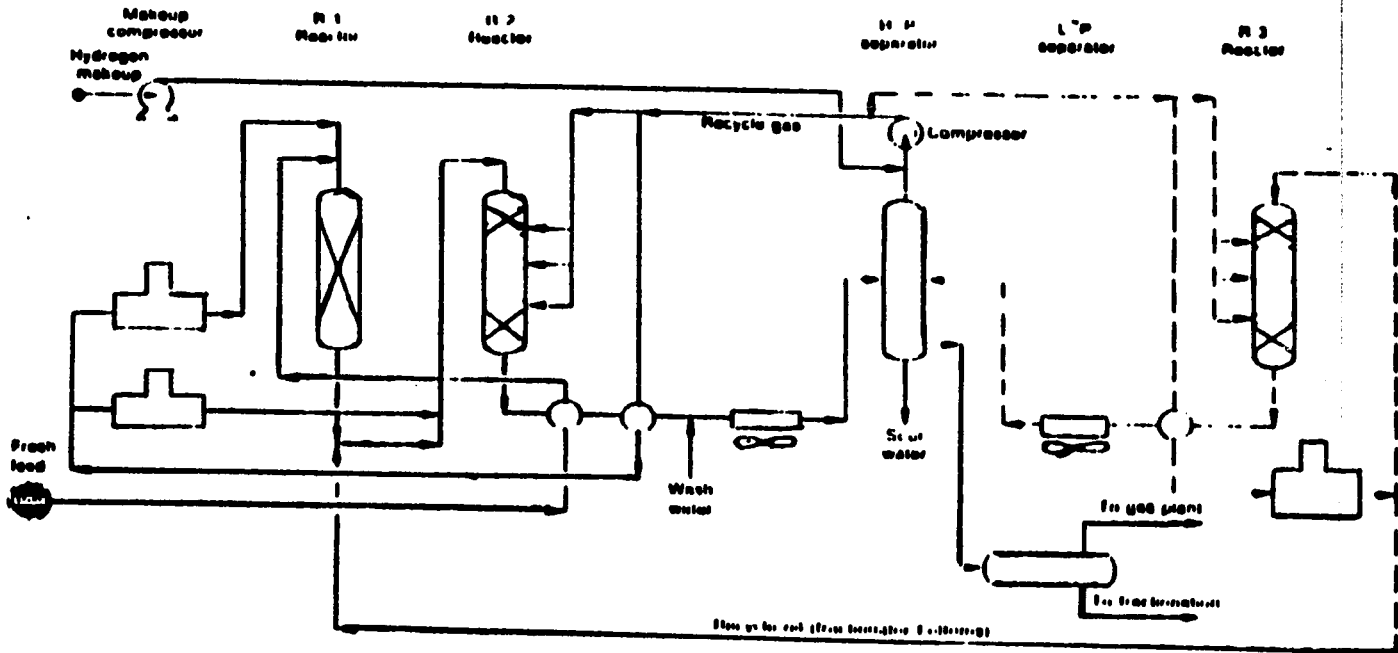


FIGURE (2.8) UNICRACKING PROCESS CONFIGURATIONS

B.T.X.Precursors : Crude oils contain varying amounts of BTX precursors, $C_6 - C_8$ or $C_6 - C_9$ naphthenes plus aromatics (N+A). These are recoverable in appropriate cut ranges of heavy naphthas that can be charged after hydrotreating to catalytic reformers. The high-boiling N+A compounds in the crude oil remain inaccessible by this means as a source of precursors. However, they can be made accessible by Unicracking heavier distillates from the crude oil, thus greatly increasing the potential of a given crude oil as a source of BTX.

During the Unicracking reactions, the catalyst provides excellent single-ring retention. That is, one of the more rings in the N+A compounds in the heavier distillates remains intact while its side chains and any associated ring are hydrocracked. In this way, the carbon numbers of the heavier N+A in the crude oil are reduced to the $C_6 - C_8$ or $C_6 - C_9$ range for BTX precursors.

Table (2.8) gives an example for an Iranian (Ahwaz) crude oil. As shown, the increase of BTX precursors by Unicracking its 650-1000°F gas oil (24 vol. percent of crude) is more than 40 percent greater than the quantity of such precursors available in the virgin naphtha (16 vol. percent of crude). The concentrations of BTX precursors in the Unicracked naphtha also are greater than in the virgin naphtha. Additional BTX precursors could readily

TABLE (2.8)

BTX PRECURSORS - STRAIGHT-RUN +
UNICRACKING

Crude source : BTX precursors from :	Ahwaz (Iranian)		Sum
	SR naphtha	VGO	
Crude cut range, °F	149-329	650-1000	
Processing	Hydrotreating	Unicracking*	
149°F + naphtha yield			
Vol. % feed to processing	100	85	
Vol. % crude	16	20.4	
N + A. vol. % crude			
C ₆ - C ₈	4.5	6.3	10.8
C ₆ - C ₉	5.9	8.4	14.3
C ₆ +			
N + A, vol.% naphtha			
C ₆ - C ₈	28	31	
C ₆ - C ₉	37	41	
C ₆	40	44	

* Product naphtha ASTM endpoint of 332°F

be obtained by Unicracking distillates both lighter and heavier than 650-1000°F fractions.

Yields of BTX precursors : The yields of BTX precursors from Unicracking are determined primarily by the type of feedstock. A rule of thumb is : " Many rings in, many rings out; few rings in few rings out." This is illustrated in Table (2.9). Ring content of the feed is roughly indexed by its UOP characterization factor*. For low characterization factors (high feed ring contents), the yield of BTX precursors become very high, reaching 69/77 vol. percent of feed for C₆- C₈/ C₆- C₉ N+A from a 9.69 UOP K steam cracked gas oil. Corresponding N+A concentrations in the 150°F naphtha reached extremely high levels, approximately 81/90 volume percent respectively.

As the characterization factor of the feed increases, its total ring content is reduced, and the yields of BTX precursors from Unicracking are reduced also. Thus, at the bottom of Table (2.9), precursors yields from Unicracking a paraffinic Libyan gas oil, having a UOP characterization factor of 12.45, are shown. As indicated, the yields of C₆- C₈/ C₆- C₉ N+A from Unicracking this feed are 22/27 vol. percent. Corresponding N+A concentrations in the 150°F naphtha are about 33/41 vol. percent respectively.

* (Cubic avg. boiling point, °R)^{1/3}/sp. gravity 60/60 °F.

TABLE (2.9)

TYPICAL YIELDS OF N+A IN 150°F
UNICRACKER NAPHTHA

<i>Fresh feed</i>		<i>Naphtha D-86 EP, OF</i>	<i>No. of stages</i>	<i>Catalyst*</i>	<i>N + A, vol.% fresh feed</i>		
<i>UOP K</i>	<i>50% pt., OF</i>				<i>C - C</i>	<i>C - C</i>	<i>Total</i>
9.69	477	348	1	NNM	68.8	76.6	83.7
10.20	484	334	1	NM	61.2	71.1	74.4
11.40	665	373	1	NNM	39.7	52.7	60.5
11.79	814	360	2	NNM	29.4	40.9	49.9
11.89	784	352	1	NM	30.8	40.0	44.8
12.45	716	340	2	NM	21.7	27.4	28.5

* NM = Noble metal; NNM = Non-noble metal

It is possible to plot the C_6 - C_8 N+A yields of Table (2.9) against feed characterization factor and obtain a reasonable smooth correlation, despite variations of Unicracking catalyst type and numbers of Unicracking stages. There is some naphtha endpoint variation in the collected data of Table (2.9), which introduces a relatively greater irregularity to the yields of C_9 and heavier N+A hydrocarbons [29].

(ii) From Lubricating Oil Base Stocks

As described earlier now the attention is also focussed on heavier fractions for the extraction of heavy aromatics. As far as lubricating oil base stocks are concerned, the aromatic constituents found in these bases are undesirable because they contribute poor viscosity Index (V.I.), low oxidation stability and tendency to form carbon residues. The removal of the aromatic constituents from an oil, results therefore in the general improvement in all these properties [31].

Of the many solvents proposed and developed over the years the following are given :

- (1) Combination of liquid SO_2 plus a solvent of the aromatic group.
- (2) Organic chemical solvents such as :

- (a) Furfural
- (b) Thenol
- (c) Nitrobenzene
- (d) Chlorex
- (e) 3-Methoxy propionitrile

Comparing any of these organic solvents, listed above, to liquid SO_2 , it has been proved that they are far more superior with respect to the extraction of aromatics with high proportion of substituent group and/or polynuclear aromatics [10].

The 3-Methoxy propionitrile was experimentally tested as a solvent in removing aromatics from the light wax distillate obtained from the vacuum distillation of Saudi Arabian residual oil. The parameters considered were operating temperature, extraction time, and oil to solvent ratio, the experimental findings are shown in Figure (2.9) [10].

(iii) From Kerosine Fractions

Extraction of aromatic hydrocarbons by selective solvents from kerosine fractions is widely used as a process for obtaining low aromatic jet-fuel-components. The aromatic extracts of this fraction are usually recommended to be used, after hydrodesulferization as a high octane fuel, and as a raw material for the petro-

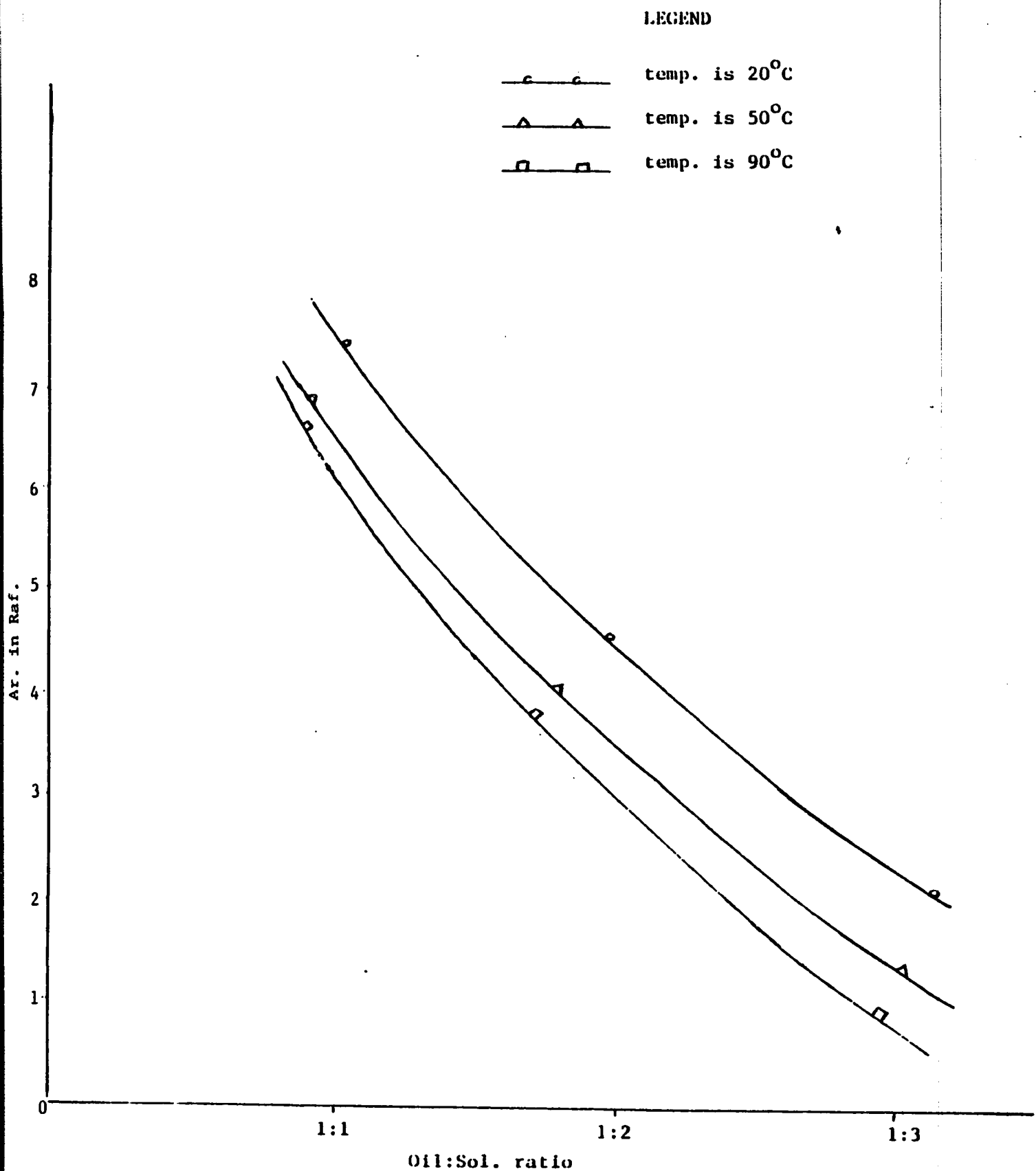


FIGURE (2.9) THE INFLUENCE OF OIL:SOL. RATIO ON THE EXTRACTION OF AROMATICS FROM L.W.D. AT DIFFERENT EXTRACTION TEMPERATURES

TABLE (2.10)

PHYSICOCHEMICAL PROPERTIES OF KEROSENE
DISTILLATE AND PRODUCTS

	Distillate	Raffinate after extraction			
		Propylene carbonate	85% aqueous solution of N-methylpyrrolidone	Mixture of methyl and ethyl carbomates (1:1)	Sulfolane*
Density ρ_4^{20}	0.8077	0.8077	0.7872	0.7865	0.7867
Kinematic viscosity, cSt					
at 20°C	1.45	1.52	1.49	1.53	1.51
at -40°C	6.13	6.34	7.03	6.90	6.85
Heat of combustion (lower local/kg)	10317	10368	10373	10370	10365
Smoke point, mm	19	26	26	25	26
Luminometer number	50.6	58.3	64.1	61.8	61.5
Content of aromatic hydrocarbons, %	24.6	17.2	16.6	14.4	14.7
Contents of bi-cyclic aromatic hydrocarbons, %	2.7	0.86	0.56	1.02	1.20
Content of sulfur, %	0.018	0.016	0.016	0.016	0.015
Raffinate yield, %	100.0	80.3	84.9	82.3	74.6

* Extraction temperature $100 \pm 2^\circ\text{C}$

chemical industry [7].

The efficiencies of sulfolane, N-methyl pyrrolidone, diethylene glycol, triethyleneglycol, propylene carbomate and a mixture of equal parts of methyl and ethyl carbomates, using kerosine distillate cut from Russian crudes for the extraction of aromatics has been studied [9]. The findings are shown in Table (2.10).

Binodal equilibrium curve for the system consisting of solvent, aromatic hydrocarbons and paraffinic-naphthenic hydrocarbons at temp from 20 to 100°C are shown in Figures (2.10 - 2.12). It has been established that the best solvent extraction properties are shown by an aqueous solution of N-methyl pyrrolidone by propylene carbonate and by mixed methyl and ethyl carbomates.

Kerosine fraction (150-250°C) from El-Morgan Egyptian Crude having an aromatic content of 20.1% by weight and a smoke point of 22 mm was treated with triethylene glycol in a counter current extraction column [7]. Extraction was carried out at different temperatures and different solvent fraction weight ratios. Optimum conditions of extraction, resulting in a fairly large extent of aromatic extraction and a high yield of good quality refined Kersoine were found to be at 110°C and 6:1 solvent: fraction weight ratio. The refined fraction is highly recommended as a component of jet fuels. Findings are shown in

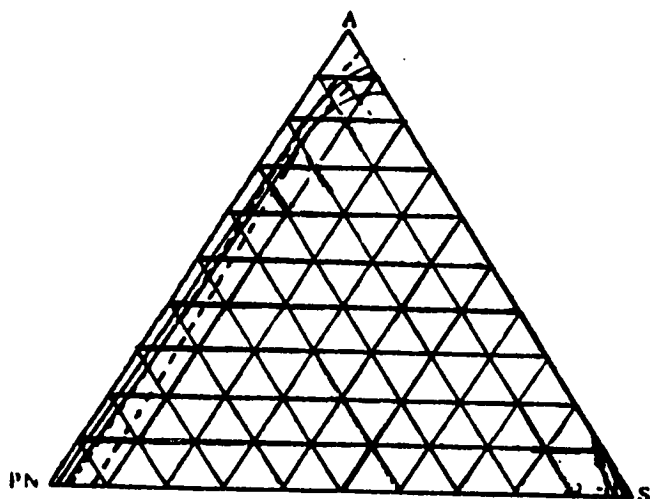


FIGURE (2.10) : PHASE EQUILIBRIUM DIAGRAM FOR SYSTEM CONSISTING OF PARAFFINIC-NAPHTHENIC HYDROCARBONS, AROMATIC HYDROCARBONS AND TRIETHYLENE GLYCOL

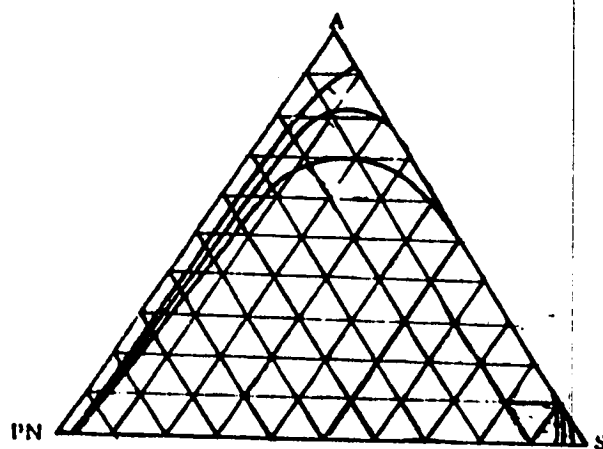


FIGURE (2.11) : PHASE EQUILIBRIUM DIAGRAM FOR TERNARY SYSTEM CONSISTING OF PARAFFINIC-NAPHTHENIC HYDROCARBONS, AROMATIC HYDROCARBONS AND PROPYLENE CARBONATES

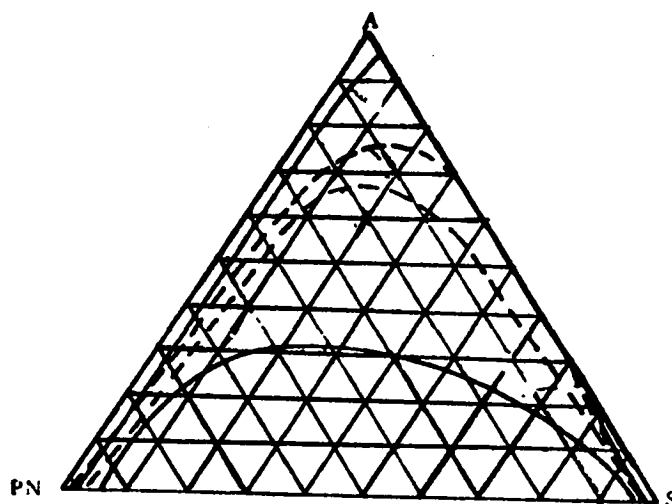


FIGURE (2.12) : PHASE EQUILIBRIUM DIAGRAM FOR TERNARY SYSTEM CONSISTING OF PARAFFINIC-NAPHTHENIC HYDROCARBONS, AROMATIC HYDROCARBONS AND N-METHYLPYRROLIDONE

Figures (2.13 and 2.14).

It may be concluded, therefore, that aromatics can be extracted, not only from lighter cuts, but also from the heavier cuts of crude oil. The choice of the lighter cuts is due to ease and availability of these cuts for extraction of aromatics. Except Abdel-Aal et al [10], nobody has published any literature for the extraction of aromatics from Saudi Arabian crude, so it becomes imperative to carry out work on the efficiencies of various solvents in extraction of aromatics from Saudi crudes (lighter cuts).

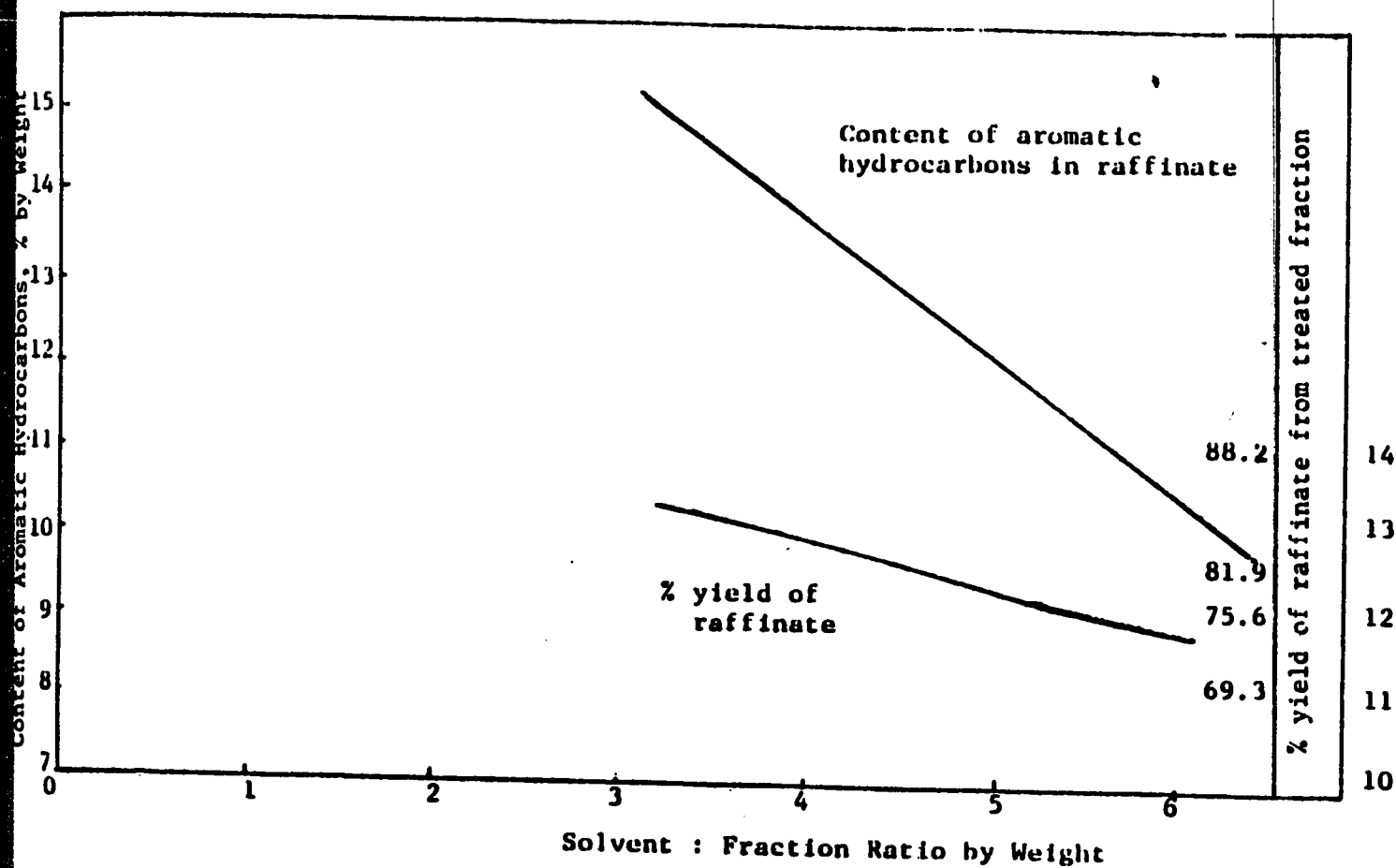


FIGURE (2.13) CHANGE OF RESIDUAL CONTENT OF AROMATIC HYDROCARBONS IN RAFFINATE AND ITS YIELD WITH CHANGE OF SOLVENT : FRACTION RATIO (AT 110 °C)

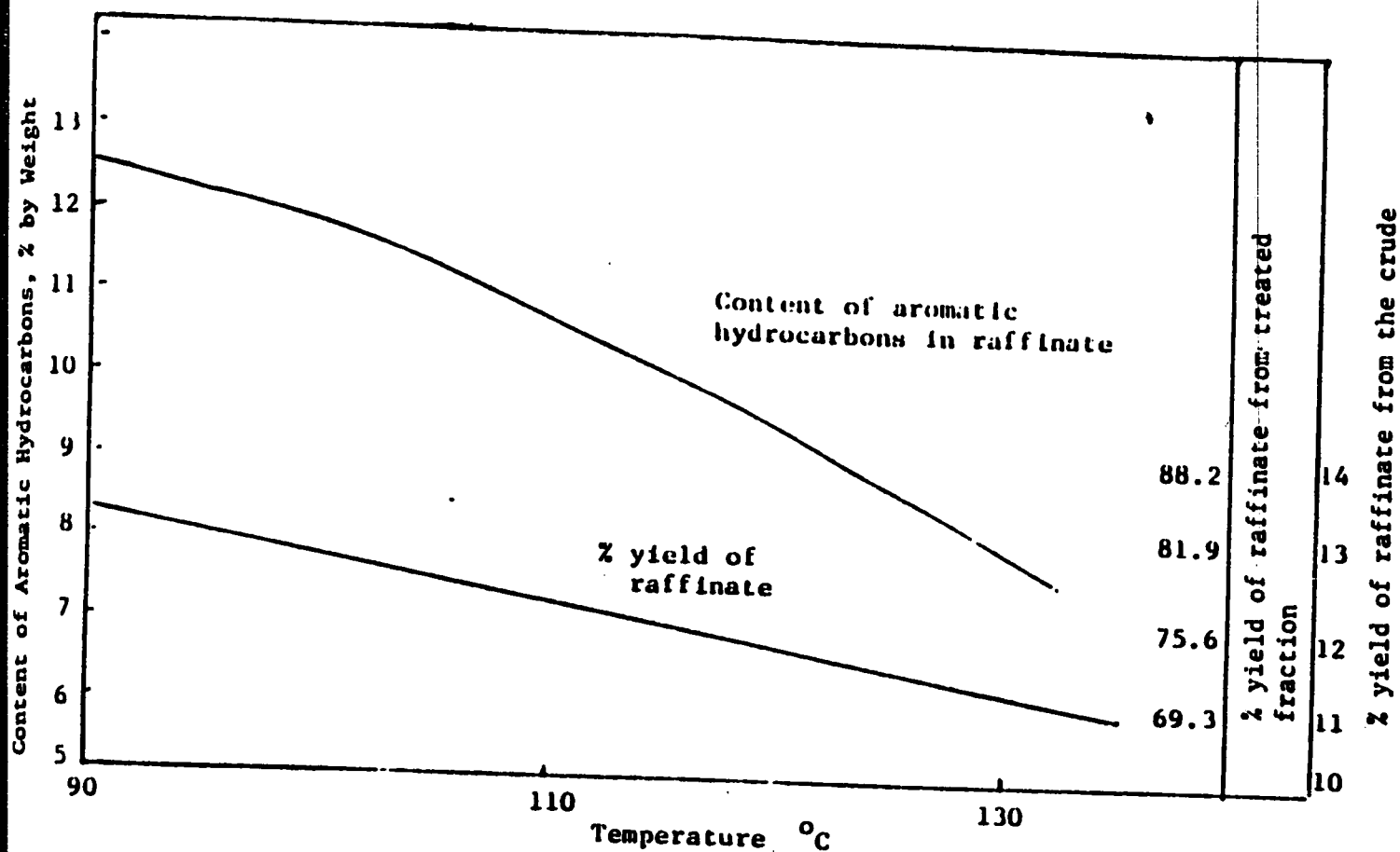


FIGURE (2.14) CHANGE OF RESIDUAL CONTENT OF AROMATIC HYDROCARBONS IN RAFFINATE AND ITS YIELD WITH CHANGE OF EXTRACTION TEMPERATURE (SOLVENT : FRACTION = 6:1 BY WEIGHT)

CHAPTER 3

SOLVENT EXTRACTION

On a technical scale, aromatics are almost exclusively separated from non aromatics of the same boiling range by liquid-liquid extraction. A pre-requisite for the application of the process is that the organic solvents used and the mixture to be separated form two phases. As solvents, only such materials that contain a polar group are of use.

The polarity shall, as for instance in the case of water, not to be too high because solubility for aromatics decreases with increasing polarity. On the other hand, solubility should not be too low, since the solubility for non aromatics increases to a greater extent than that for aromatics with decreasing polarity. For economic reasons solvents with a boiling point, which exceeds that of the aromatics to be extracted, are given preference. [11].

In general the criteria of separation, using liquid-liquid extraction as compared to distillation, is based on solubility rather than pressure difference of the species involved in a mass transfer operation. Liquid-liquid extraction system can be categorized into two main classes.

- (i) Where the mutual solubility of the solvent and the feed containing component is to be extracted negligible. This case could be represented by the

extraction of pyridine from water using chlorobenzene as a solvent. Equilibrium relationship is a simple one and problem of this type can be solved using classical graphical MacCabe-Thiele Method.

- (ii) Where the partial miscibility of the solvent and the feed is considerable. Equilibrium relationship in such systems are normally represented by triangular coordinates.

It is clear that proper solvent selection is critical in determining whether solvent extraction will be economically competitive for a particular separation. The choice usually involves a compromise between conflicting properties, as it is rare to find a solvent that can be described as truly ideal. Some of the parameters are selectivity, capacity, solvency, reversibility, cost, physical properties and safety.[32]

Through the years a host of selective solvents for the physical group of separation in extraction and extractive distillation have been proposed and selected. Among the criteria for selection are such obvious and practical properties as stability, chemical indifference, availability, toxicity and price have been featured, but it is the basic solvent properties, such as selectivity and solvent capacity, which characterize a solvent. Since we are here looking for the high boiling solvent (heavy solvents), and wide range

feedstock, the boiling point and the molecular weight selectivity also assume some importance [33,34,35].

For most of the current solvents, selectivity is a matter of polarity of the solvent molecule. Therefore, the sequential order of affinity to the various groups of hydrocarbon species is always the same, irrespective of solvent. The affinity decreases in the order : dicyclic aromatics, monocyclic aromatics, polycyclic naphthenes, dicyclic naphthenes, naphthenes, olefins, paraffins. Selectivity can be defined in several ways. A suitable definition in the case of aromatic extraction is the ratio of the distribution coefficient of solute A and B [36].

The amount of solvent which can be contained in the solvent phase is a factor in determining the solvent circulation rate in plant. A quantitative measure of this solvent capacity could be the Distribution Coefficient [32,37].

In selecting a solvent, high selectivity is naturally desirable. A low light/heavy selectivity is required for the processing of a wide range feedstocks. The object is less clear as far as solvency is concerned. Since, while high solvent capacity looks attractive, this implies a lower selectivity. To decide on a suitable criteria for solvent selection, the extraction process has to be looked into more detail.

3.1 Requirements for Separation by Extraction

For the separation of a wide range fraction, liquid-liquid extraction is inevitably required on account of the limitations to the light/heavy selectivity of all processes including distillation. If extraction is applied, solubility of the hydrocarbons in the solvents must be such that two liquid phases exist which requires that the solvent capacity at least for the raffinate part is not too high. If on the other hand solvency is too low for the aromatics large quantities of solvent are required [38,39].

The conditions of extraction pertinent to hydrocarbon system can be represented in the well known ternary phase diagrams Figures (3.1 to 3.3). With the open system it is possible to produce pure aromatics, but with other type is not. However, one figure implies that the solubility of the extract is quite low and that high solvent ratios are required. Moreover, the actual solvent ratios would be considerably higher than those deducible from the final extract solubility figure, since a sizeable internal recycle and build-up in the counter current process will occur [9]. With the closed system, extraction could in principle go as far as the plait point, where the hydrocarbon load is 50 to 70%. In the case of all physical solvents, selectivity is largely lost at low loads. For practical purposes loading beyond 30 - 35% is generally inattractive. Disregarding any recycle and build-up, the solvent to extract

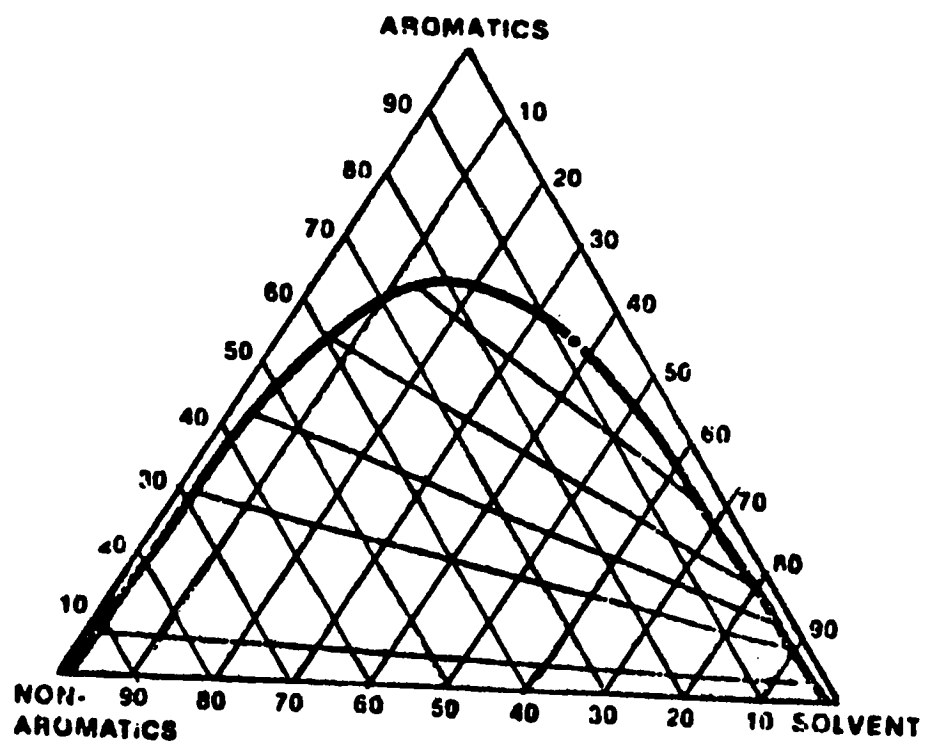


FIGURE (3.1) TERNARY PHASE DIAGRAM
(OPEN SYSTEM)

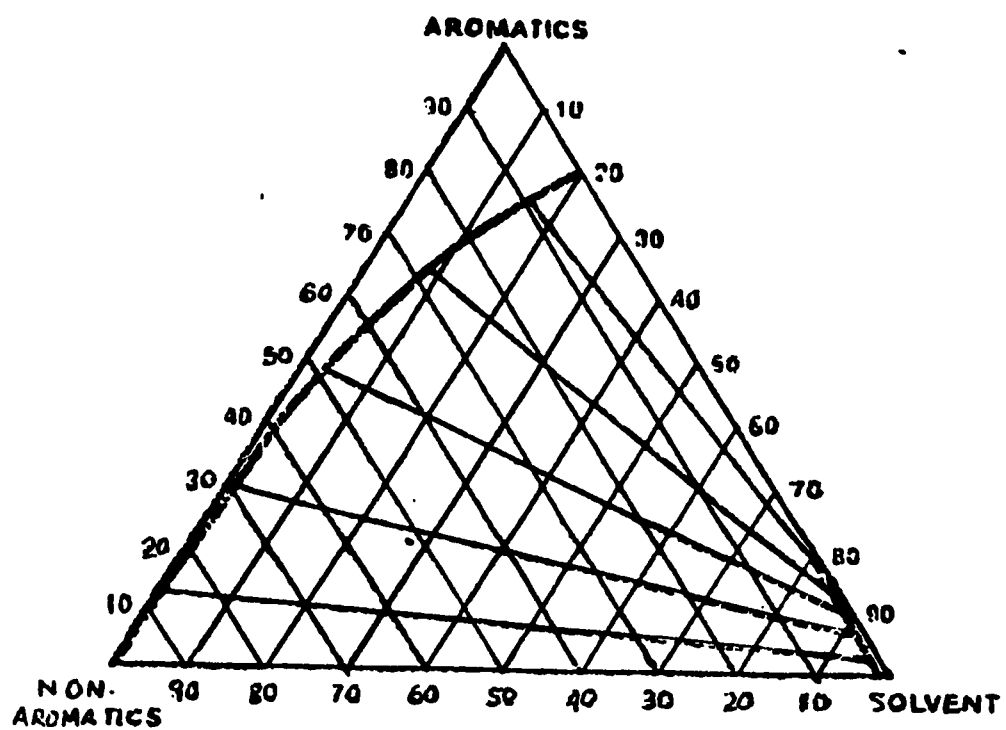


FIGURE (3.2) TERNARY PHASE DIAGRAM (CLOSED SYSTEM MEDIUM SOLUBILITY)

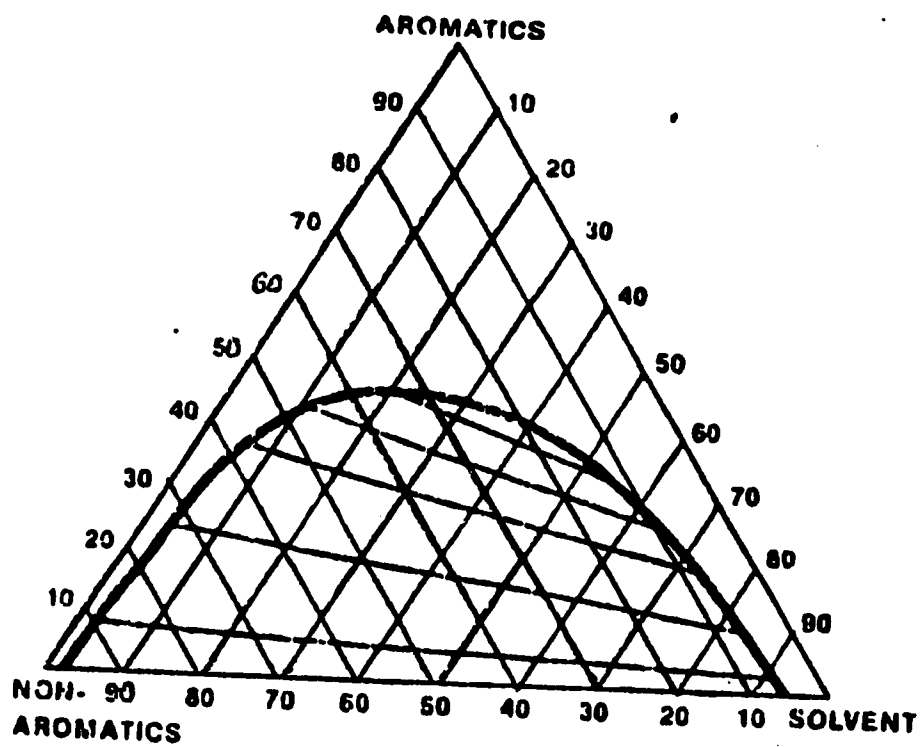


FIGURE (3.3) TERNARY PHASE DIAGRAM (CLOSED SYSTEM HIGH SOLUBILITY)

ratio must therefore be larger than 3. Taking a normal build-up of half the extract into account, the minimum solvent/extract ratio reaches the order of 4.5. This limit is universal [40].

In the solvent requirement at the raffinate end of the extractor, the solubility of the highest aromatic in the feed sets the limit to the required solvent to raffinate ratio. For the solvents having less solvency for the highest aromatic to be recovered, extra solvent will be supplied above the minimum requirement at the bottom part of the extractor, whereas in solvent systems with higher solvency one will have to apply the minimum amount and because of the relation of selectivity to solvency, solvent will have less selectivity than the optimum solvent [41].

This argument is very important. We may rephrase it by saying that under conditions, like near the bottom of an extractor, where the solvent has to carry the extract and to provide selectivity, the maximum load is given rather, by the amount which a solvent tolerates before losing its selectivity properties than by the solubility property, as long as the latter is large enough. For higher solvent capacity selectivity suffers with no compensation otherwise. For less solvent capacity more solvent than the theoretical minimum is required [41,42].

The above derivations are simplification of a complicated case, but the requirement evolves that an advantageous solvent has to have the highest possible group selectivity within a certain range of the solvent capacity.

3.2 Ways to Influence Basic Solvent Properties

If the solvent does not meet the exact requirements of an application there are three ways to cope with the situation :

- (i) To accept the less than optimum fit of solvent properties with requirements.
- (ii) To find another more suitable solvent.
- (iii) To modify the basic solvent properties in the desired direction.

In some applications it might be desirable to slightly modify the solvent properties. Some of the possible means are the influence of temperature, of water content, and of mixing with other solvent.

Temperature :

The solvent properties vary with the operating temperature. A hotter solvent has more solvency and less selectivity. The trend is, however, less favourable than the general trend constituted by all solvents together. Naturally, in a process design the temperature

chosen has consequences for a number of other aspects, so that the final selection has to be made with the overall picture in view [38].

Water Content :

In essence, water can be regarded as a solvent with reasonable selectivity and very low solvency. Owing to its extreme properties, relatively small additions of water will have a noticeable effect on solvent properties, but the water/solvent system can simply be regarded as a mixed solvent. In most of the process schemes, water is used to strip or wash streams, and so is actually always present. Addition of somewhat more water than would in any case be in the solvent, does not introduce a new processing medium to be taken care of. The other less advantageous aspect is that water in hydrocarbon environment, is quite volatile and will be distilled off upon stripping, thereby using up the heat of vaporization which has to be provided [9].

Mixed Solvents :

Solvent mixtures are used in several commercial processes, but now and then the question has been posed whether by synergistic effects, some special advantages could be gained by using solvent mixtures. As a matter of fact, one could hardly expect the basic properties of

solvent mixtures, if, plotted on a graph of solvent power vs group selectivity, to fall exactly on a straight line between the points of the two pure solvents. With regard to the advantage of tailoring a solvent by blending, the fact should not be overlooked that the two solvents may behave differently towards various auxiliary steps in the process, such as water wash of products, steam stripping, corrosion, stability and behaviour in the recovery column, and in a design these aspect will have to be considered [42].

3.3 Secondary Solvent Properties

Besides the primary properties, selectivity and solvency, solvents must conform to a number of practical requirements, all obvious in themselves. But contrary to the primary properties, the requirements for secondary properties are not that rigid as long as certain standards are met. Compensation are possible between reasonable and outstanding properties. The balance of advantageous properties will, however, be reflected in the overall operating cost.

Solvents are in general organic chemicals, the thermal stability of which is not limited. It should be borne in mind that the solvent is circulated continuously, exposed to heating, cooling and shear and that it is more desirable to reach an operating life of years. So the standard of stability are

set extra-ordinarily high and most of the organic molecules with the polar groups required for selectivity would not qualify.

Beside thermal and mechanical stability, chemical indifference is important. None of the agents which the solvent can be expected to come in contact with, should attack the solvent, nor form irreversible compounds with it under conditions normally encountered. Here too, even quite slow reaction rates are detrimental and standards of indifference have to be set high. For aromatics extraction the most common agents to be considered are water and steam, olefinic and sulfur compounds, media with low and high pH, rust and iron sulfide, molecular and dissolved oxygen and volatility.

All solvents have a certain volatility and solubility in the products, as a consequence of which some solvent remains in the products, due to solvent loss and product contamination this solvent has to be recovered. This is normally done by water washing. This procedure is based on a certain affinity of solvent to water. This affinity is proportionally related to solvency/selectivity behaviour of the solvent. Solvent with low solvency are most easily taken up by water. Solvents with optimum solvency are still completely mixable with water, washing can serve the purpose. High solvency solvents pose more of a problem in this respect.

Solvent with too high a volatility imposes limits to the boiling range of the extraction feedstocks, or alternatively require costly means to separate the extract from the solvent of the other secondary solvent properties, we may just mention toxicity and handling/storage requirement.

CHAPTER 4

EXPERIMENTAL

The experimental studies were carried out according to the scheme shown in Figure (4.1). The four Saudi crudes namely : extra Arab light, Arab light, Arab medium and Arab heavy were first subjected to True Boiling Point (TBP) fractionation, and a naphtha cut of the boiling range start-200°C was collected for each of them. Aromatic contents from the naphtha cut for each crude were determined. Among the four fractions of the respective crude, Arab light fraction was selected for the extraction of aromatics utilizing a group of selective solvents.

The experimental studies carried out in this thesis can be broadly divided into following :

- (i) Crude oil fractionation
- (ii) Aromatics determination
- (iii) Solvent extraction.

4.1 Crude Oil Fractionation

The apparatus used for crude fractionation was Semi-Cal Series 3650 Serial 298 made by Podbielniak Inc., Ill. USA, and the method adopted was ASTM D2892-78 [43]. This method assays crudes. A True Boiling Point (TBP) developed by the California

SAUDI ARABIAN CRUDE OIL

ARAB EXTRA
LIGHT(BERRI)ARAB
LIGHTARAB
MEDIUMARAB
HEAVYT.B.P.
FRACTIONATIONSt.Run Naptha
St-2000CARAB EXTRA
LIGHT(BERRI)ARAB
LIGHTARAB
MEDIUMARAB
HEAVY

AROMATICS DETERMINATION

ETHY. GLYCOL

3 MOPN

Arab Light
St. Run Naptha

PHENOL

SULFOLANE

TOLUENE

AROMATICS EXTRACTION

AROMATICS

FIGURE (4.1) EXPERIMENTAL SCHEME

Research Corporation [44] is designed to provide reliable data regarding the volumetric and gravimetric yield of distillate from crude petroleum throughout the temperature range covered by the distillation. Distillate fraction and residuum obtained during the procedures may be used for analytical studies.

Outline :

A 2.5 liter sample is weighed and distilled in a distillation unit equipped with a column having a fractionating efficiency of 14 theoretical plates. A reflux ratio of 5:1 is maintained throughout the atmospheric distillation. Simultaneous readings are obtained of the volume of distillate recovered as product, distillation temperature weight and specific gravity are determined for each distillate fraction and the residue.

Apparatus :

Distillation unit consisting of kettle with heater, packed column, still head including condenser, secondary condenser (vapor trap). The schematic diagram in Figure (4.2) illustrates apparatus for performing the distillation as follows :

- (i) Distillation kettle of 5 liter capacity along with the provision for the measurement of the temperature of the liquid in the kettle to a precision of 1°C was used. Heat output from the kettle heater is adjustable and capable of sufficient control that the boil-up rate can be either held approximately constant or varied without extreme fluctuation during the operation.
- (ii) Packed column of 50 mm in inside diameter and 914 mm in length and having a fractionating efficiency of 14 theoretical plates is used. It is well illustrated to provide near adiabatic operation. Connection of the column to the kettle is leak-free under all operating conditions.
- (iii) Still head, includes a condenser with sufficient cooling capacity to condense essentially all vapors evolved through the column except some pentanes and lower boiling components. Physical arrangement of the condenser and column was such that condensate from the condenser returns by gravity flow to the top of the packing. Provision includes for automatically diverting a variable but known proportion of the total condensate as distillate product. The apparatus provides for repetitive diversion of total condensate as product for a measured time and non-diversion of

total condensate as reflux for a measured time, both the frequency of diversion and the duration of diversion during each cycle was adjustable. A thermocouple capable of temperature measurement with precision of 0.5°C was located in the vapor space immediately above, but not in contact with, the column packing or the other interior surface.

- (iv) Secondary condenser or alternatives vapor collection system having sufficient capacity to retain essentially all propanes and butanes evolved during the distillation.
- (v) Distillate receivers, calibrated in such manner that volume determination can be made with precision of 1.0 ml for all volumes. Provision includes changing the distillate receivers.

Sampling :

The four Saudi crudes namely: , Arab light, extra Arab light, Arab medium and Arab heavy were obtained from Aramco. The drums of these crude were rolled well to ensure even mixing, a 2.5 liter samples were drawn from each drum and were placed in refrigerator to condense the vapor formed during transportation. Typical characteristics of each crude is determined and is reported.

Procedure

After determining the typical characteristics of each crude, 2.5 liter of sample was charged into the kettle by opening the needle control valve, with the stopcock fully opened. A graphited silicone grease was used as a lubricant for ground-glass connections. Circulation of liquid coolant through the condenser was maintained at 10°C. Heat was turned on and the auto-transformer was adjusted to a low value. Temperature of the reflux was recorded at the time reflux liquid was first observed to return from the condenser to column. At this time timer was started which automatically control the reflux ratio. The fractions were collected and simultaneously temperature was recorded till 200°C.

4.2 Aromatic Determination

The method of ASTM D 1019-78 was adopted for the determination of aromatics in naphtha cut (0-200°C) obtained from True Boiling Point (TBP) fractionation.

This method covers the determination of olefinic plus aromatic hydrocarbons in gasolines, naphthas, kerosines and other petroleum distillates. In petroleum distillates, the proportion of nonhydrocarbon material is generally low enough

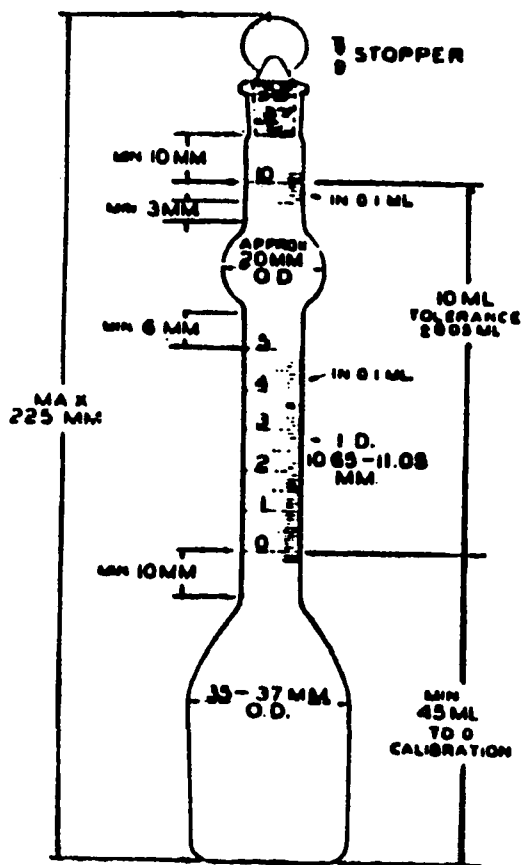
so that the acid absorption can be taken as a measure of total olefinic plus aromatic hydrocarbons and, in the absence of olefins i.e. when bromine number is less than 1, as a measure of aromatics, after an empirical correction for co-absorbed saturates has been applied [45]. The solubility correction is subject to variation depending on the material analyzed. Also, the concentration of volume may include certain minor effects such as volume change which occurs when hydrocarbons of different types are mixed; these effects are usually considerably less than the precision of the method, and, therefore negligible.

Outline :

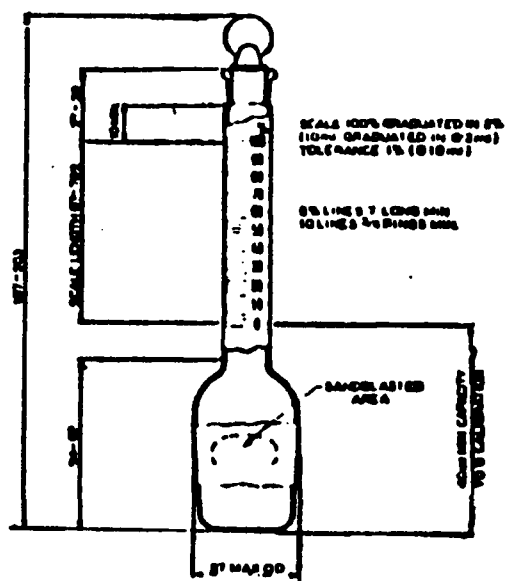
A measured volume of sample contained in a specific flask is shaken in a prescribed manner at the temperature of melting ice, with a solution of phosphorus pentoxide in concentrated sulfuric acid. After the sample has been reacted the flask is centrifuged to separate phases and the unreacted portion is measured.

Apparatus :

- (i) Standard and precision sulfonation flasks of heat-resistant glass, well annealed and meeting the requirements shown in Figure (4.3).



Precision Sulfonation
Flask



Standard Sulfonation
Flask

FIGURE (4.3) SULFONATION FLASKS

- (ii) Pipets of 5 and 10-ml capacities, calibrated to deliver $5.0 \pm .02$ ml and 10.0 ± 0.04 ml of water at 20°C respectively.
- (iii) Centrifuge, capable of whirling two or more filled sulfonation flasks at a speed that can be controlled to give a relative centrifugal force of between 250 and 400 at the bottom of the flasks.
- (iv) Mechanical shaker and ice-water bath.

Reagents

- (i) Sulfonation Acid - A mixture of 70 weight percent H_2SO_4 (95 to 96 percent) and 30 percent P_2O_5 . This is done by adding the content of 1 lb (454 g) package of P_2O_5 to 575 ± 5 ml of acid contained in an Erlenmeyer flask. After stirring only a small amount of residue remains, the beaker is covered while the mixture cools to room temperature and then the mixture is decanted into acid bottles provided with closure which protect the reagent from dilution with moisture from the atmosphere, preparation of reagent was done rapidly so as to minimize absorption of moisture from the air during preparation.

(ii) Sulfuric Acid (95-96 weight percent).

Procedure :

25 \pm 1 ml of the sulfonation acid was introduced into the standard sulfonation flask which was then placed in ice water for 10 min. and the temperature is recorded. 10 ml of sample was introduced in the flask slowly down the flask in order to minimize mixing with acid. 10 min after the introduction of sample, the flask was shaken for 10 minutes, intermittently dipping in ice water and venting it momentarily while still in the ice water bath, then was immediately removed from the bath and centrifuged for 3 min. H_2SO_4 (95 to 96 percent) was next poured down the side of the neck of the flask until the hydrocarbon layer was entirely within the graduated portion of the neck, then the flask was centrifuged for an additional 5 min. The acid-hydrocarbon mixture was then brought to a temperature within 1°C of that at which the sample was measured by immersing the sulfonation flask for 15 min. in water maintained at the desired temperature. The scale was read by placing the flask in front of a plain nonglary light-coloured background illuminated by a diffused light.

Calculations :

As the Bromine Number of the distillates is less

than 1 therefore experiment accounts for only aromatic contents [45].

The Aromatic Contents, volume percent [45]

$$= [(V-R)100/V] - [10C/V]$$

where

V = volume of sample, ml

R = volume of residue, ml and

C = correction for solubility of residue in the acid.

4.3 Solvent Extraction

The apparatus used in this work consisted of the following main components :

- (a) Extraction column, shown in Figure (4.4).
- (b) Thermostat bath
- (c) Mechanical device for agitation inside the column
- (d) Refractometer.

The specifications of the solvents used in the extraction process are given as follows.

- (i) 3-Methoxy propionetrile

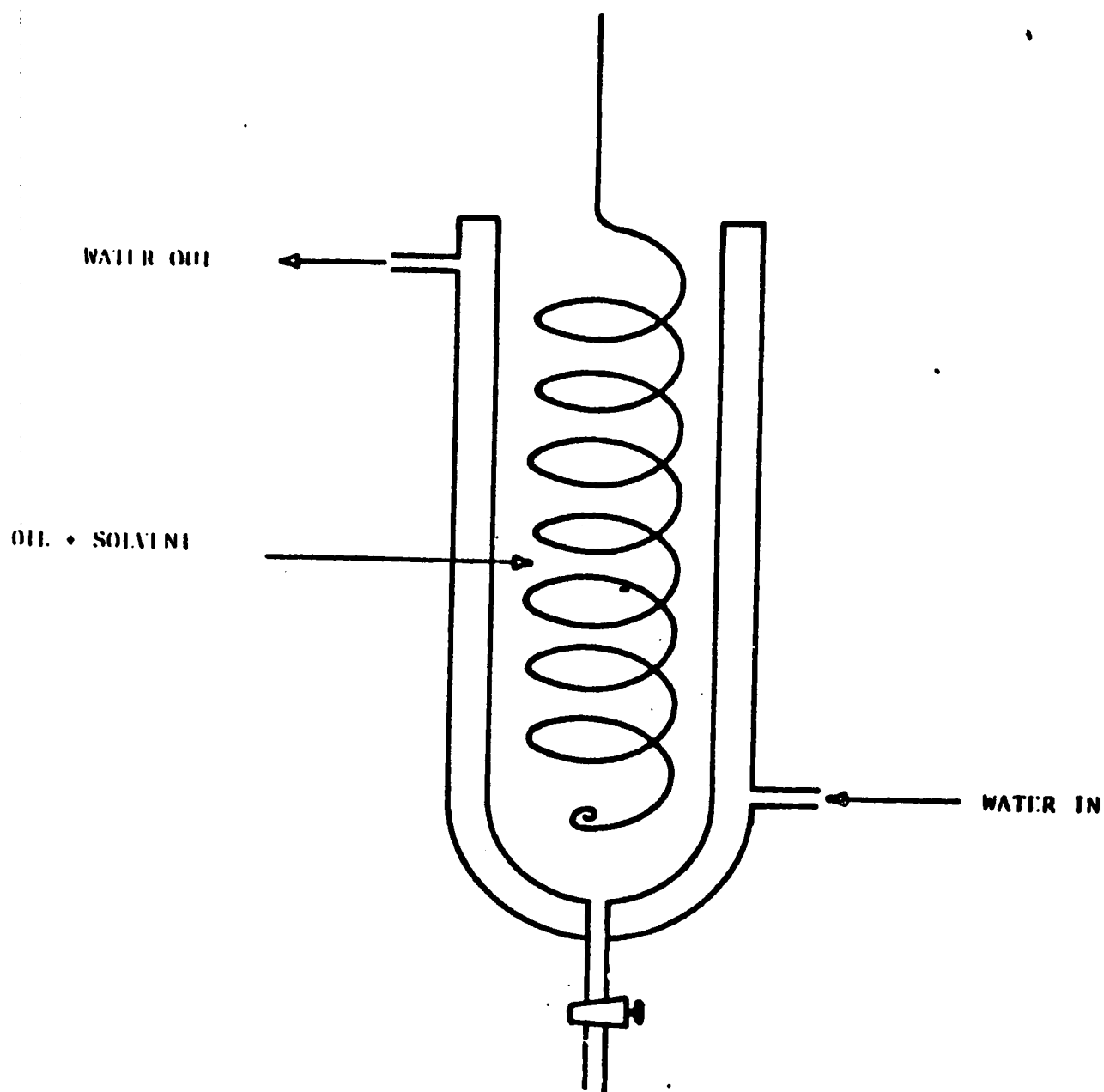


FIGURE (4.4) EXTRACTION COLUMN

Grade	Commercial
Boiling range	163-165 °C @ 762 mm hg.
Molecular wt	85.11
Density	0.94 kg/liter
Formula	C ₄ H ₇ NO

(ii) Ethylene Glycol

Grade	Commercial
Boiling range	195 - 197 °C
Molecular wt	62.07
Density	1.11 kg/liter
Formula	CH ₂ OHCH ₂ OH

(iii) Dimethyl Sulfoxide

Grade	Commercial
Boiling range	72-73 °C
Molecular wt	78.13
Density	1.10 kg/liter
Formula	(CH ₃) ₂ SO

(iv) Nitrobenzene

Grade	Commercial
Boiling range	210.9 °C - 211.4 °C
Molecular wt	123.11
Density	1.21 kg/liter
Formula	C ₆ H ₅ NO ₂

(v) Phenol

Grade	Commercial
Boiling range	181.8 - 182.4 °C
Molecular wt	94.11
Density	1.071 kg/liter
Formula	C ₆ H ₅ OH

(vi) Morpholine

Grade	Commercial
Boiling range	127-129 °C
Molecular wt	87.12
Density	1 kg/liter
Formula	C ₄ H ₉ NO

(vii) Sulfolane

Grade	Commercial
Boiling range	285 - 288 °C
Molecular wt.	120.17
Density	1.26 kg/liter
Formula	CH ₂ .(CH ₂) ₃ . SO ₂

The solvents were dried using anhydrous calcium chloride and then purified by repeated distillation. A fairly constant boiling point material was collected for use as a solvent throughout this research.

Procedure :

An outline of the experimental procedure is given in the following order :

- (a) The thermostat bath was switched on and adjusted to the required experimental temperature.
- (b) Two flasks, one containing the solvent and other containing the distillate were suspended in the bath for at least 30 minutes to attain its temperature.
- (c) The extraction column, on the other hand, was brought to the operating temperature - before admitting the samples - by circulating water from the bath inside the heating jacket of the column.
- (d) Both samples of destillate and solvent were mixed in the column under the influence of a variable - speed agitator. Time was recorded.
- (e) Extraction was allowed to proceed under the above conditions for the prescribed duration of time.
- (f) Seperation of phases into extract and raffinate was accomplished by allowing the contents of the extraction column to settle for 60 minutes.
- (g) The Refractive Index (R.I) was determied for samples of extract and known aromatics in solvent using refractometer. The aromatic contents in each phase was next evaluated from the caliberation curves.

Parameters :

It is clear that wise solvent selection is critical in determining whether solvent extraction will be economically competitive for a particular separation. The choice usually involves a compromise between conflicting properties, as it is rare to find a solvent that can be described as truly ideal [32].

The parameters considered in this work are

- (i) Operating Temperature : The effect of this parameter on the extraction of aromatics is of vital importance, since it is this parameter which determines the utility load and its cost along with the extent of extraction. [37]
- (ii) Solvent-to-Oil Ratio (S:O) : The effect of this parameter on the extraction of aromatics is of prime importance, since it is the S:O ratio that determines the capacity of an extraction unit [38].
- (iii) Selectivity : This is the first property ordinarily studied in deciding the applicability of a solvent [38]. The solvent should be as selective as possible for the desired solute over impurities, so as to reduce or eliminate the need for scrubbing [32].

Selectivity could be quantitatively defined in several ways, for chemists a suitable definition is the log of

the ratio of the activity coefficient of heptane and toluene in the solvent. The definition followed throughout this work is [38].

$$\text{Selectivity} = \frac{\text{wt. fraction aromatics in extract}}{\text{wt. fraction aromatics in raffinate}} \times$$

$$\frac{\text{wt. fraction non aromatics in raffinate}}{\text{wt. fraction non aromatics in extract}}$$

Solvent Capacity :

Unless the solvent has the capacity to dissolve relatively large quantities of the preferentially extracted solute, in addition to have high selectivity, it will likely be uneconomical to use because of the large quantities that must be circulated through the extraction system [38]. Therefore high value of solvent capacity is clearly desirable, as this will make possible loading to a high concentration of solute, thereby lowering the amount of solvent required in the circuit. This will reduce the equipment size and solvent losses and may reduce the cost of solvent recovery, if by distillation.

Solvent capacity is given by distribution coefficient [32] and is given as :

$$\text{Solvent Capacity} = \frac{\text{wt. fraction aromatics in extract}}{\text{wt. fraction aromatics in raffinate}}$$

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Crude Oil Fractionation

The four Saudi Arabian Crude Oils, namely, Arab extra light (Berri), Arab light, Arab medium and Arab heavy were subjected to different test methods before being fed to True Boiling Point (TBP) fractionation apparatus. The typical characteristics of each crude is given in Table ((5.1) to (5.4)).

Considerable variation in the typical characteristic of each crude from the other is observed. The gravity ($^{\circ}\text{AP1}$) exhibits an increase from 28, for Arab heavy to 38.0 for Arab extra light (Berri) crude oil. This represents an increase of more than 26 percent. The ash (ppm) increases from 46 for Arab extra light (Berri) to 132 for Arab heavy crude oil. This shows a gain of about 65 percent.

The Reid vapor pressure in lbs increases from 5.10, for Arab extra light (Berri), to 8.80 for Arab heavy crude oil. This depicts an increase of about 42 percent. The sulfur (wt. percent) increases from 1.21, for Arab extra light (Berri), to 2.90 for Arab heavy crude oil. This gain is more than 58 percent. The viscosity (sus @ 21°C) increases from 43.8, for Arab extra light (Berri) to 179.5 for Arab heavy crude oil.

TABLE (5.1)

**TYPICAL CHARACTERISTICS OF ARAB
EXTRA LIGHT (BERRY) CRUDE OIL**

<i>Tests</i>	<i>Test Methods</i>	<i>Results</i>	
Gravity, °API	ASTM D 287	38.0	
Ash, ppm	ASTM D 482	46.0	
Reid vapor pressure, lbs	ASTM D 323	5.10	
Sulfur, wt. %	ASTM D 129	1.21	
Viscosity, sus @ 21°C	ASTM D 445	43.8	
Viscosity, sus @ 38°C	ASTM D 445	38.0	
TBP Distillation Yield	ASTM D 2892	<u>Temp. °C</u>	<u>Vol. percent</u>
		50	2.4
		75	5.3
		100	9.9
		125	15.1
		150	22.3
		175	27.1
		200	33.1
		225	40.8
		250	44.1
		275	48.9

TABLE (5.2)
TYPICAL CHARACTERISTICS OF
ARAB LIGHT CRUDE OIL

<i>Tests</i>	<i>Test Methods</i>	<i>Results</i>	
Gravity, °API	ASTM D 287	33.7	
Ash, ppm	ASTM D 482	42.0	
Reid vapor pressure, lbs	ASTM D 323	8.10	
Sulfur, wt. %	ASTM D 129	1.80	
Viscosity, sus @ 21°C	ASTM D 445	56.1	
Viscosity, sus @ 38°C	ASTM D 445	44.8	
TBP Distillation Yield	ASTM D 2892	<u>Temp. °C</u>	<u>Vol. percent</u>
		50	2.0
		75	4.9
		100	9.1
		125	14.4
		150	21.1
		175	26.2
		200	30.1
		225	34.5
		250	38.9
		275	43.9

TABLE (5.3)

TYPICAL CHARACTERISTICS OF
ARAB MEDIUM CRUDE OIL

<i>Tests</i>	<i>Test Methods</i>	<i>Results</i>
Gravity, °API	ASTM D 287	30.8
Ash, ppm	ASTM D 482	102.0
Reid vapor pressure, lbs	ASTM D 323	6.20
Sulfur, wt. %	ASTM D 129	2.54
Viscosity, sus @ 21°C	ASTM D 445	80.00
Viscosity, sus @ 38°C	ASTM D 445	54.60
TBP Distillation Yield	ASTM D 2892	54.60
	<u>Temp. °C</u>	<u>Vol. percent</u>
	50	1.8
	75	4.1
	100	8.6
	125	13.1
	150	20.1
	175	24.3
	200	27.1
	225	31.5
	250	36.1
	275	40.3

TABLE (5.4)
TYPICAL CHARACTERISTICS OF
ARAB HEAVY CRUDE OIL

<i>Tests</i>	<i>Test Methods</i>	<i>Results</i>	
Gravity, °API	ASTM D 287	28.0	
Ash, ppm	ASTM D 482	132.0	
Reid vapor pressure, lbs	ASTM D 323	8.8	
Sulfur, wt. %	ASTM D 129	2.9	
Viscosity, sus @ 21°C	ASTM D 445	179.5	
Viscosity, sus @ 38°C	ASTM D 445	96.0	
TBP Distillation Yield	ASTM D 2892	<u>Temp. °C</u>	<u>Vol. percent</u>
		50	1.5
		75	3.6
		100	7.9
		125	12.4
		150	17.9
		175	20.0
		200	23.2
		225	27.3
		250	31.7
		275	35.4

This increase accounts for 75 percent.

The True Boiling Point (TBP) fractionation yield exhibits descending order from Arab extra light (Berri) to Arab heavy crude oil. The decrease in yield (vol.percent) is from 33.1, for Arab extra light (Berri), to 23.2 for Arab heavy crude oil. This accounts for a decrease of about 30 percent.

5.2 Aromatics Determination

Aromatic contents from the light fraction (Boiling range 23-200°C) were determined for the four Saudi Arabian Crudes, namely, Arab extra light (Berri), Arab light, Arab medium and Arab heavy, the findings are reported in Table (5.5).

The maximum aromatic contents are found in Arab extra light (Berri) Crude oil fraction (Boiling range 23-200°C). The increase in aromatic content (vol.percent) is from 9.09, for Arab heavy to 14.30 for Arab extra light (Berri) crude oil fraction. The percentage increase of aromatic contents of the said fraction is more than 36 percent.

The aromatic contents and the yield of Arab extra light (Berri) crude oil justifies its selection as the most appropriate feedstock for aromatic production, but Saudi Arabian government's policy restricts market of said crude as it is used as a premium crude oil. The restriction on availability of this crudes compels to focus attention on Arab light crude

TABLE (5.5)**AROMATIC CONTENTS IN SAUDI ARABIAN CRUDES**

<i>Crude Oil</i>	<i>Distillate Boiling Range °C</i>	<i>Aromatic Contents Volume Percent</i>
Arab Extra Light (Berri)	23-200	14.30
Arab Light	23-200	12.96
Arab Medium	23-200	9.73
Arab Heavy	23-200	9.09

oil fraction, as a feedstock for aromatics production as it competes the requirement of yield and aromatic content with the other Saudi Arabian Crude Oils. So for further investigation Arab light crude oil fraction will be considered.

5.3 Solvent Extraction

This section deals with the investigation of the efficiencies exhibited by different selective solvents in extracting aromatic hydrocarbons from the lighter fraction (boiling range 23-200°C) of Arab light crude oil. A total of 50 experimental runs were made. The solvents considered are :

- (i) 3-Methoxypropionitrile
- (ii) Ethylene glycol
- (iii) Dimethyl sulfoxide
- (iv) Nitrobenzene
- (v) Sulfolane
- (vi) Phenol

The experiments carried out in this work were designed to take into consideration the following significant parameters.

- (i) Operating temperature
- (ii) Solvent to oil ratio (S:O)
- (iii) Selectivity and
- (iv) Solvent capacity.

(1) *3-Methoxypropionitrile*

(i) Operating Temperature : The extraction temperature was varied over the range of 20°C - 80°C . The effect of operating temperature on the percentage of aromatics in extract is shown in Figure (5.1). At a solvent-to-oil ratio of 3:1, it is found that the percentage of aromatics in extract increases from 62.3 to 69.9 by increasing the operating temperature from 20°C to 80°C . This represents a gain of more than 10% of the aromatic contents in the extract operating at 20°C .

(ii) Solvent-to-Oil Ratio (S:O) : The solvent-to-oil ratio was varied over the range of 1:1 to 3:1. Figure (5.2) shows the effect of solvent-to-oil ratio on selectivity at different temperatures. Operating at a solvent-to-oil ratio of 3:1 and temperature of 50°C the selectivity reduces from 7.6 to 7.34 at the same temperature but at solvent-to-oil ratio of 1:1. This exhibits a decrease of about 4% in selectivity.

(iii) Selectivity : As shown in Figure (5.2), selectivity is found to decrease with the increase in temperature. Operating at a temperature of 20°C the selectivity reduces from 7.6 to 7.33 at the same solvent-to-oil ratio but at a temperature of 50°C . This represents a decrease of about 4 percent. Similar decrease in the selectivity of solvent with an increase in temperature is most

○—○ S:O 3:1
△—△ S:O 2:1
□—□ S:O 1:1

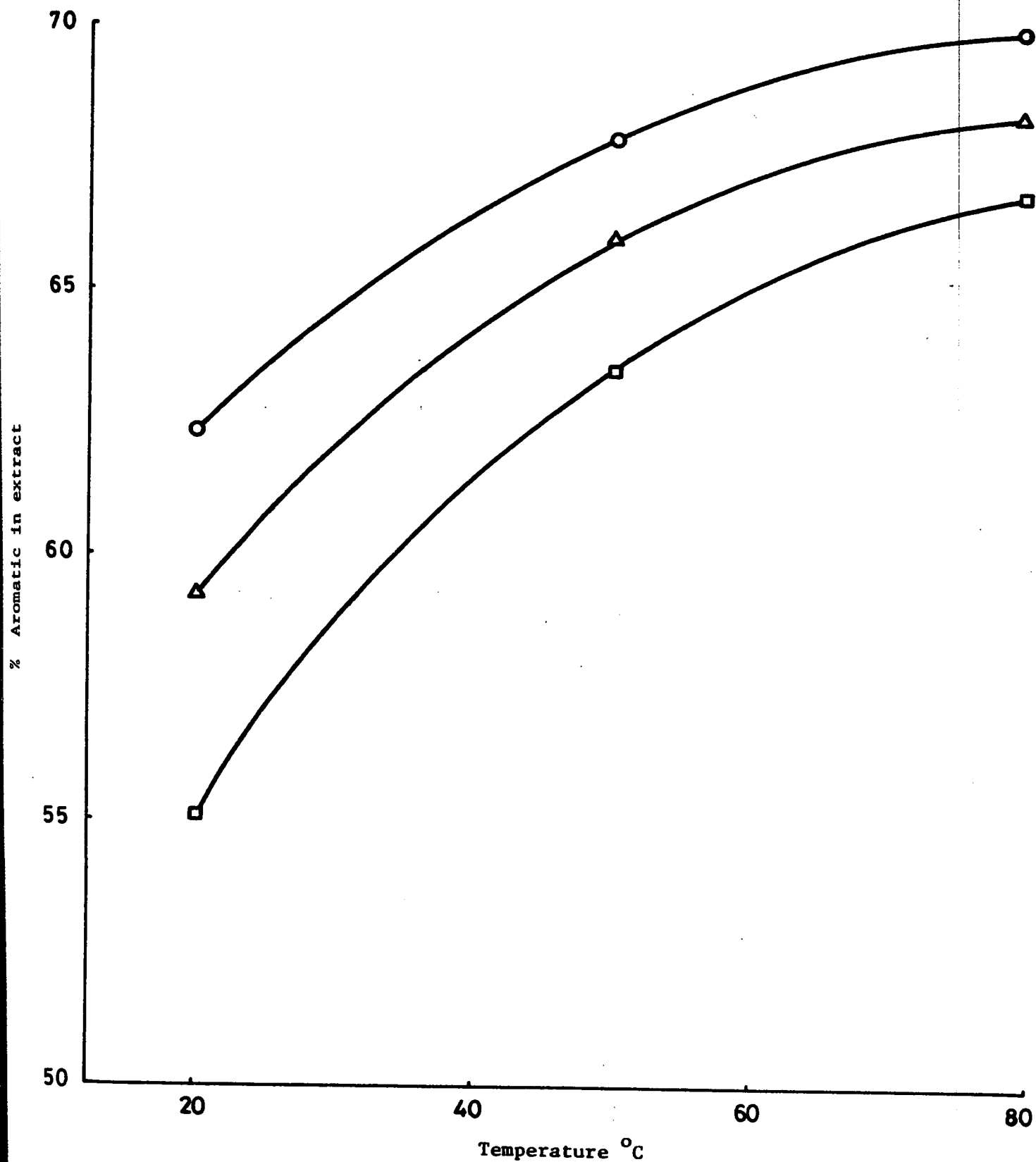


FIGURE : 5.1 EFFECT OF OPERATING TEMPERATURE ON THE PERCENTAGE OF AROMATICS IN EXTRACT (3-MOPN)

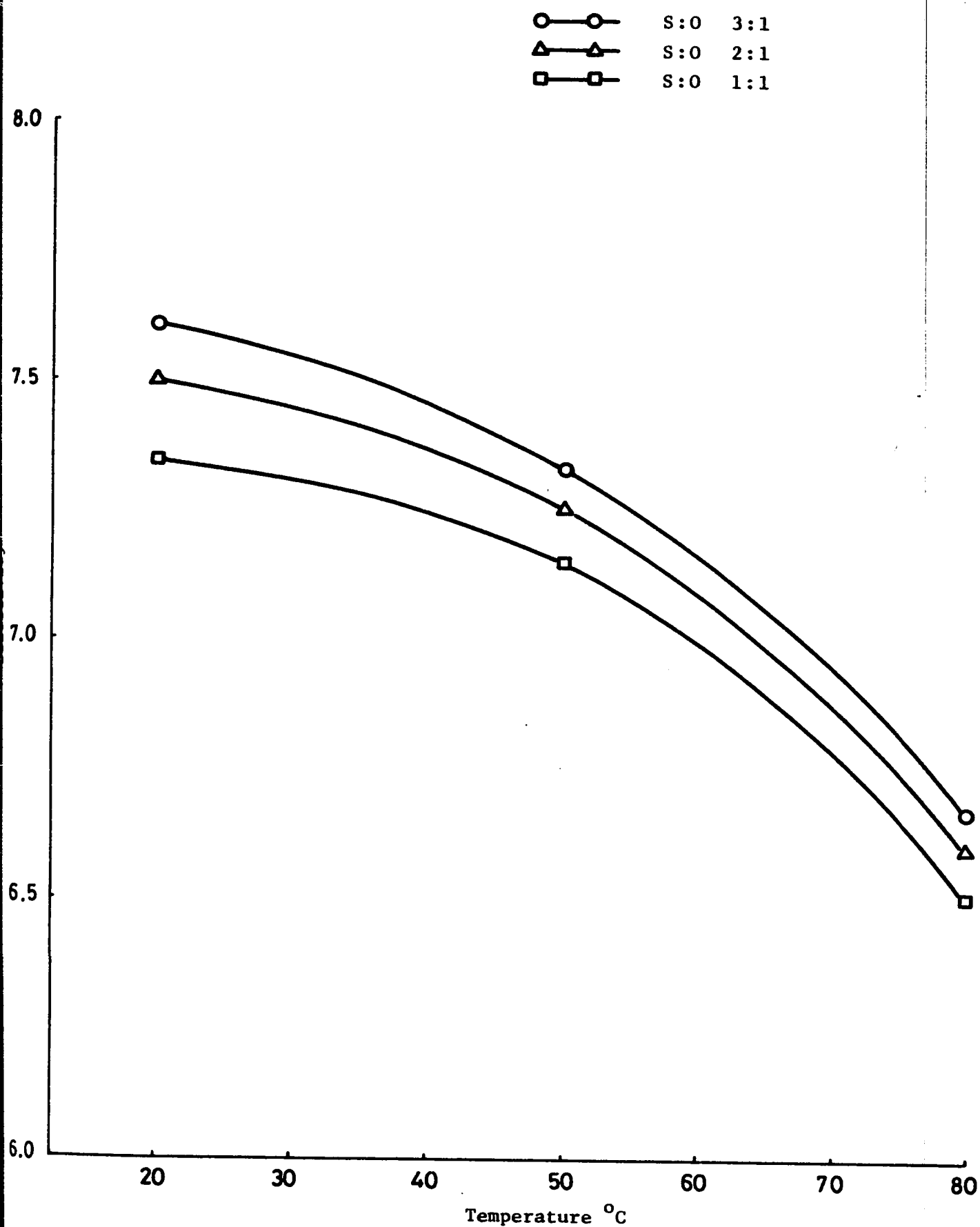


FIGURE : 5.2 EFFECT OF OPERATING TEMPERATURE ON THE SELECTIVITY AT THREE SOLVENT:OIL RATIOS (3-MOPN)

likely behavior for other S:O ratios.

(iv) Solvent Capacity : The solvent capacity is found to be decreasing with increasing selectivity in the temperature range (20°C - 80°C) with solvent-to-oil ratio of 3:1. This behavior is shown in Figure (5.3). With the increase in temperature solvent capacity is observed to be increasing at the cost of selectivity. Traversing from 20°C to 80°C the selectivity decreases from 7.6 to 6.67 and solvent capacity increases from 0.32 to 0.34 which depicts 12% decrease for the former and 6% increase for the latter:

(2) *Ethylene Glycol* :

(i) Operating Temperature : The extraction temperature was varied over the range of 20°C - 80°C . The effect of operating temperature on the percentage of aromatics in extract is shown in Figure (5.4). At a solvent-to-oil ratio of 3:1, it was found that the percentage of aromatics in extract increases from 50.0 to 64.8 by increasing the operating temperature from 20°C to 80°C . This represents a gain of 23% of aromatic contents in the extract operating at 20°C . Almost same behavior is exhibited at other solvent-to-oil ratios.

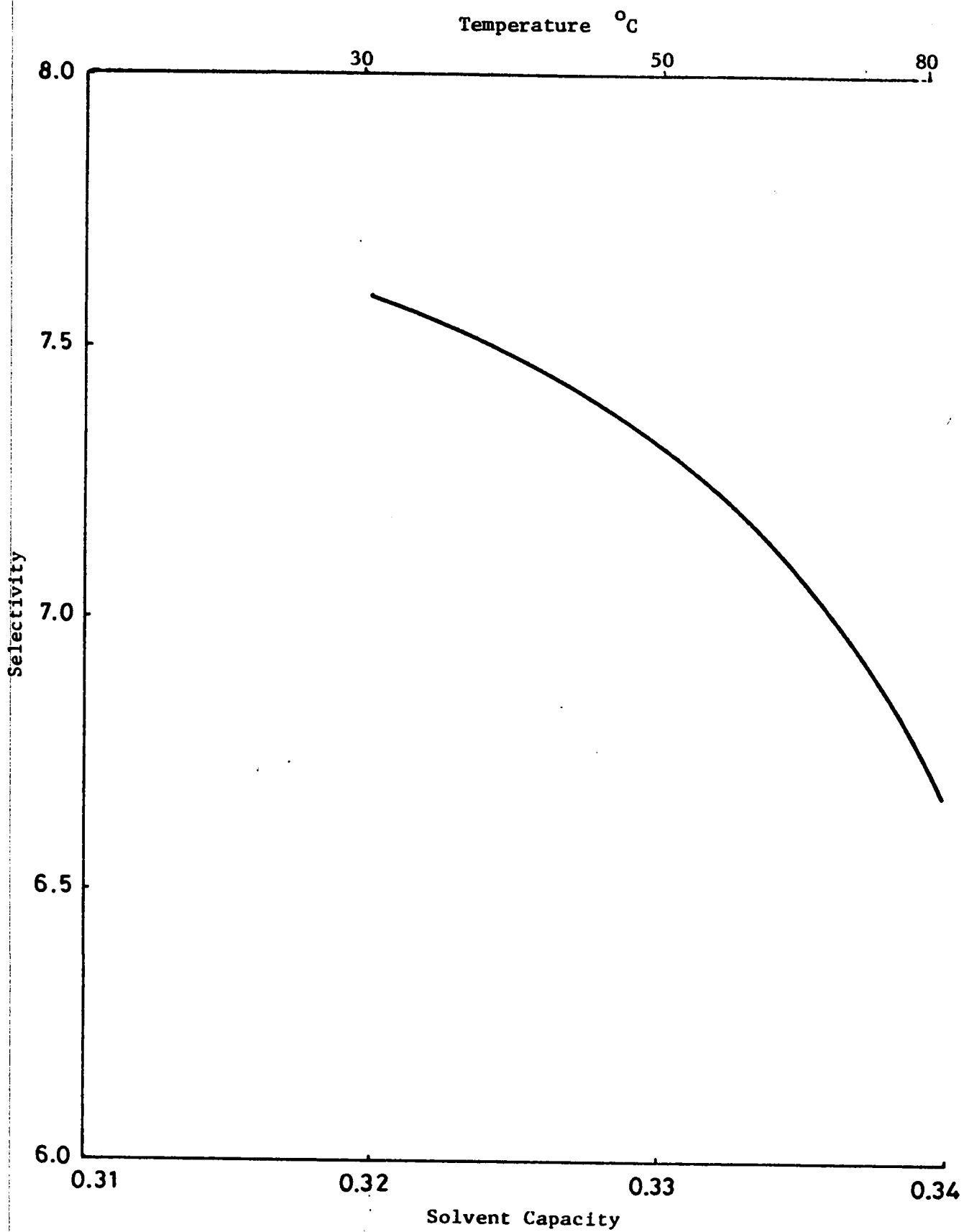


FIGURE : 5.3 SELECTIVITY VERSUS SOLVENT CAPACITY (3-MOPN)

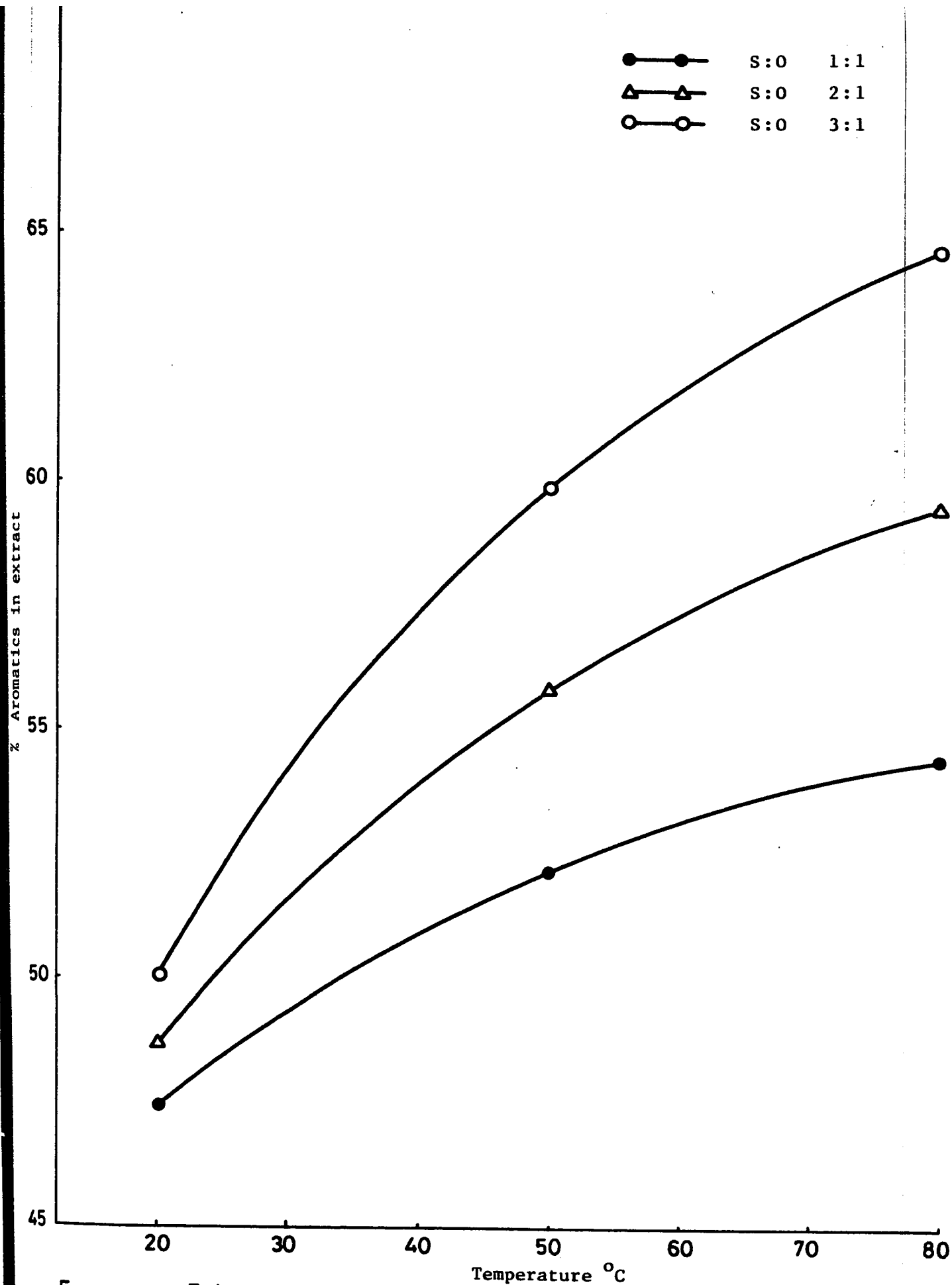


FIGURE : 5.4 EFFECT OF OPERATING TEMPERATURE ON THE PERCENTAGE OF AROMATICS IN EXTRACT (ETHYLENE GLYCOL)

(ii) Solvent-to-Oil Ratio (S:O) : The solvent-to-oil ratio was varied over the range of 1:1 to 3:1. Figure (5.5) exhibits the effect of solvent-to-oil ratio on selectivity at different temperatures. Operating at a solvent-to-oil ratio of 3:1 and temperature of 20°C the selectivity reduces from 7.56 to 7.29 at the same temperature but at a solvent-to-oil ratio of 1:1. This represents a decrease of about 4% in selectivity.

(iii) Selectivity : As shown in Figure (5.6) selectivity is found to be decreasing with the increase in temperature at solvent-to-oil ratio of 3:1. The similar behavior is shown at other solvent-to-oil ratios. Operating at a temperature of 20°C the selectivity decreases from 7.55 to 6.26 at the same solvent-to-oil ratio but at a temperature of 80°C. This represents a decrease of about 17%.

(iv) Solvent Capacity : Following the same trend as before, selectivity is found to be inversely proportional to the solvent capacity. The behavior is shown in Figure (5.6). At solvent-to-oil ratio of 3:1 and traversing from 20°C to 50°C shows the increase in solvent capacity from .015 to .025, a gain of about 40%.

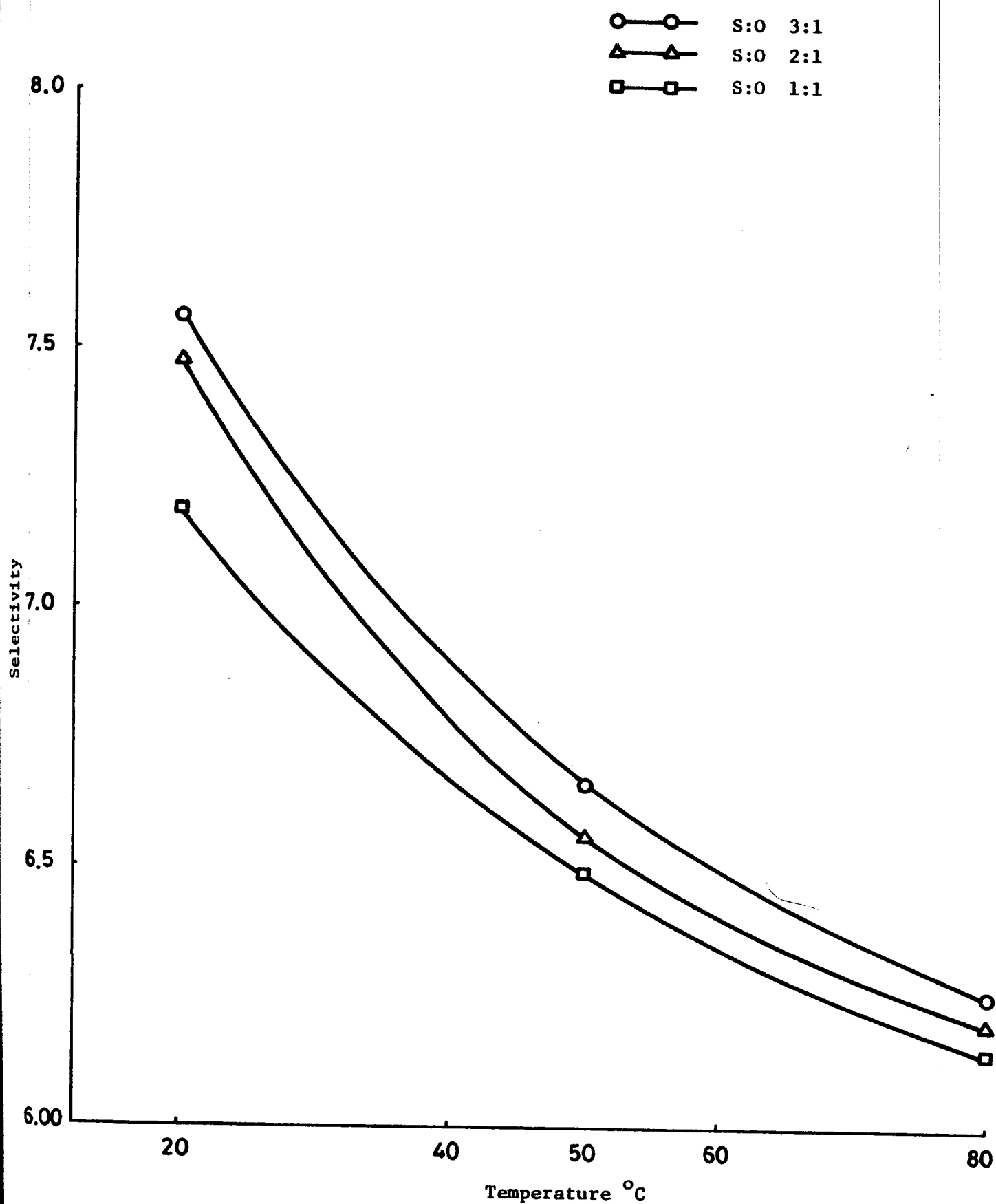


FIGURE : 5.5 EFFECT OF OPERATING TEMPERATURE ON THE SELECTIVITY AT THREE SOLVENT:OIL RATIOS (ETHYLENE GLYCOL)

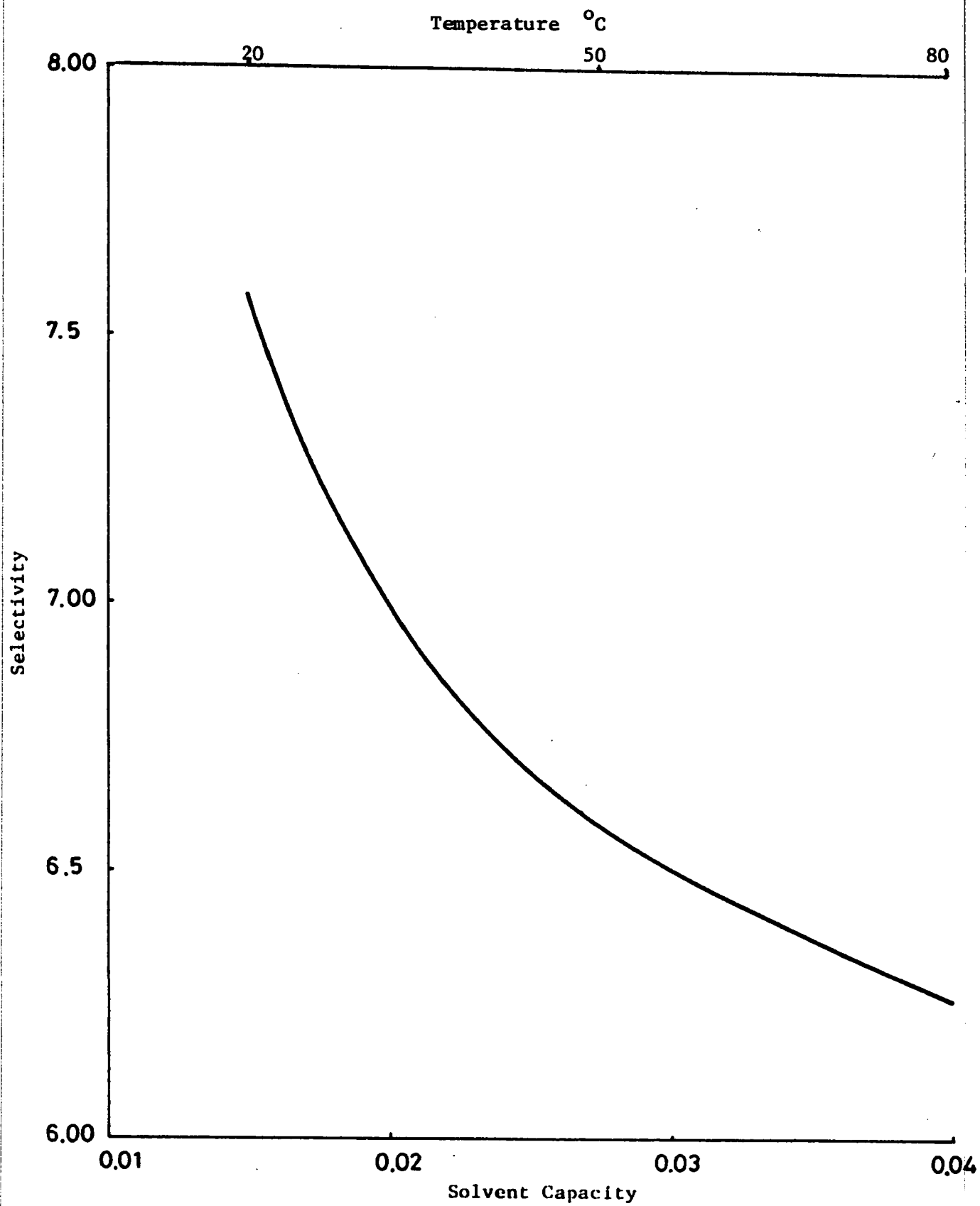


FIGURE : 5.6 SELECTIVITY VERSUS SOLVENT CAPACITY
(ETHYLENE GLYCOL)

(3) *Dimethyl Sulfoxide* :

(i) Operating Temperature : The extraction temperature was varied over the range of 20°C - 80°C . The effect of operating temperature on the percentage of aromatics in extract is shown in Figure (5.7). At a solvent-to-oil ratio of 3:1, it is found that the percentage of aromatics in extract increases from 55.9 to 60.1 by increasing the operating temperature from 20°C to 80°C . This represents a gain of about 7% of the aromatic contents in the extract operating at 20°C . Similar increase of aromatic content in extract, at increased temperature can be observed at 2:1 and 1:1 solvent-to-oil ratios.

(ii) Solvent-to-Oil Ratio (S:O) : The solvent-to-oil ratio was varied over the range of 1:1 to 3:1. Figure (5.8) shows the effect of solvent-to-oil ratio on selectivity. At a solvent-to-oil ratio of 3:1 and temperature of 20°C the selectivity reduces from 9.0 to 8.08 at the same temperature but at solvent-to-oil ratio of 1:1. This exhibits a decrease of about 10%. Similar behavior can be seen at other operating temperatures.

(iii) Selectivity : As shown in Figure (5.9) selectivity is found to be decreasing with the increase in temperature. Operating at a temperature of 20°C , the selectivity

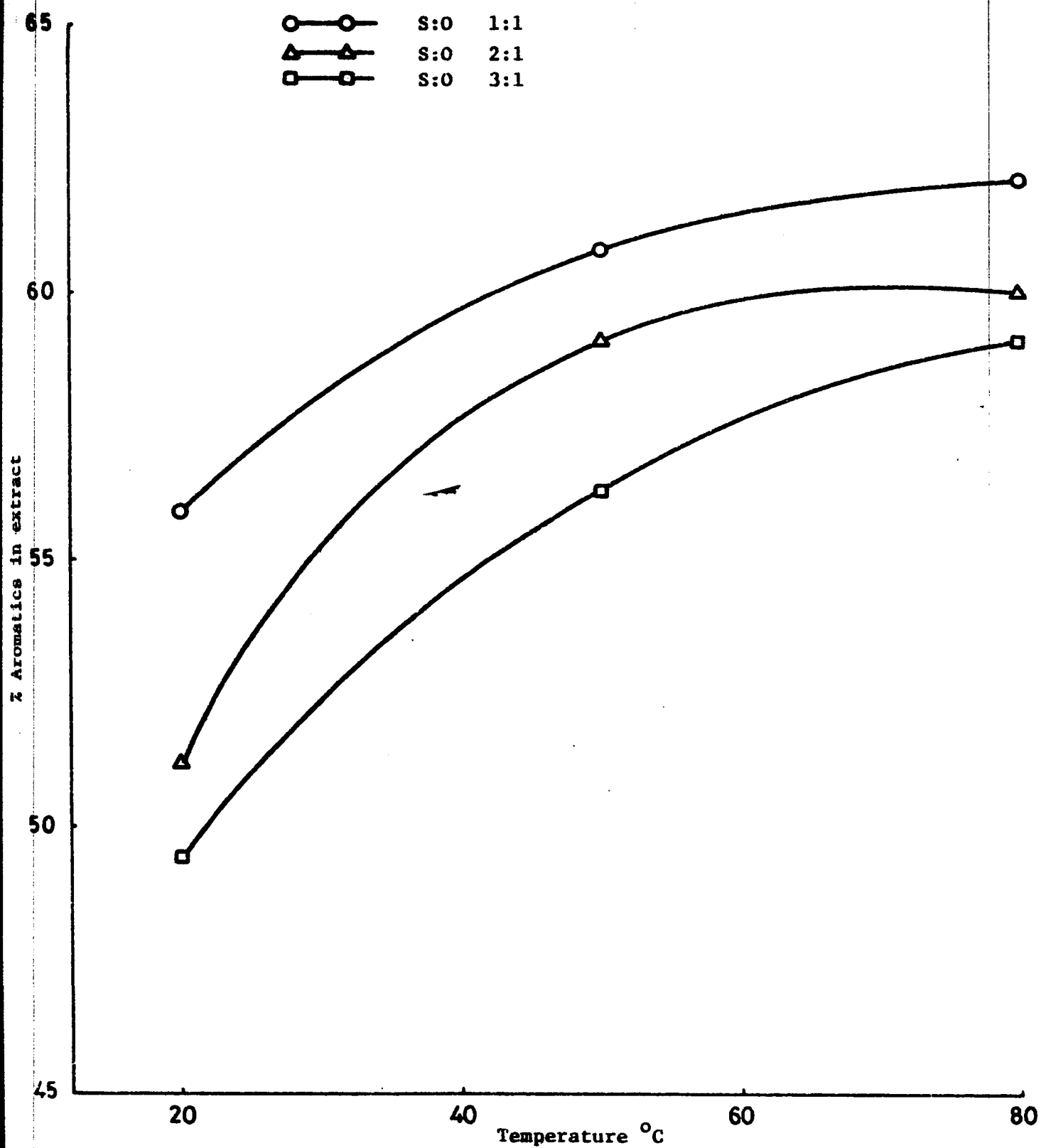


FIGURE : 5.7 EFFECT OF OPERATING TEMPERATURE ON THE PERCENTAGE OF AROMATICS IN EXTRACT (DMSO)

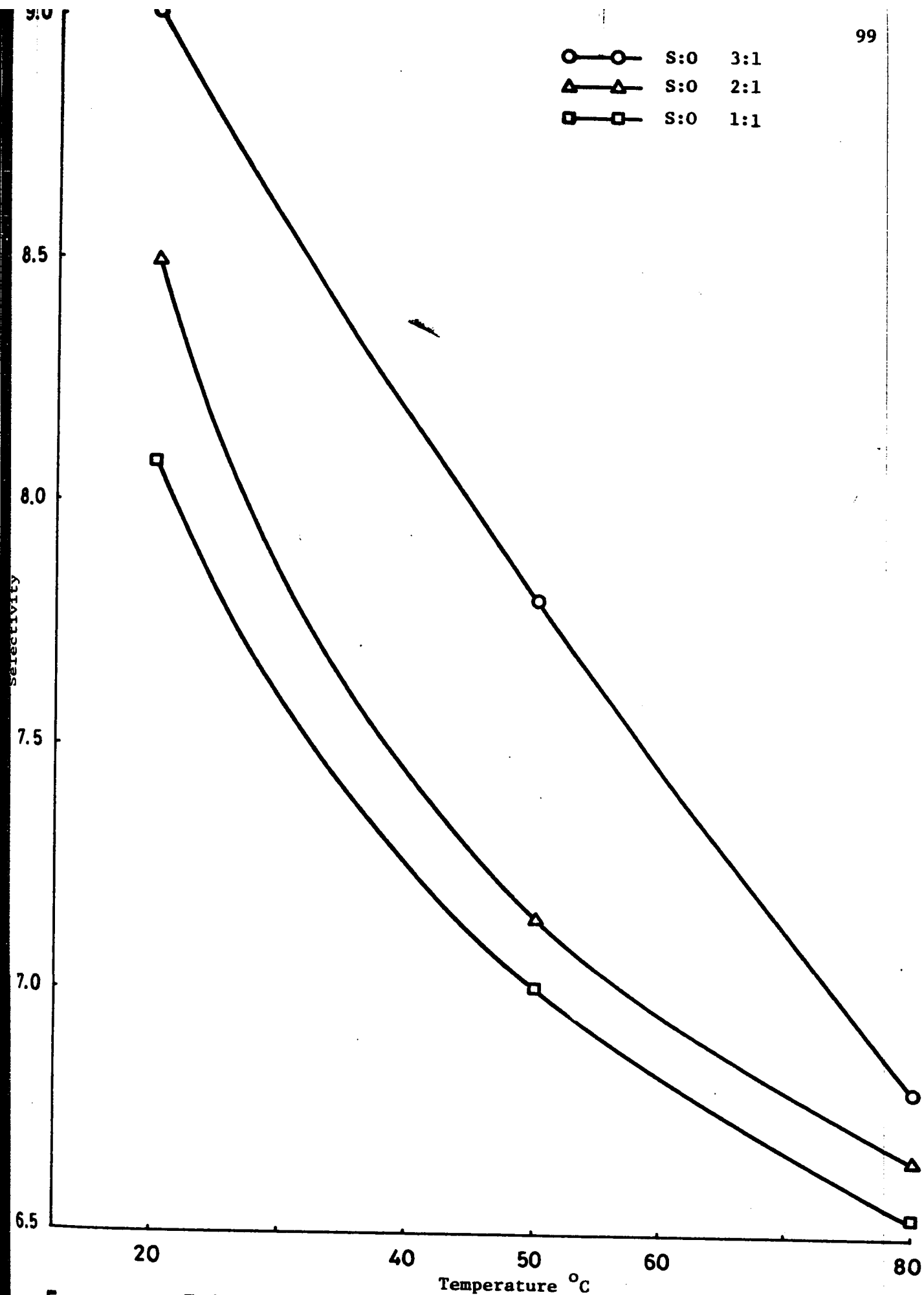


FIGURE : 5.8 EFFECT OF OPERATING TEMPERATURE ON THE SELECTIVITY AT THREE SOLVENT:OIL RATIOS (DMSO)

reduces from 9.0 to 7.8 at the same solvent-to-oil ratio but at a temperature of 50°C. This represents a decrease of more than 13%. Similar decrease in the selectivity of the solvent with an increase in temperature is most likely behavior for other solvent-to-oil ratios.

(iv) Solvent Capacity : The solvent is found to be decreasing with increasing selectivity in the temperature range (20°C - 80°C) with solvent-to-oil ratio of 3:1. This behavior is exhibited in Figure (5.9). Traversing from 20°C to 80°C the selectivity decreases from 9.0 to 6.8 and the solvent capacity increases from 0.2 to 0.29 which shows 24% decrease for the former and 31% increase for the latter.

(4) *Nitrobenzene* :

The study of nitrobenzene as a solvent for extraction of aromatics requires severe operating conditions. When the normal operating conditions were followed, the solvent does not seem to form two separate phases which makes its use impossible as a solvent for extracting aromatics following the normal operating conditions. The homogeneous phase requires severe operating conditions and additional processes to separate aromatics from non-aromatics and the solvent.

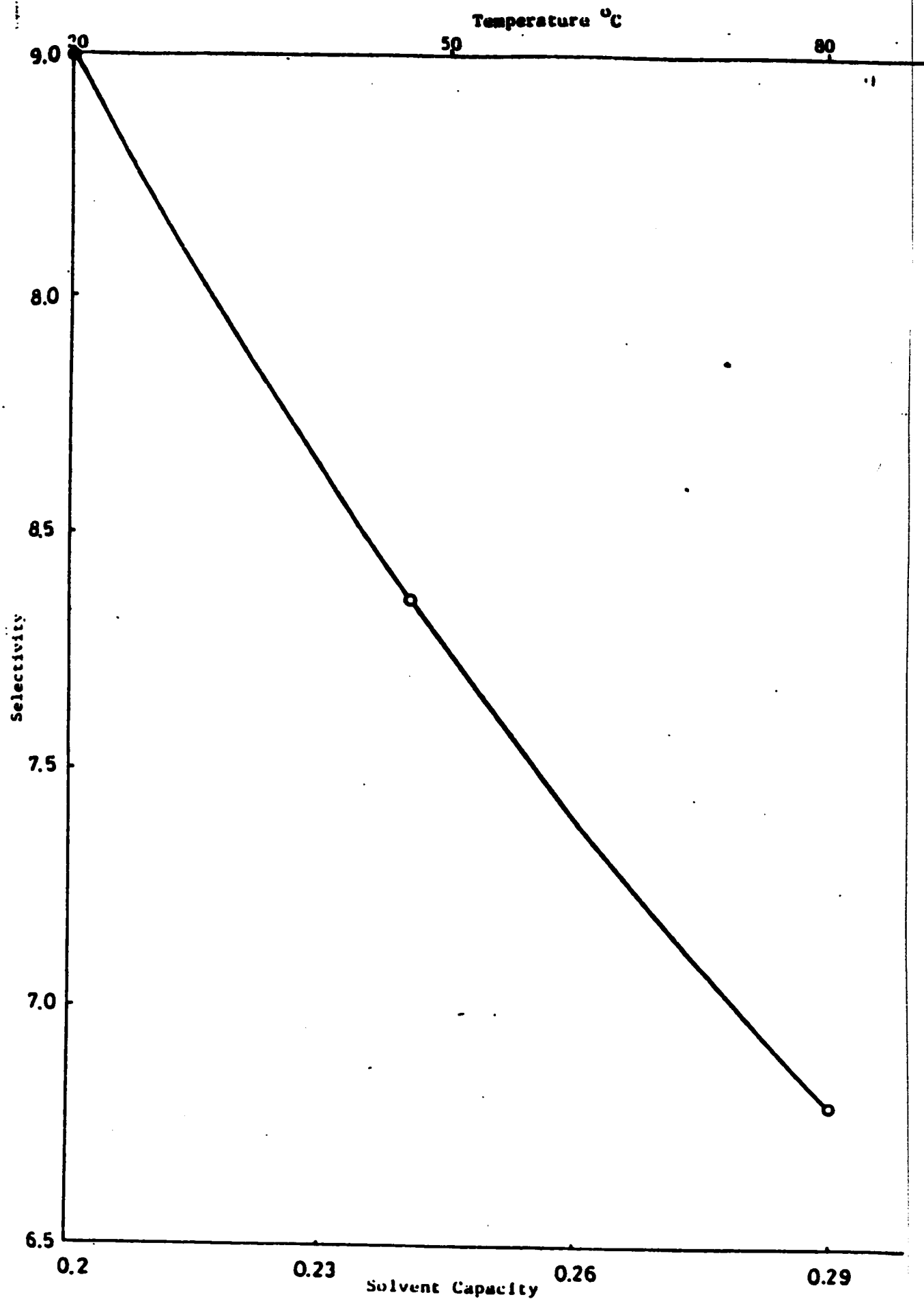


FIGURE : 5.9 SELECTIVITY VERSUS SOLVENT CAPACITY (DMSO)

(5) *Sulfolane* :

(i) Operating Temperature : The extraction temperature was varied over the range of 75°C - 125°C . The use of high temperature is due to the increased solidification point of the solvent. The effect of operating temperature on the percentage of aromatics in extract is shown in Figure (5.10). At a solvent-to-oil ratio of 3:1, it is found that the percentage of aromatics in extract increases from 50 to 55.3 by increasing the operating temperature from 75°C to 125°C . This represents a gain of about 10% of the aromatic contents in the extract operating at 75°C . Similar increase in the percentage of aromatic contents in extract is exhibited at other solvent-to-oil ratios.

(ii) Solvent-to-Oil Ratio (S:O) : The solvent-to-oil ratio was varied over the range of 1:1 to 3:1. Figure (5.11) shows the effect of temperature on selectivity at three different solvent-to-oil ratios. Operating at a solvent-to-oil ratio of 3:1 and temperature of 100°C the selectivity reduces from 7.32 to 6.86 at the same temperature but at solvent-to-oil ratio of 1:1. This gives a decrease of more than 6%.

(iii) Selectivity : As shown in Figure (5.11), selectivity is found to be decreasing with the increase in

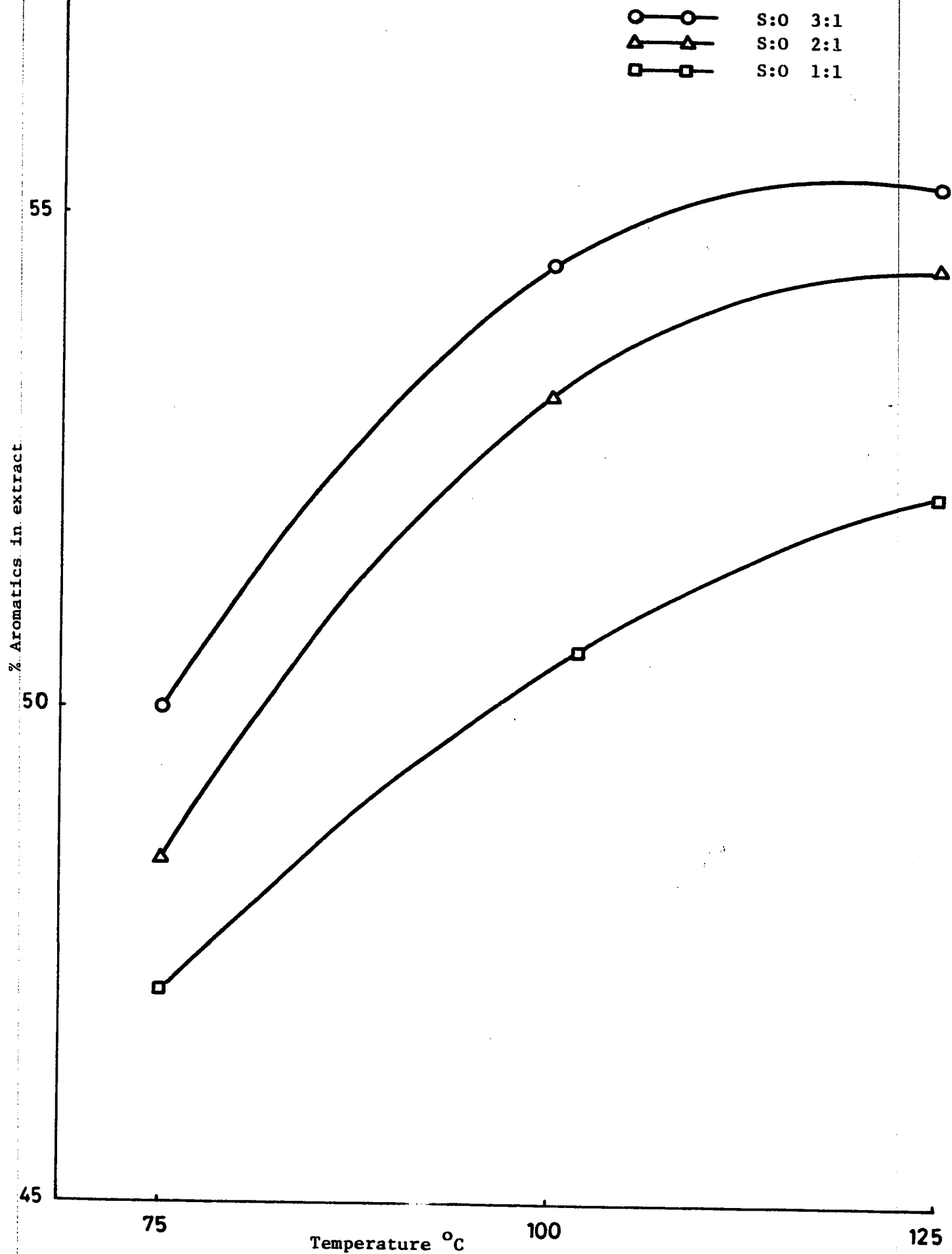


FIGURE : 5.10 EFFECT OF OPERATING TEMPERATURE ON THE PERCENTAGE OF AROMATICS IN EXTRACT (SULFOLANE)

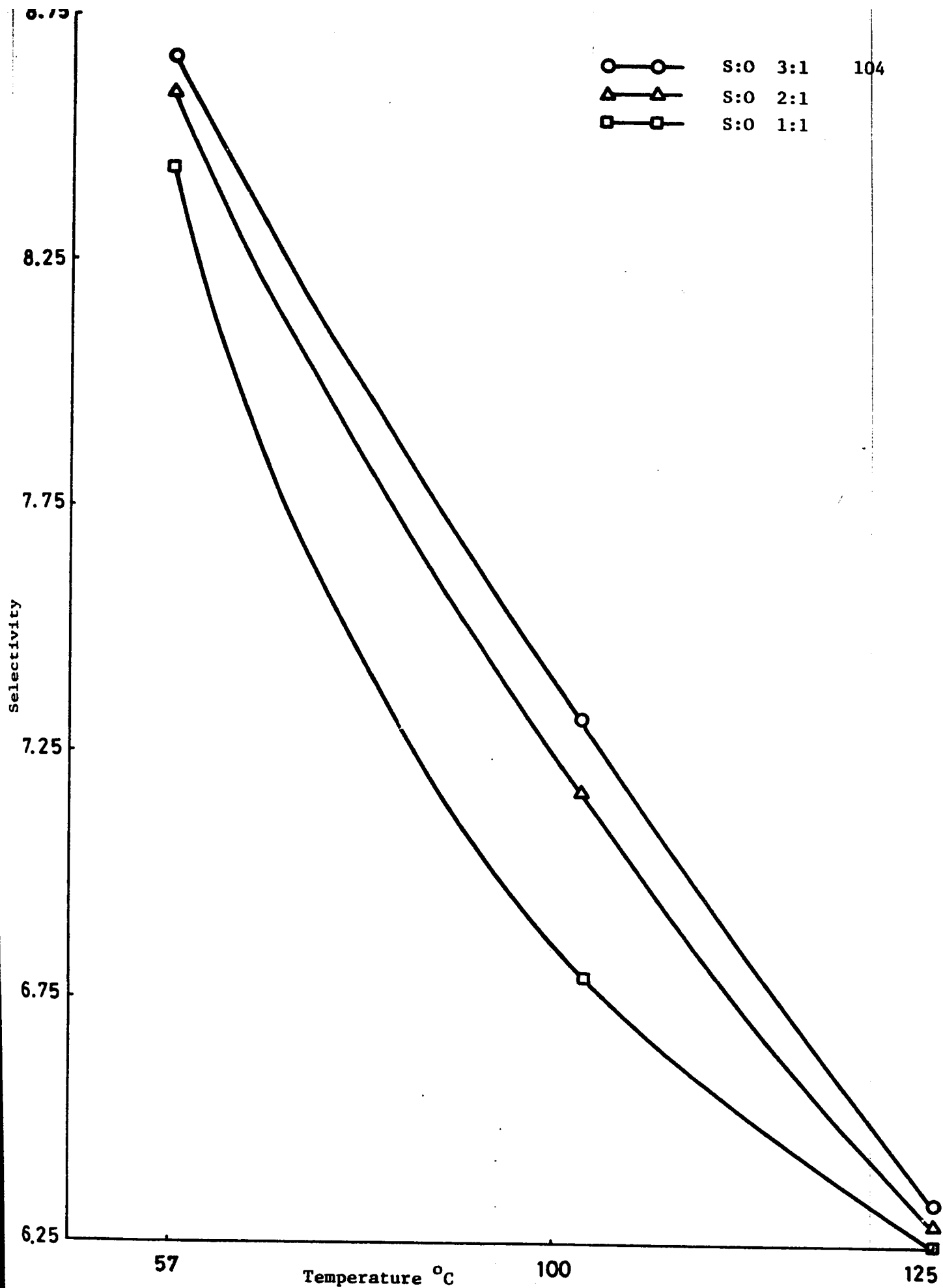


FIGURE : 5.11 EFFECT OF OPERATING TEMPERATURE ON THE SELECTIVITY AT THREE SOLVENT:OIL RATIOS (SULFOLANE)

temperature. Operating at a temperature of 75°C the selectivity reduces from 8.66 to 6.33 at the same solvent-to-oil ratio of 3:1 but at a temperature of 125°C . This represents a decrease of about 27%. Similar decrease in the selectivity of solvent with an increase in temperature is most likely behavior for other solvent-to-oil ratios.

(iv) Solvent Capacity : The solvent capacity is found to be decreasing with increasing selectivity in the temperature range (75°C - 125°C) with solvent-to-oil ratio of 3:1. This is shown in Figure (5.12). With the increase in temperature solvent capacity is found to be increasing at the cost of selectivity. Traversing from 75°C to 125°C the selectivity decreases from 8.66 to 6.33 and solvent capacity increases from 0.23 to 0.33, which depicts 27% decrease for the former and more than 30% increase for latter.

(6) *Phenol* :

Experimental findings indicate that when phenol is used as a solvent in extracting aromatics a three phase mixture is formed. The aromatic contents were found to be distributed in these three phases when normal operating conditions were followed.

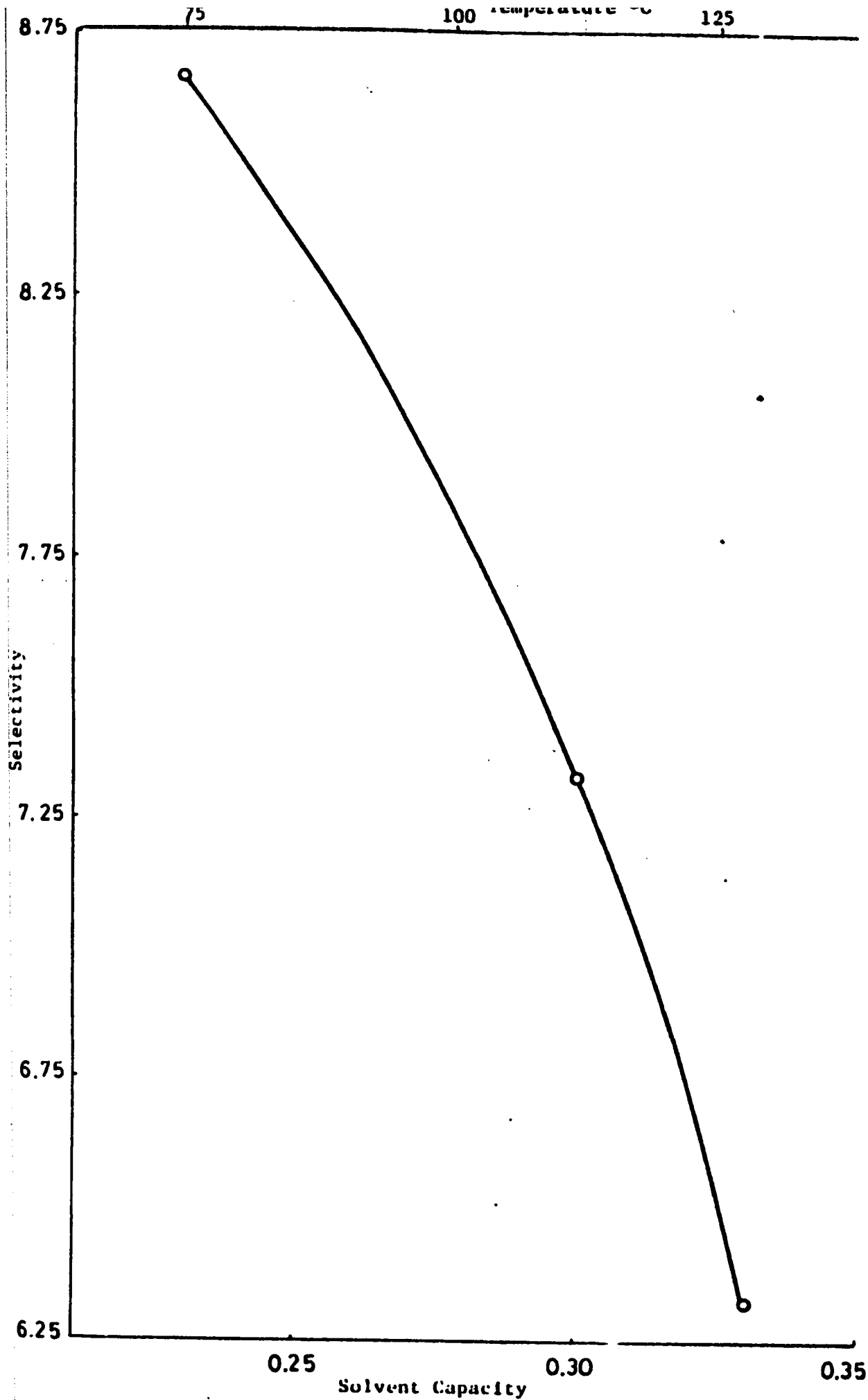


FIGURE : 5.12 SELECTIVITY VERSUS SOLVENT CAPACITY (SULFOLANE)

5.4 Solvent Selection with Regard to Domain of Application

In Figure (5.13) the two important properties, selectivity and solvent power, are plotted for four solvents, namely, 3-Methoxypropionitrile, Ethylene glycol, Dimethyl Sulfoxide and Sulfolane used for the extraction of aromatic hydrocarbons from light fraction (boiling range 23-200°C) of the Arab light crude oil.

The qualifications of a solvent for a certain purpose, the extraction of aromatics from hydrocarbon streams, results from a complex of related properties. In the field of primary properties, 3-Methoxypropionitrile and Ethylene glycol does not occupy favourable combination of selectivity and solvent capacity as compared to Dimethyl Sulfoxide and Sulfolane as shown in Figure (5.13).

Sulfolane as compared to Dimethyl Sulfoxide has just about the right solvent capacity for hydrocarbon with fairly good selectivity, together with such desirable properties as high density, low heat capacity and a boiling point high enough to permit simple separation of solvent from extract. The commercial feasibility of using sulfolane as a solvent in extracting aromatic hydrocarbons has been well proven. Since 1965, over sixty sulfolane extraction units have been licensed through 1974, the total licensed sulfolane plants have aromatics product capacity exceeding 422,000 BPSD (20.2 million M.T.A).

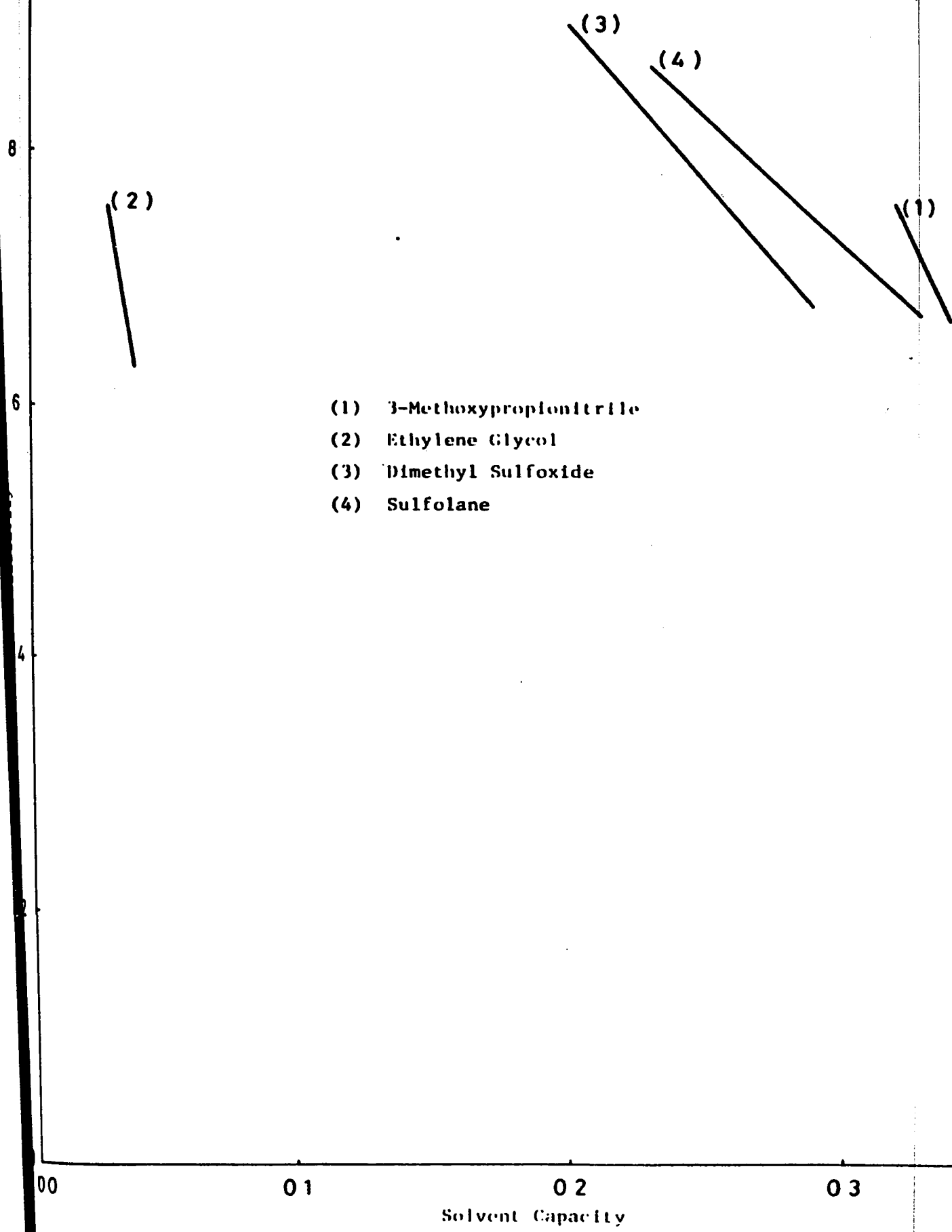


FIGURE : 5.13 : SOLVENT SELECTION WITH REGARD TO DOMAIN OF APPLICATION AT S:O RATIO OF 3:1

CHAPTER 6

ECONOMIC APPRAISAL OF AROMATICS RECOVERY

6.1 Introduction

Developing countries, especially those with abundant petroleum and natural gas resources have shown increasing interest in the development of petrochemical industries. In Saudi Arabia it is reflected by huge petrochemical complex to be built in Jubail. Recently the petrochemical industry has shown a very high rate of growth in the world economy. It is a dynamic industry which supplies intermediate products for a number of other industries and provides substitute for traditional material such as steel, lumber, paper, natural fibres, soap etc. [46].

The Saudi Basic Industries Corporation (SABIC) plans to produce Ethylene, Ethylene dichloride, PolyethyleneLD & HD, Ethanol, Methanol and Caustic soda at gigantic petrochemical complex, at Jubail, with the intention to utilize its natural resources to convert such resources into products useful to all citizens, and to have them as an additional source of income beside petroleum [47].

Aromatics are a basic intermediate in the production of a wide variety of chemicals as shown in Figures (6.1 & 6.2). In the course of building a petrochemical industry, a developing country must consider the point at which it will be economical to install facilities for the production of aromatic hydrocarbon [48].

6.2 Aromatics; Supply vs. Demand

There is a severe competition between the two major forces in the aromatics market : producer or sellers for outlets of their products and buyers or consumers for the material available. The forces are further complicated in that some producers and sellers are also consumers and likewise some buyers and consumers are themselves producers. These driving forces commonly referred to as integration, must be considered as each "side" develops a strategy for future planning [49].

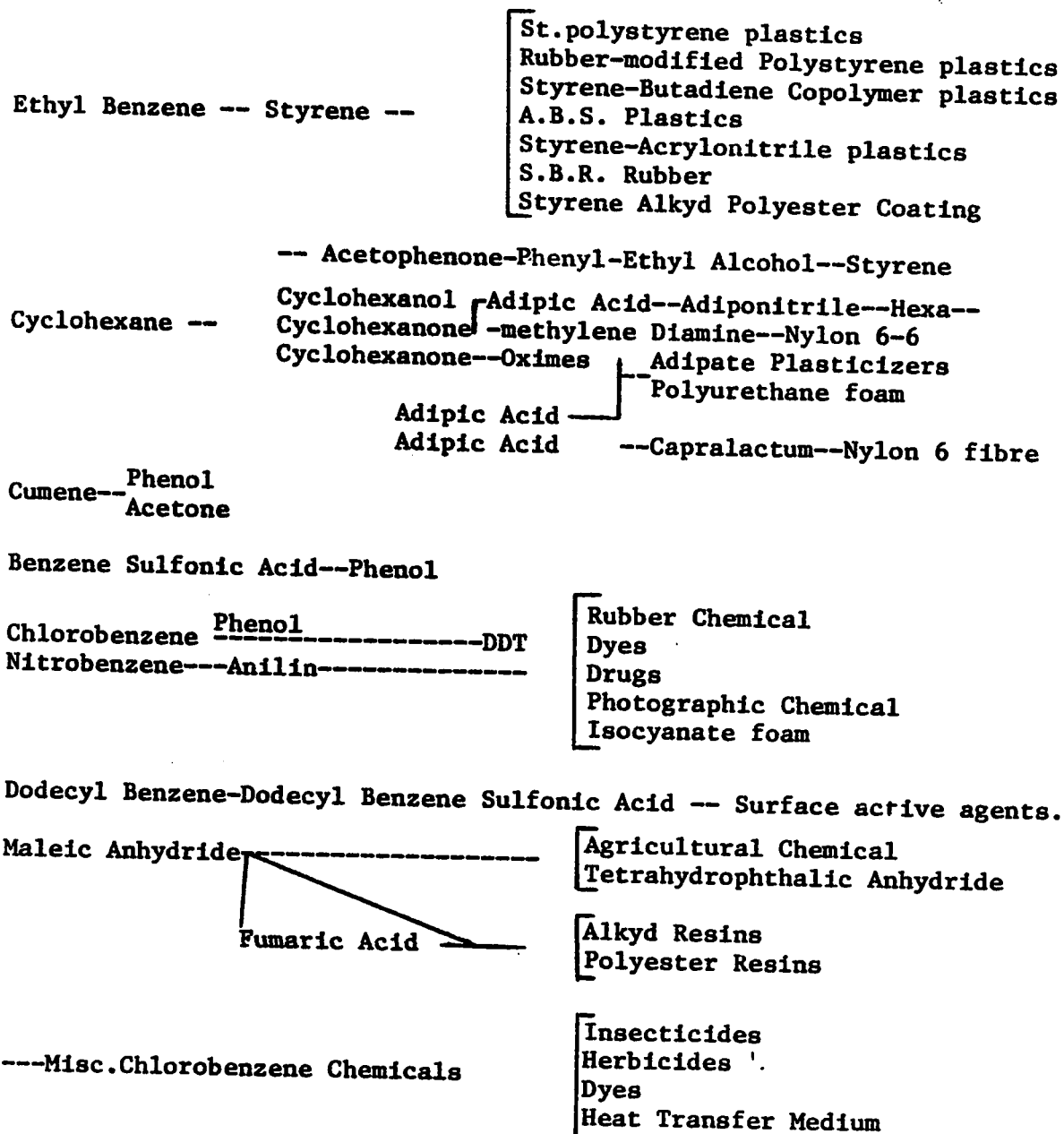
Now let us review the situation for the each member of aromatic series.

Benzene :

As shown in Figure (6.3) the U.S. benzene products capacity will grow to 1.7 MM metric tons/year by 1982. Consumption capacity should gain about 1 MM metric tons/year. Thus there could be about 1 MM metric tons/year surplus. However, the merchant market appears to be growing in absolute volume as well as percent of

FIGURE (6.1)

CHEMICALS FROM BENZENE



consumption and production capacity. Over one-half of the consumption capacity can be filled from the merchant market.

We can see from Figure (6.3) that Western Europe is likely to grow 330 M metric tons/year both in additional consumption and production capacity with a close balance projected. Also, in Western Europe the merchant market appears to be leveling off at about 40% by 1982. This market is very similar to that of the United States with a small surplus of 330 M metric tons/year in production capacity. Also, it resembles Western Europe in that there is little change in plant construction likely over the period 1978 to 1982. The merchant market should hold onto its 60% share of consumption capacity.

The benzene buyer should have ample supplies. Some of the potential production capacity surplus of about 2 MM metric tons/year can be used for exports. Plant construction appears adequate and the merchant market should hold about 50% of the consumption capacity.

From the analysis above, it would appear that there is little need for a buyer to consider backward integration. There is a potential that because of long supply, merchant sellers of benzene may be tempted to integrate forward to improve their profit picture [49].

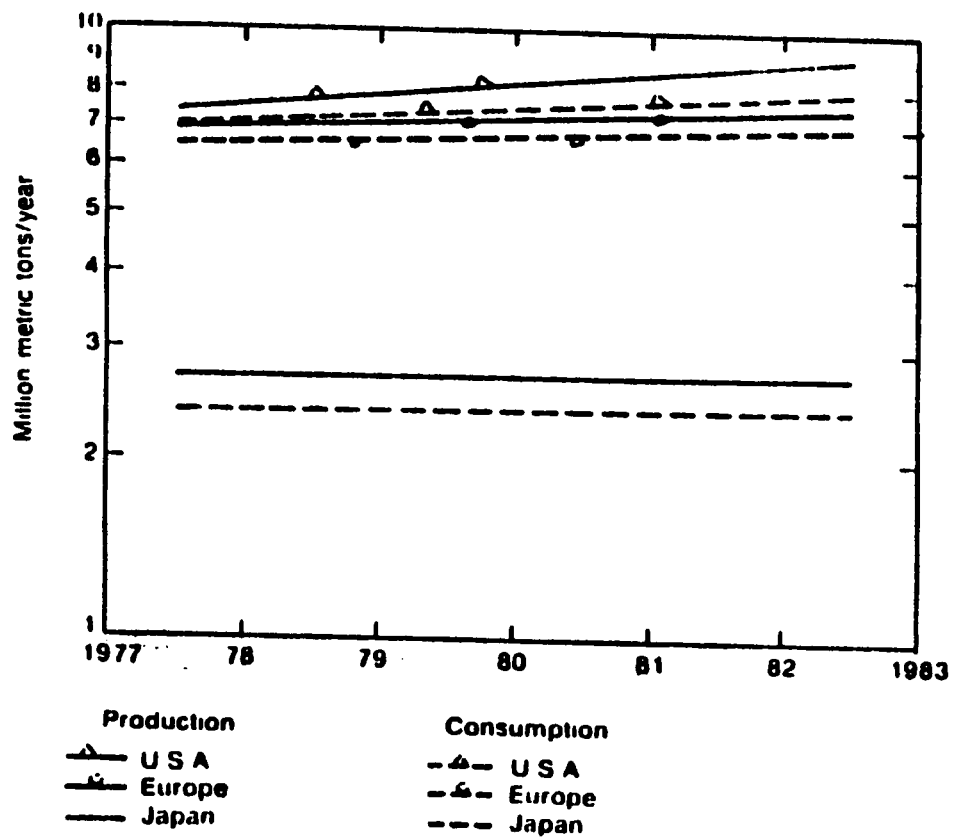


FIGURE (6.3) BENZENE CAPACITIES, PRODUCTION & CONSUMPTION

A major petrochemical producing company and a leading international bank have studied the advantages and disadvantages of establishing a commodity exchange for chemicals, to operate like the copper and Cocoa markets. The most suitable chemical for this use is benzene [50]. Benzene was taken as a model because it seemed to typify what in the petrochemical industry is called a commodity chemical. This is because it has a high volume product with a fair number of buyers and sellers in a competitive market with no tariff barriers. Benzene is a raw material. It is easily stored and transported, and is sold largely to the same specification; this is believed to be true for more than three-quarters of the benzene consumed in Western Europe. It is not produced and consumed in totally different areas, but this is not completely true either of some products like sugar, which has been successfully traded on exchange for years.

Toluene :

Octane improvement will be one of the major problems facing refiners over the next decade. Extracted toluene has traditionally been the highest octane number component available and has been widely used by many refiners as an aid to optimization of blending the various grades of gasoline [51].

Table (6.1) compares the blending properties of toluene with specification of the two expected unleaded grades. Compared to premium grade, toluene's octane is higher by almost 10 numbers. Table (6.2) shows the estimate of "The Pace Company, Consultant and Engineers, Inc., Houston", for the supply and use of extracted high purity toluene for 1978. The major source of toluene is that extracted from refinery. This extraction is nearly always done in conjunction with the recovery of benzene and xylenes from reformat. Recovery of benzene and xylenes for use as petrochemicals generally justifies the extraction operation.

Toluene, probably more than any other commodity, illustrates the continual competition between energy and petrochemical producers for available hydrocarbons. Toluene is very sensitive to conditions in the gasoline market. Because of toluene's position as a unique swing material for the petrochemical industry, conditions in the gasoline market rather quickly influence a wide number of petrochemicals. Toluene's value as a gasoline blending component is an important factor in establishing market price. This value can be estimated by blending toluene with unleaded regular gasoline to yield an unleaded premium grade as shown in Table (6.3).

TABLE (6.1)

TOLUENE PROPERTIES

	<i>Octane</i> <i>(R + M)/2</i>	<i>RVP</i>	<i>Minimum</i> <i>% off</i> <i>Ca 212°F</i>
Regular unleaded	88	9.0	43
Premium unleaded	93	9.0	43
Toluene	102.9	2.0	20

TABLE (6.2)**TOLUENE SUPPLY/DEMAND (mbpcd)**

	1972	1978
Production		
Reforming	70.2	75.3
Olefin plant	2.8	14.2
Other + imports	14.3	9.2
	<hr/> 87.3	<hr/> 98.7
Demand		
TDA	26.5	26.3
Solvents	16.8	11.7
Chemicals + exports	8.9	15.5
To gasoline	41.1	45.2
	<hr/> 87.3	<hr/> 98.7

As shown in Table (6.4) gasoline prices and toluene blending value are expected to increase throughout 1979. The period of late 1978 through early 1979 represented an example of strong competition between gasoline and petrochemical producers for limited supplies of toluene [51]. With gasoline selling at ceiling prices, refiners have no effective economic limitation to the price they can pay for toluene since ceilings can be increased to pass the full cost of purchased toluene on the consumers.

Looking to the future, Table (6.5) shows expected toluene balances for 1980 and 1985. After meeting chemical and solvent demands, the amount available for gasoline is expected to grow only modestly. Supplies are expected to grow from extracted reformat and pyrolysis by-products, but this will be largely offset by increased requirement of toluene to be dealkylated to benzene. Thus toluene's part in meeting the impending octane shortage is expected to be essentially neutral - supplies available for gasoline will neither increase nor decrease [52].

In United States toluene is completely different market as there is essentially no integration in the non-hydrodealkylation market as it is 100% merchant. Also, extraction capacity greatly exceeds consumption capacity. About one third of this surplus serves to European export

TABLE (6.3)

TOLUENE BLENDING VALUE
(4th quarter 1978)

	Octane (R + M)/2	RVP	% off @ 212°F	Volume	
				(bbls.)	(¢/gal.)
Unleaded regular	88.0	9	43	100.0	42.9
Toluene	102.9	2	20	85.7	
C ₅ /160 SR	74.5	9	110	17.3	36.9
n-Butane	90.7	59	110	12.1	23.0
Unleaded premium	93.0	9	43	215.1	46.4

= 55.7¢/gallon

TABLE (6.4)

EFFECT OF TOLUENE PRICE ON
 MAJOR PETROCHEMICALS
 (4th quarter 1978)

<i>Direct effects</i>	<i>Fourth quarter</i>	<i>10¢ gal. increase in toluene price</i>	
		<i>%</i>	<i>%</i>
Benzene, ¢/gal	80.0	+ 12.6	+ 15.8
Cumene, ¢/lb.	12.5	+ 1.5	+ 12.0
Phenol, ¢/lb.	18.0	+ 1.9	+ 10.6
Styrene, ¢/lb.	18.5	+ 1.5	+ 8.2
Polystyrene, ¢/lb.	25.5	+ 1.5	+ 5.9

TABLE (6.5)

PROJECTED TOLUENE SUPPLY/DEMAND
(Mbpcd)

	<i>1978</i>	<i>1980</i>	<i>1985</i>
Production			
Reforming	75.3	75.3	90.2
Olefin plants	14.2	15.5	21.2
Other + imports	9.2	8.9	9.8
Total	98.7	99.7	121.2
Demand			
TDA	26.3	28.7	42.4
Solvents	11.7	11.7	12.9
Chemicals + exports	15.5	11.4	12.5
To gasoline	45.2	47.8	53.4
Total	98.7	99.7	121.2

and the balance is returned to gasoline pool as shown in Figure (6.4) [49].

In Western Europe this market is completely reversed to that of the United States. Consumption capacity exceeds production capacity but a balance appears likely by 1982 as refinery patterns are altered. The merchant market is about 75 percent and very little toluene is presently returned to the gasoline pool as shown in Figure (6.4).

From Figure (6.4) it can be noticed that the consumption of non-HDA toluene is not shown. This is estimated to hold at 40 M metric tons/year from 1978 to 1982. In Japan, the merchant market also captures about 75 percent of the consumption capacity with extraction capacity greatly exceeding the petrochemical demand for toluene.

Therefore, a toluene buyer should see no reason for backward integration into toluene with the present worldwide potential production surplus. However, any strategic plan should closely monitor the octane demand for motor gasoline. While this remains unsettled, it could be a strong factor in the overall demand equation.

With toluene supplies remaining constant through 1985, the demand for octane improvement and petrochemical feedstocks will determine the expected increase in toluene market price [51].

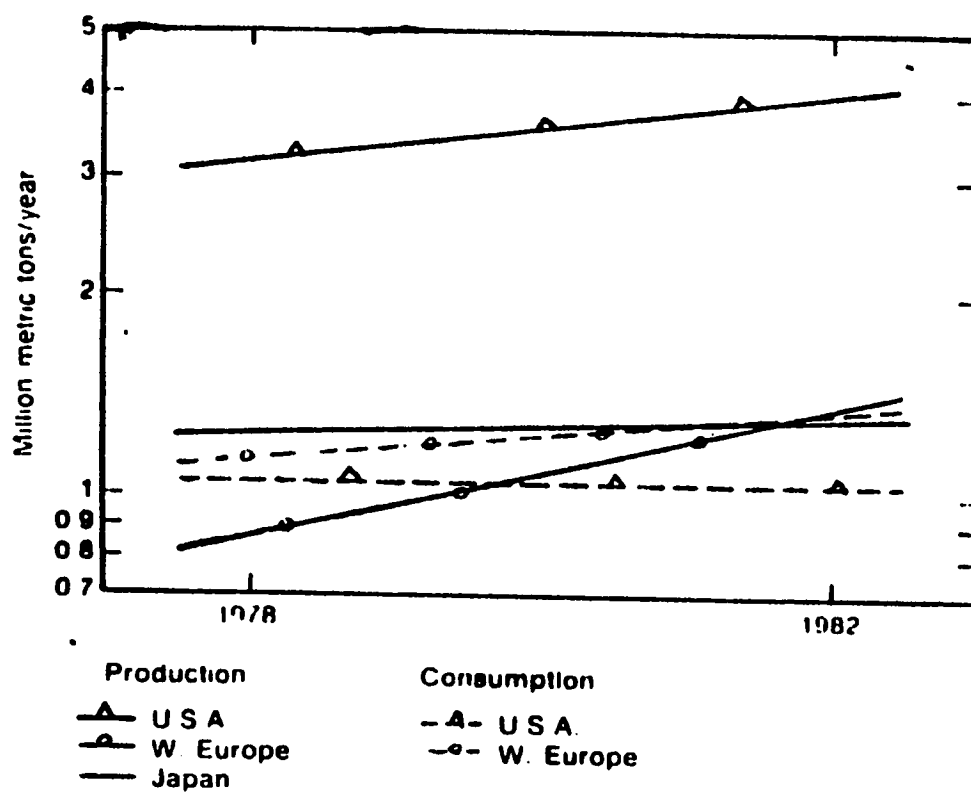


FIGURE (5.4) TOLUENE CAPACITIES, PRODUCTION & CONSUMPTION

Xylene Isomers :

The production capacities shown in Figure (6.5) are for the isomers and not for whole xylenes. As shown, U.S. production capacity will exceed consumption capacity at about the same increment through 1982. However, the merchant market is expected to decline to the 30% level of consumption. In Western Europe the isolation capacity is expected to stay below consumption capacity and the merchant market to shrink to around 50%. Apparently Western Europe will continue imparting xylene isomers through 1982. The Japanese data are incomplete and are not discussed here. European aromatic buyers will be net importers for the next several years with these coming mainly from the United States and Japan. While production excess capacity potential exists, the aromatic buyers faces a shrinking merchant market in toluene and xylene isomers which could present a problem [53].

Aromatic Prices

Both aromatics seller and buyer share the major issue - aromatics price. An acceptable price for each derivative varies with each maker and can differ within the same company for various derivatives. A price may prove very profitable for an established producer with a well-maintained and paid-out plant and not cover debt service for a new producer. Price acceptability becomes an

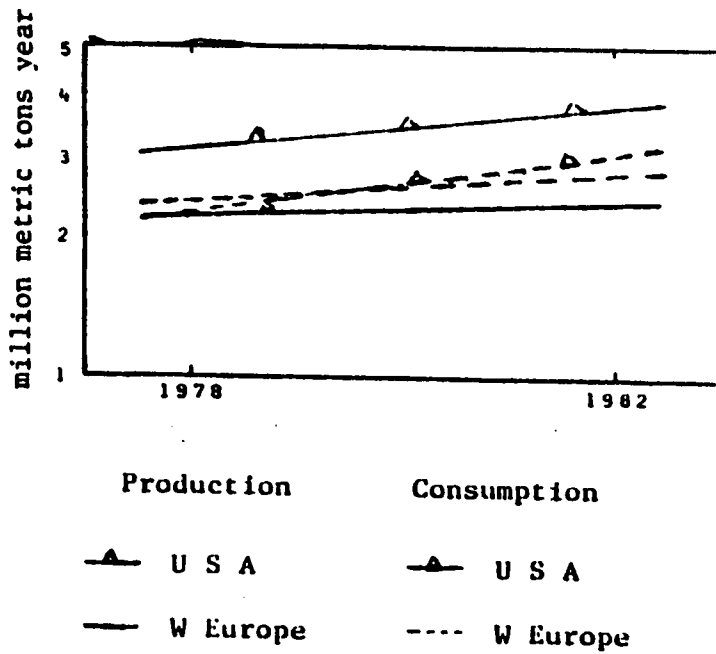


FIGURE (6.5) MIXED XYLENE CAPACITIES,
PRODUCTION & CONSUMPTION

individual matter.

Since aromatics are closely related to motor gasoline which is closely related to crude oil, a historical plot comparing relative U.S. prices is shown in Figure (6.6).

In 1972 \$US., the price of U.S. crude run to stills and wholesale motor gasoline shows a \$10/metric ton differential in 1960 increasing to \$32/metric ton by 1977.

Toluene (again in 1972 \$U.S.) increased from \$15/metric ton over motor gasoline to \$76/metric ton. The xylene isomers are about the same although not shown here.

Benzene, with more variances, indicates a \$45/metric ton differential over motor gasoline, dropping to \$12/metric ton in 1971, and by 1977 this differential widens to \$186/metric ton above motor gasoline.

An aromatics buyer must assess these facts and relate them to his product prices and business goals. A seller must relate these prices to his costs [49].

6.3 Production of Aromatics in Saudi Arabia

General Outlook :

The potential yield of aromatics from Saudi Arabian Crude Oil fractions using different selective solvent was discussed in previous chapters. They are indicative of the level of aromatics that can be obtained from the Saudi Arabian Crude oil fractions.

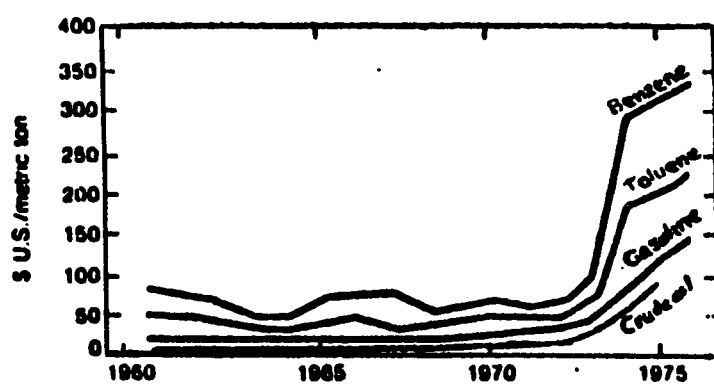


FIGURE (6.6) U.S. HISTORICAL PRICING

The production of aromatics from petroleum is highly capital-intensive i.e., a large capital investment is required per unit of production and economics of scale are important therefore, a developing country considering the installation of aromatics production facilities must carefully calculate whether or not the foreign-exchange savings and continuity of supply are offset by higher production costs associated with a small-scale unit.

Before examining economic factors, a brief description of flow scheme for aromatics production would be appropriate. Figures(6.7) shows the flow scheme [54].

In scheme a C_6 - C_8 petroleum fraction is charged to a hydrotreating unit for destruction of sulfur, nitrogen, and oxygen, containing compounds. The purified naphtha is then charged to a platforming unit, in which the most important reactions for aromatics production are the dehydrogenation of naphthenes and the dehydrocyclization of paraffins. The catalytic reformat is fed to an extraction unit for recovery of benzene, toluene, and C_8 aromatics. Excess toluene and C_8 aromatics are converted to benzene in a hydrodealkylation unit.

Feasibility Study :

The economic of producing aromatics vary significantly according to the cyclic content of the feed. Lower cyclic content result in higher feed capacities for the same

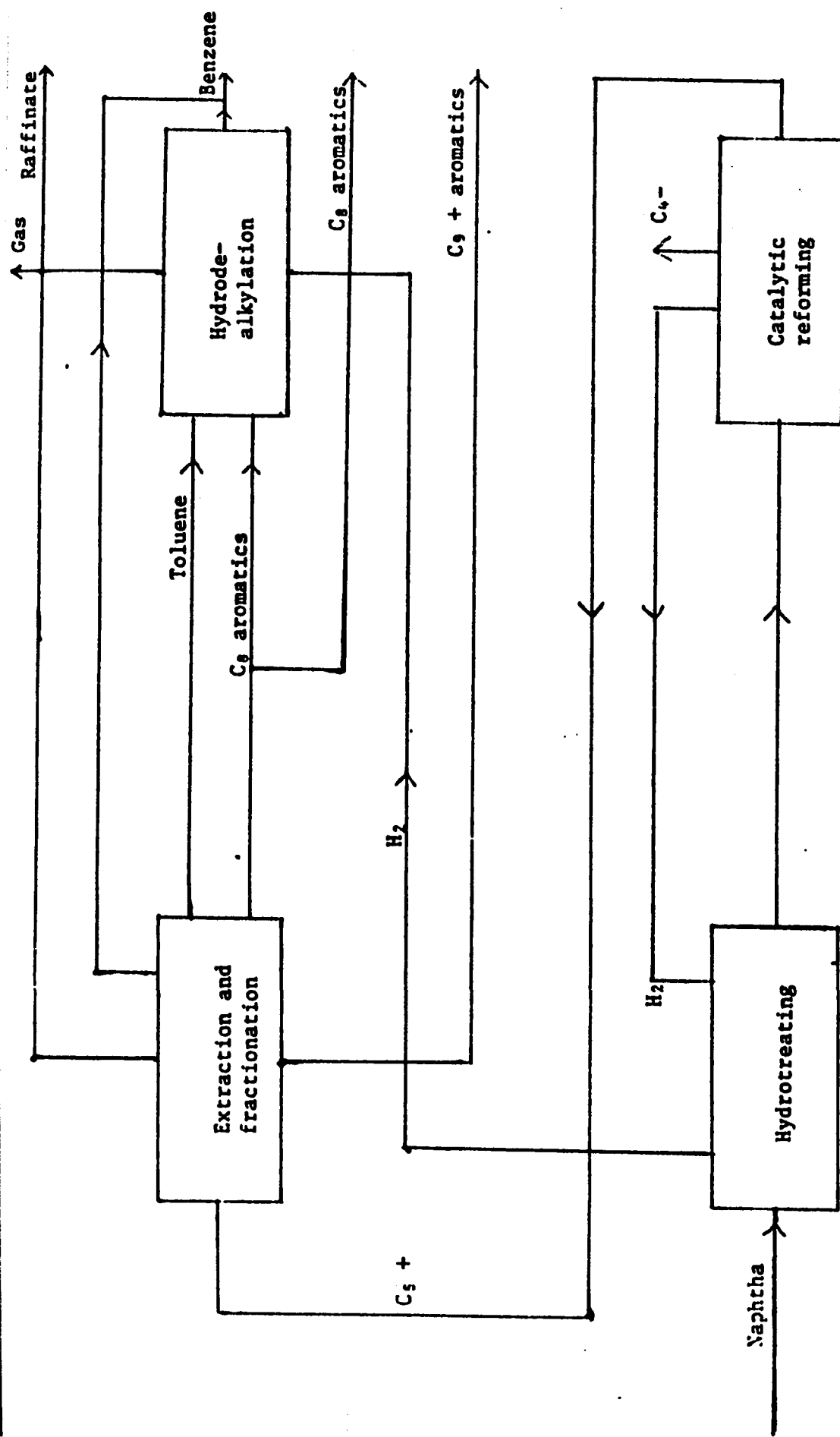


FIGURE (6.7) FLOW SCHEME

level of aromatics production and require more severe operations in the catalytic reforming unit in order to achieve a significant level of aromatics production [55]. Reforming yields are shown in Table (6.6) [56] for two light Arabian naphtha cuts. The first is C₆- 280°F. Cut and the second is C₆- 300°F. Yield of xylene are about the same in both cases.

The economics will be based upon operations of the particular proprietary process units with which we are familiar, i.e. unifining (hydrotreating), UOP Platforming (catalytic reforming), sulfolane (aromatic extraction) and Hydeal(hydrodealkylation). The following assumptions are made :

1. Installing in an existing refinery, with availability of existing offsite facilities;
2. Air cooling with allowance for trim water cooling, and electric drives on pumps and compressors;
3. Straight-line depreciation over ten years, with no salvage value;
4. Borrowed capital at an interest rate of 6% on unpaid balance, with repayment in equal instalments over ten years;
5. Naphtha feed, raffinate from the extraction unit and C₉+ aromatics valued at \$ 260 per ton;
6. Fifteen per cent desired annual rate of return on

TABLE (6.6)

REFORMER YIELD*

<i>Naphtha feed</i>	<i>145° 300°F wt % as feed</i>	<i>145° 280°F</i>
Benzene	5.8	6.0
Toluene	18.6	19.8
Ethythenzene	5.2	5.5
O-Xylene	7.1	7.6
M-Xylene	12.1	12.8
P-Xylene	4.7	4.8
C ₉ -Aromatics	5.9	2.4
* Light Arabian naphtha feedstock		

investment, with a project life of ten years.

In working from the naphtha value to aromatics cost, discounted cash flow is used to account for this 15% return on investment. This concept, which is now widely used for the evaluation of projects in the petroleum and chemical industry, may be compared with an annuity. Thus, an initial outlay is made; this outlay to be returned over a period of years along with "cash flow" at a given rate on the unpaid balance. The high required rate of return of 15% for this period reflects the risks inherent in such an investment owing to the possibilities of technological obsolescence of the process, later installation of a unit with more favourable economics of scale, change in markets, change in position of the company, or less of production due to damage to the unit. However, these risks are less for an aromatics production unit than for other types of chemical plants, since benzene is an important basic intermediate and the technology of aromatics production is well developed.

Economics are presented for the processing of Light Arabian naphtha by scheme shown in Figure (6.7). The capacity of the complex has been set at 30,000 tons of chemical aromatics annually. Estimated yields and utility requirements are shown in Table (6.7). The scheme includes hydrodealkylation of all of the toluene and as much of the C_8 aromatics as is possible with the available hydrogen.

TABLE (6.7)

ESTIMATED YIELDS AND UTILITY REQUIREMENTS
LIGHT ARABIAN NAPHTHA

Feed, tons annum	94,000
Products, tons/annum	
Benzene	20,680
Toluene	-
C ₈ aromatics	9,320
C ₉ + aromatics	5,000
C ₅ + raffinate	32,000
C ₄ and lighter gases	27,000
Estimated utilities	
Fuel, 10 ⁶ kcal/hr	23
Cooling water, m /hr	130
Power, kWh	1,270

The scheme's total includes benzene and xylenes in the ratio of about 5:1, assuming that it is desired to recover para-xylene or ortho-xylene for further processing and thus giving the xylenes chemical value. The by-product aromatics could be sold as solvents, say, or if the raffinate (about 86 F-1 octane with 3 ml TEL) could be used for motor fuel blending, the economics would be improved.

Table (6.8) summarizes the estimated capital investments costs. These costs are taken from generalized correlations, which are based on Gulf Coast, U.S.A. and Nelson Cost Index [57].

The calculation of direct operating cost is shown in Table (6.9). The assumed on-stream efficiency is 330 stream days per annum, or 90%.

Table (6.10) shows the back-calculation of the cost of producing aromatics in order to achieve the desired 15% rate of return. The cash flow required is based on achieving a 15% of return over ten years on the unpaid balance of the total investment plus working capital, assuming a residual or "salvage" value equivalent to the working capital. From this cash flow is subtracted aromatization to arrive at an after-tax profit figure. An assumed tax rate of 50% is used to determine the before-tax profit. Operating expenses are added and by-product credits subtracted to arrive at the aromatic cost. This figure is divided by 30,000 annual tons to arrive at a cost per ton.

TABLE (6.8)
ESTIMATED INVESTMENT*

	\$
Unifining and platforming units	3,000,000
Sulfolane and aromatic fractionation	3,200,000
Hydeal unit and feed H clean up	2,700,000
Material and labour subtotal	8,900,000
Design, engineering and contractor's charges	1,800,000
Process erected cost	10,700,000
Intermediate and product storage	1,000,000
Initial catalysts and chemicals	550,000
Total Investment	12,250,000
Working Capital allowance	1,300,000

* Costs are for the year 1979.

TABLE (6.9)

CALCULATIONS OF DIRECT OPERATING COST

330 STREAM DAYS ANNUM

	<i>Unit Value</i> \$	<i>Dollars per</i> <i>Calendar day</i>
Labour		
Operating labour	3.00/hr	430
Supervision		86
Laboratory		
Estimated at		80
Utilities		
Fuel	9.2/10 ⁶ kcal	4,600
Cooling water	0.02/m ³	55
Power	0.06/kWh	1,655
		<hr/> 6,310
Chemicals		
Calalyst and sulfolane		395
Maintenance		660
TOTAL DIRECT OPERATINV COST		7,961

TABLE (6.10)

CALCULATION OF AROMATIC VALUE
IN U.S. DOLLARS PER ANNUM

1. Cash flow for 15% return on the investment	2,032,500
2. Amortization on investment	1,225,000
3. Profit required (1-2)	807,500
4. Income taxes, 50% of pre-tax profit	807,500
5. Pre-tax profit (3+4)	1,615,100
6. Pay out period total investment/1	6 years
7. Total operating expenses	
Feedstock at \$ 260/t	24,440,000
Direct operating cost (Table 6.4)	2,905,765
Allowance for overhead	449,000
Taxes and insurance 2½% of equipment	291,000
Amortization, 10% of total investment	1,225,000
Interest, 6% on unpaid balance	345,000
	<hr/>
TOTAL OPERATING EXPENSES	29,655,765
8. Required total revenue (5+6)	31,270,865
9. By-product credits at \$ 260/t	9,620,000
10. Fuel gas produced at \$ 9.17/10 ⁶ kcal	3,057,000
11. Product cost (7-8-9)	18,593,865
Product cost/t \$ 620.00	

Market :

Saudi Arabia has a large geographical size but a relatively low population density. This is sparsely populated country because a vast expanse of its land is arid desert unfavourable to living conditions.

The big obstacle in setting up aromatic extraction plant is the limited local market demand because of the small and scattered population. It is clear that a sizeable local market is necessary before the manufacture of aromatics can be justified economically. Although per capita consumption of a variety of commodities is increasing, possible future trends and tendencies cannot be predicted with accuracy. The primary market for aromatics lies in the consuming industries : plastic processing plants, rubber plants, paint and detergents manufacture. Currently Alkyl Benzene Sulfonate (ABS) is manufactured in Jeddah using imported Alkyl Benzene as a starting raw material.

The problem of small market size is tackled in Saudi Arabia with an appreciable amount of success. One technological approach adopted is the integration of several process into a single petrochemical complex where the units are so designed to give low construction cost, the other more realistic approach adopted is the creation of joint ventures between government agency and private companies with access to foreign markets and know-how.

The establishment of joint ventures is now universally adopted in order to secure a particular process technology from a company which has no market outlets or the necessary capital for the venture. It is becoming much harder to break into the already highly competitive market of aromatics so, in order to embark on an export scheme of any nature. One must bear in mind the fluid state of venture and the risks that beset it. Market research must, therefore, be intensified in the developing countries especially neighbouring Arab countries in order to coordinate a policy which is adaptable to the shift in the international scene.

The experimental studies have shown the potential level of aromatics in Saudi Arabian Crude oil fraction, so it is proposed that Saudi Arabian government must take the initiative and invite a consultant firm with the pertinent technical experience of aromatic extraction from indigenous petroleum distillates.

Conclusion

In aromatics production, product transfer prices highly depend on feedstock price. If naphtha feedstock is valued at current Ras Tanura export value, aromatic products would be more expensive. Naphtha price concessions are basic to the project viability.

The cost of transportating aromatics can be quite significant when compared with production costs. Owing to its low flash point and toxic properties, benzene is quite expensive to transport. Neverthelss, it is clear that a small aromatic plant serving a local chemical industry will be economically attractive as compared to large aromatic plants located at distance, because of the transportation cost.

Some general conclusion may be drawn, however,

- (1) Aromatics yield and concomitant economics can vary widely depending upon the naphtha sources;
- (2) Plant capacity has a very significant effect on aromatics production costs, particularly in the range of aromatic capacities that a developing country would wish to consider;
- (3) Lower feed naphtha prices and freight costs can offset the economic effects of a large difference in plant capacities; when balance of payments and reliability of supply are also taken into account, the installation of a smaller-scale aromatics plant in a developing country, like Saudi Arabia, is worth-while for consideration.

CHAPTER 7

SUMMARY AND CONCLUSIONS

The following conclusions may be drawn from the study of the efficiencies of different selected solvents used for the extraction of aromatic hydrocarbons from Saudi Arabian Crudes light fraction.

- (1) The experimental determination of aromatic contents shows that the most suitable crude oil for the production of aromatics in Saudi Arabia is Arab Light Crude oil, as its aromatic contents are 12.96 volume percent. The Saudi Arabian Crude oils considered for investigation were Extra Arab light (Berri), Arab light, Arab medium and Arab heavy crude oil.
- (2) The study of efficiencies of different selected solvents shows that the most appropriate and selective solvent for the extraction of aromatic hydrocarbons from Arab light crude oil fraction is sulfolane. The study includes a total of 50 experiment runs on the extraction of aromatics from the light fraction (boiling range 23-200°C) of Arab light crude oil using different selective solvents and at different temperatures and solvent-to-oil ratios. The solvents considered were 3-methoxypropionitrile, Dimethylsulfoxide, Phenol, Nitrobenzene, Ethylene Glycol

and Sulfolane. The temperature range was from 20-80°C and the solvent-to-oil ratio was varied over the range of 1:1 - 3:1.

- (3) The feasibility study for the large scale production of B.T.X (Benzene, Toluene, Xylene) aromatics in Saudi Arabia indicates that the viability of such venture is subjected to arrival at a satisfactory naphtha price. The capacity set is 30,000 tons of chemical aromatics annually, and the estimated investment is 12.25 million dollars, this reveals a total direct operating cost of 7,961 dollars per callender day with aromatics product cost of 620 dollars per ton.

This study can be further extended in terms of extracting aromatics from Saudi Arabian reformat using the same solvents studied in this work along with other selective solvents namely : N-methylpyrrolidone and Tetraethylene Glycol.

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