RECOVERY OF BICYCLIC AROMATICS FROM LIGHT CYCLE OIL BY LIQUID-LIQUID EXTRACTION

A DISSERTATION

Submitted in partial fulfillment of the requirements for the award of the degree of

INTEGRATED DUAL DEGREE

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CHEMICAL ENGINEERING

(With Specialization in Hydrocarbon Engineering)

By

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Candidate's Declaration

I hereby declare that the work, which is being presented in the dissertation entitled **"Recovery of bicyclic aromatics from light cycle oil by liquid-liquid extraction"** in the partial fulfilment of the requirements of the award of the Integrated Dual Degree in Chemical Engineering with specialization in "Hydrocarbon Engineering", is an authentic record of my own work carried out during the period from July 2010 to May 2011 under the supervision of **Dr. I.D. Mall,** Professor and Head, Chemical Engineering Department, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Date : 27-06-2011 (Prabhjot Kaur)

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Certificate

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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Abstract

A lot of valuable bicyclic aromatic components, including 2, 6-dimethylnaphthalene (2,6 DMNA), are usually present in some refinery streams such as light cycle oil (LCO). In this work, the separation of naphthalene, a bicyclic aromatic component, by solvent extraction method from a model oil (p-xylene, iso-octane and naphthalene) using furfural and NMP as solvent has been investigated. A four factor Box-Behnken design was used to study the individual and interactive effects of four main parameters namely paraffinic content in model oil (P/F): 0.7-0.8; solvent to feed ratio (S/F): 0.5-1.0; temperature (T): 20-40 °C; time (t): 1-3 h for furfural and 1-7 hr for NMP on yield and selectivity of naphthalene. Gas chromatography- ~~mass spectrometry~~ was carried to analyse the composition of raffinate and extract phase. Various polynomial models were fitted to chalk out the best model for the system. Pareto analysis of variance (ANOVA) and other statistical tests were performed to check the soundness of the model. Furfural was found to be a better solvent than NMP, both in terms of yield and selectivity. The operating conditions leading to maximum aromatic recovery have been optimized. It was found that P/F=0.7, S/F=0.5, Temperature=24.41°C and time=2.98 h for furfural and P/F=0.76, S/F=0.76, Temperature=21.93°C and time=4.07 h for NMP yield optimum extraction condition, with lowest possible solvent requirement.

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Prabhjot Kaur

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Nomenclature

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P/F	*Paraffin to feed ratio*
S/F	*Solvent to feed ratio*
T	*Extraction Temperature*
t	*Time*
P	*Pressure*
x_i	*Mole fraction of component i in raffinate phase*
y_i	*Mole fraction of component i in extract phase*
Y_i	*Yield of component i*
m_i	*Distribution coefficient if component i*
E	*Volume of extract phase*
R	*Volume of raffinate phase*

Subscript and superscript

N	*Naphthalene*
I	*Iso-octane*

Greek Symbol

β_i	*Selectivity of component i*
γ_i	*Activity coefficient of component i*

1. INTRODUCTION

1.1. Interest and background

The separation of aromatic hydrocarbons (benzene, toluene, ethyl benzene and xylenes) from C_4 to C_{10} aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. The conventional processes for the separation of these aromatic and aliphatic hydrocarbon mixtures are liquid extraction, suitable for the range of 20–65 wt.% aromatic content, extractive distillation for the range of 65–90 wt.% aromatics and azeotropic distillation for high aromatic content, >90 wt%. Typical solvents used are polar components such as sulfolane, n-methyl pyrrolidone (NMP), n-formyl morpholine (NFM), ethylene glycols, propylene carbonate. This implicates additional distillation steps to separate the extraction solvent from both the extract and raffinate phases, and to purify the solvent, with consequently, additional investments and energy consumption.

Recently, it is stressed that petroleum is used as a raw material rather than energy in view of efficient resource utilization. LCO, specifically, which includes lots of raw materials, is used only as a fuel. 2, 6-dimethylnaphthalene (2,6-DMNA) in LCO is paid attention as raw materials for engineering plastic (PEN plastic), polymer liquid crystal, etc. Hence, it is very significant that 2, 6-DMNA in LCO can be separated and recovered by dearomatization of LCO. Also, as the cetane number of raffinate oil can be improved by dearomatization of LCO, it may be used as diesel oil.

The major advantages of NMP over traditional solvents, such as phenol and furfural, include the nontoxic nature, the high solvent power, the ease of recovery from solutes, and its high selectivity for aromatic hydrocarbons. The key role of this solvent in commercial extraction of mono- and polyaromatics has aroused some research about the equilibrium behaviour of model mixtures containing aliphatics and aromatics with application to dearomatization by NMP as the solvent. Of all commercial extraction solvents for aliphatic-aromatic separations, sulfolane is considered to be the strongest competitor to NMP for its higher selectivity.

Extraction method using solvent such as sulfolane (SUL) and diethylene glycol (DEG), etc., is mainly used for separating aromatic groups from petroleum products with low boiling temperature such as naphtha and gasoline. In solvent extraction of aromatic components in LCO, solvents such as SUL and DEG are difficult to recover by distillation alone after extraction operation because the boiling point between extraction solvent and extract component overlap. Therefore, there are few solvent extraction reports for dearomatizing of petroleum product with high boiling temperature such as LCO.

Benham et al [1967] reported dearomatization of LCO by solvent extraction. They used the mixture of furfural and water as an extraction solvent for dearomatizing of LCO, and the mixture of xylene and naphtha as a re-extraction solvent for recovering extract components in the extract phase, i.e., redex process. This process was for mainly improving the cetane number of raffinate oil and, subsequently, experimental review on separating and recovering each aromatic component by extraction and re-extraction was found to be unsatisfactory. Kim et al [2003] investigated separation of valuable bicyclic aromatic components (carbon number 10–12) in LCO by solvent extraction method. The distribution equilibrium between LCO and solvent was measured by using SUL, DMSO, DEG, and DMF as extraction solvent. DMSO was found to be a suitable solvent to extract bicyclic aromatic components in LCO. Furthermore, the effect of operation factors on separating bicyclic aromatic components was investigated by equilibrium extraction using DMSO. With increasing the moisture content in solvent, the distribution coefficient of bicyclic aromatic components decreased and the selectivity based on n-nonane increased. Increasing operation temperature resulted in decreasing the distribution coefficient and the selectivity of bicyclic aromatic component. The lower the carbon number, the higher the distribution coefficient and the selectivity based on n-nonane. Extraction operation resulted in increasing the paraffin concentration of raffinate phase, and subsequently increasing the cetane number of raffinate phase. It appeared that it could be used as diesel oil.

1.2 Refinery and diesel fuel

The fuels for the three dominant transportation means: cars, trucks or trains, and airplanes- are gasoline, diesel fuel, and jet fuel, respectively. The corresponding

powering systems are based on spark-ignition (SI), compression ignition (CI), and gas turbine engines, respectively.

Table 1.1Comparision of Diesel fuel with Gasoline and Jet fuel

Fuel	Distillate fraction	Boiling Range, °C	Sulfur wt%	Engine for use	Quality indicator
Gasoline Jet fuel Diesel	Gasoline Kerosene L Gas Oil	30-225 160-300 160-380	0.035 0.1-0.4 0.05	Spark Ignition Gas turbine Compression Ignition	Octane N Specs Cetane N

Over the years bulk composition of diesel fuels has been well characterized. The main components of diesel fuels are saturated and aromatic hydrocarbons. Saturated hydrocarbons are dominant diesel components that include normal paraffins (n-paraffins), isoparaffins, and cycloparaffins (naphthenes). N-paraffins have high cetane numbers and are desirable molecules in diesel fuels from a combustion point of view. High boiling n-paraffins, however, cause cold flow problems if present in excess. Aromatic compounds are mainly benzenes, indans, indenes, naphthalenes, biphenyls, acenaphthenes, phenenthrenes, anthracenes, and the naphthenophenantherenes. Diaromatic hydrocarbons are the most abundant aromatic components in the diesel fuels. Trace amounts of polycyclic aromatic hydrocarbons (3+ring aromatic compounds) such as chrysenes, pyrenes, benzanthracenes, and perylenes can also be present.

1.2.1 Meeting diesel fuel requirements: There are various solutions for meeting the parameters in diesel fuel in the design of the fuel. These solutions range from fractionation, adding improvers, and more complex hydroprocessing. Using modern developments in hydro-processing it is possible to convert low-grade blend stocks, such as FCCU or thermal cracker product streams to good diesel precursors.

1.2.2 Increasing cetane value: The simplest way to improve the cetane number is to use an appropriate ignition improvement additive. These are mainly alkyl nitrates. Paraffins already have high cetane value respond best to the additives. Aromatics on the other hand, which have a low cetane number, have a poorer response. Figure shows the relationship between molecular types and cetane number.

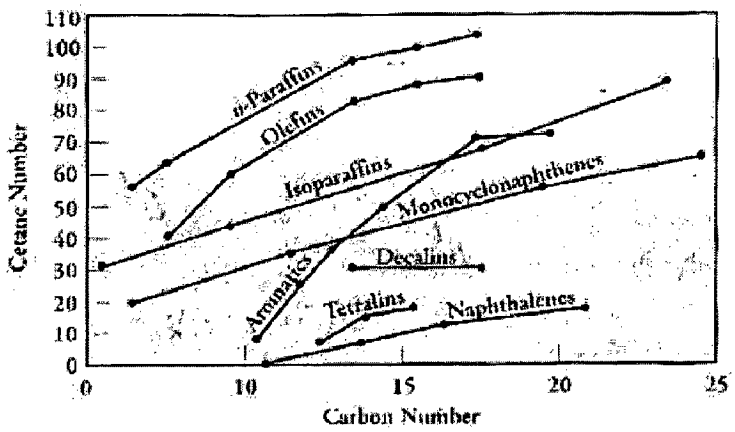

Figure 1.1Cetane number corresponding to various molecular types

1.2.3 Reducing aromatic content:

With the increasing demand for diesel fuel, refineries will need to use streams normally routed to heating oil of fuel as components for diesel product blend. These streams are of lower quality and in particular contain higher quantity of aromatics that will be acceptable as diesel blend stocks without severe treating to improve their blending characteristics. While high severity hydro-treating to remove sulphur and nitrogen helps in reducing aromatics in acceptable diesel blend stocks, it will not be sufficient to improve the quality of the heating oil and fuel oil blend stocks to meet the diesel pool requirement. Hydro-treating using nickel-molybdenum catalyst (de-aromatization process) is being considered for the purpose of upgrading these poorer blend stocks.

1.2.4 Aromatic feedstock

The production of aromatic feedstock originates from the catalytic reforming of a refinery stream of a heavy naphtha range (say 120°C – 420°C) and rich in naphthalene. A typical stream that meets the criteria would be a naphtha stream from a hydrocracker. Thus in meeting these petrochemical, needs a hydrocracker forming part of a fuel refinery configuration. This unit would be operated to maximize naphtha production. This would mean running the unit on a low space velocity with higher oil recycle rate (that is most recovered product heavier than the naphtha would be recycled back to the reactors).

Another source of high naphthalene feed to the catalytic reformer would be hydrotreated catalytic cracker naphtha. Of course the hydrotreating of unsaturates has a high demand on the refinery's hydrogen system, but this is balanced to some

extent by additional hydrogen produced in reforming the naphthenes. Should the refinery configuration include a thermal cracker and/or a steam cracker, the hydrotreating of the naphtha cut from these units also yield high naphthene catalytic reformer feed stock.

Catalytic reforming of high naphthene content naphtha produces aromatics but there is only present some unreacted paraffins and some naphthenes. The downstream petrochemical units that separate and purify the aromatic reformate are expensive both in capital and operating costs. The specification of the BTX (Benzene, Toluene, Xylene) feed therefore is very stringent and excludes non aromatic components as much as possible. Another process may therefore be included in the refinery configuration to: clean up the aromatic feed stream before leaving the refinery. This is an aromatic extraction plant. This is a licensed process using a solvent to separate the paraffins and aromatics by counter current extraction. The rich aromatic stream is then forwarded to the BTX plant where benzene and o-xylene are separated by fractionation while the p-xylene is usually separated by crystallization. The meta-xylene may also be recovered by super distillation but more often than not it is converted into o-xylene in an isomerisation unit.

1.3 Fluid catalytic cracking

Fluid catalytic cracking (FCC) is the most important conversion process used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases and other products. Cracking of petroleum hydrocarbons was originally done by thermal cracking which has been almost completely replaced by catalytic cracking because it produces more gasoline with a higher octane rating. It also produces by-product gases that are more olefinic, and hence more valuable, than those produced by thermal cracking.

The fluid catalytic cracking unit (FCC) is still a main conversion unit in many refineries. It is able to process very large amounts of heavy oil fractions, and it is flexible enough to direct production preferentially to gases (propylene, butenes), gasoline or diesel, with minor modifications of the unit or the operation conditions. However, the light cycle oil (LCO) fraction obtained by FCC is high in aromatics, sulfur and has a low cetane index. This implies that hydrotreatments are always

necessary before blending this fraction into the final diesel pool. By doing this, sulfur content will be decreased, and the aromatics content reduced, but converting them to naphthenes. An additional increase of the cetane may be achieved with the selective opening of the naphthenic rings obtained by hydrogenation. Despite the low quality of the LCO, and due to the processing capacity of the FCC unit, it would be interesting, especially from an economic point of view, to improve the quality of this fraction during the process itself.

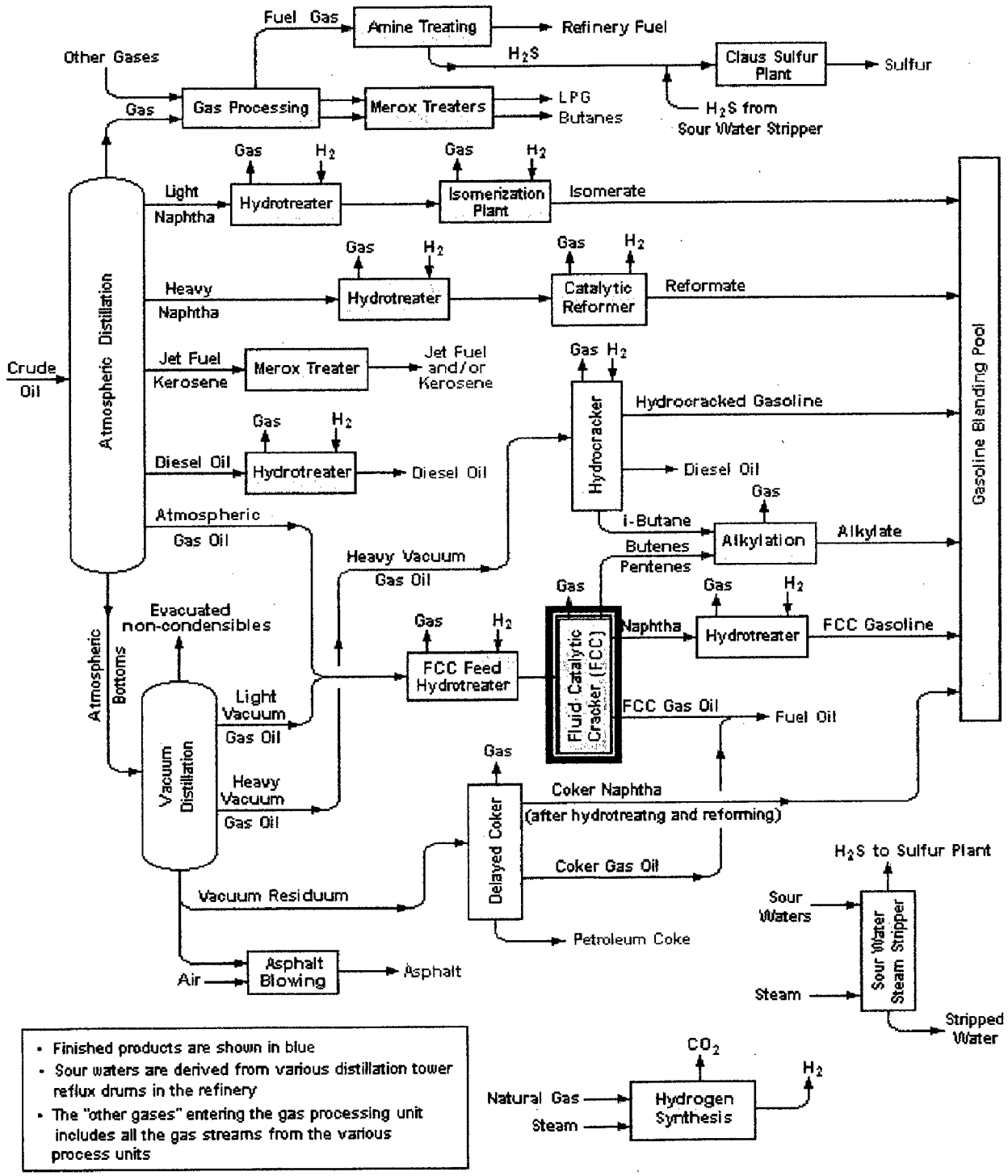

Figure 1.2 Schematic flow diagram of typical oil refinery

The FCC catalyst is a complex mixture containing an active zeolite, a matrix that can participate in the overall cracking process at different levels, a binder, and different additives for specific functions. Whereas the zeolite properties will affect more to the composition of gases and gasoline, the matrix will have a direct influence on the properties of the heavier LCO fraction. It is known that their chemical composition and textural properties play an important role in the final selectivity of the catalyst. Concerning the aromatics content in LCO, during the FCC process aromatic compounds may end up in the LCO fraction following two different pathways: they may be directly obtained by cracking of the heavy hydrocarbons present in the feedstock, or they may be formed by secondary reactions such as cyclation/dehydrogenation of primary cracking products. The process variables and the nature of the catalyst will have a direct influence on the extension of these two pathways.

The feedstock to an FCC is usually that portion of the crude oil that has an initial boiling point of 340°C or higher at atmospheric pressure and an average molecular weight ranging from about 200 to 600 or higher. This portion of crude oil is often referred to as heavy gas oil. The FCC process vaporizes and breaks the long-chain molecules of the high-boiling hydrocarbon liquids into much shorter molecules by contacting the feedstock, at high temperature and moderate pressure, with a fluidized powdered catalyst.

1.4 Light cycle oil

Table 1.2 Identification of Light Cycle Oil

(http://www.lyondellbasell.com/techlit/techlit/refining/REV-AP2050_LIGHT_CYCLE_OIL_LCO.pdf)

Trade Name	Light Cycle Oil (LCO)
CAS Number	64741-59-9
Product Family	Petroleum Hydrocarbon Middle Distillate
Synonyms	LCO, FCCU LCO, FCCU Light Cycle Oil, Middle Distillate Cutter Oil, Untreated Diesel Fuel Blending Component, Light Catalytic Cracked Distillate (Petroleum), C9-C25 Petroleum Hydrocarbons.

1.4.1 Characterization of LCO (Light Cycle Oil)

The total worldwide installed FCC capacity is approximately 14 million BPSD, with an overall production of about 3 million BPSD of LCO. The majority of FCC capacity is in North America, followed by Europe and Asia. Operating severity varies depending upon the market. For example, North American refiners operate their FCC units at high severity to maximize gasoline production with LCO yield of less than 20%, whereas European refiners operate a lower severity for greater LCO production.

1.4.2 Physical and Chemical Properties

Table 1.3 Physical and Chemical properties of Light Cycle Oil

Physical State	Liquid
Color	Transparent, slightly yellow to amber
Odor	Characteristic, Kerosene like
Specific Gravity	0.94 to 0.95 at 60° F
Ph	Not applicable
Vapor Density	AP 50 (Air = 1 at 70□ F)
Boiling Point/Range	150° to 415° C (302° to780° F) (ASTM D-2887)
Melting/Freezing Point	LT - 12°C (10°F) (ASTM D-97)
Vapor Presure	0.8 to 1.8 mm Hg at 20° C (68° F) or LT 0.1 Reid-psia at 38° C (100° F)
Viscosity (cSt @ 40□ C)	3 to 7.5 (ASTM D-445)
Solubility in Water	Negligible to slightly soluble in cold water (LT 0.005 to 0.04 %)
Volatile Characteristics	Volatile Organic Compounds (VOCs) Content = 30% below 400°F 825 95 gm/L

Cracked products such as LCO and Coker distillates have a considerably lower cetane value compared to straight run distillates derived from most of the world's crude sources. LCO cetane ranges from 15-25, compared to 40-60 for the straight

run distillates produced from the same crude. The sulfur content in average light cycle oils can range from 0.2 to 2.5 wt%. A detailed sulfur speciation of LCO shows that a significant portion of the sulfur is found in alkyldibenzothiophenes (DBT), The aromatics content of LCO from FCC units in a normal gasoline-oriented operation can be as high as 80 wt-percent. The organic nitrogen is almost entirely composed of non-basic aromatic compounds, such as carbazoles, with a concentration range of 100-750 ppm. The components of LCO boil in the diesel range with a 95% point of 360°C or higher, representing thermally stable cracked hydrocarbons that are not further reacted in the FCC process.

Over 70% of the aromatic hydrocarbons present in LCO have two rings, while the remainder is typically evenly split between single ring and 3-plus ring aromatics. Two and 3+ ring aromatics combust poorly in the diesel engine. They have very low cetane values and are the root cause of the low blending quality of LCO.

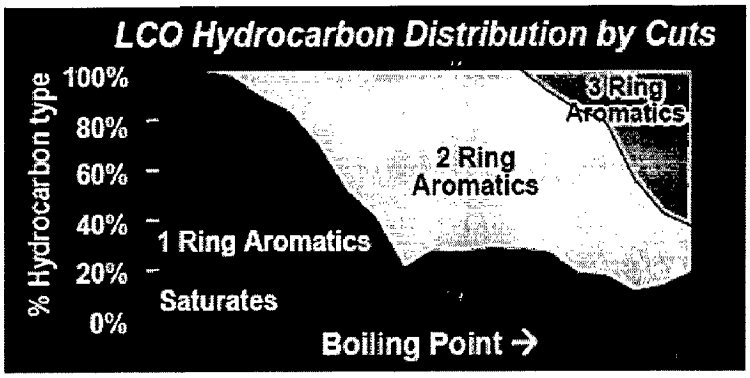

Figure 1.3 Hydrocarbon distribution of LCO

It is necessary to saturate and open the di-aromatic rings to increase the fuel value of products from LCO upgrading. These reactions are a fundamental pathway in hydrocracking reaction chemistry and thus this process is ideal for converting LCO to a higher quality diesel product.

1.4.3 LCO in the clean fuels refinery

A high cetane index of FCCU light cycle oil (LCO) is desirable since the higher the index, the more LCO can be blended into the more valuable road diesel fuel. Many factors affect the gasoline octane and LCO cetane index. Feed quality, catalyst type and unit operating conditions all play major roles in affecting the quality of FCCU products. More stringent environmental legislation is forcing refiners to significant changes in their plant strategies. Most of these modifications concern the quality of their liquid fuels, both gasoline and diesel. Although desulfurization is still the main

issue, other restrictions have to be considered, such as lower product densities, higher cetane numbers and lower levels of polynuclear aromatics (PNAs)

1.5 Liquid-liquid extraction

1.5.1 Process

It is a mass transfer operation in which a liquid solution (the feed) is contacted with an immiscible liquid (solvent), diluent A and a solvent B which are miscible. The object is to recover solute. Two streams result from this contact: **the extract**, which is the solvent rich solution containing the desired extracted solute and **the raffinate,** the residual feed solution containing little solute.

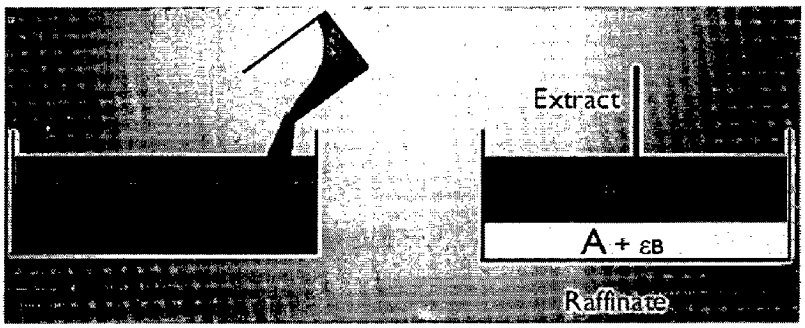

Figure 1.4 Formation of extract and raffinate phases in liquid-liquid extraction

The following need to be carefully evaluated when optimizing the design and operation of the extraction processes.

- Solvent selection
- Operating Conditions
- Mode of Operation
- Extractor Type
- Design Criteria

1.6 Polyethylene naphthalate (PEN)

Table 1.4 Various properties of PEN

(http://en.wikipedia.org/wiki/Polyethylene_naphthalate)

Physical and chemical properties:		**Electrical Properties**	
APPEARANCE:	Yellowish-white solid fiber.	DIELECTRIC CONSTANT @1MHZ	3.2 @ 10KHz
PHYSICAL STATE:	Solid	DIELECTRIC STRENGTH (KV MM^{-1})	160 @ 0.075mm
ODOR:	No specific odor	DISSIPATION FACTOR @ 1MHZ	0.0048 @ 10KHz
MOLECULAR WEIGHT:	>20,000	SURFACE RESISTIVITY (OHM/SQ)	10^{14}
SPECIFIC GRAVITY (water = 1.0):	>1.3	VOLUME RESISTIVITY (OHMCM)	10^{15}
CHEMICAL FORMULA:	$(C_{14}H_{10}O_4)_x$	**Mechanical Properties**	
SOLUBILITY IN WATER (weight %):	Insoluble	COEFFICIENT OF FRICTION	0.27 - biax film
MELTING POINT:	255°C	ELONGATION AT BREAK (%)	60 - biax film
pH:	Not applicable	TENSILE MODULUS (GPA)	5-5.5 - biax film
BOILING POINT:	Not applicable	TENSILE STRENGTH (MPA)	200 - biax film

(Poly(ethylene 2,6-naphthalate) is a polyester with good barrier properties (even better than Polyethylene terephthalate). Because it provides a very good oxygen barrier, it is particularly well-suited for bottling beverages that are susceptible to oxidation, such as beer. It is also used in making high performance sailcloth.

Production: Polyethylene Naphthalate (PEN, Poly(ethylene-2,6-naphthalene dicarboxylate, CAS No: 25853-85-4) is a polyester polymer of Naphthalene Dicarboxilate and Ethylene Glycol.

There are two major manufacturing routes for PEN, i.e. an ester or an acid process, named according to whether the starting monomer is a diester or a diacid of naphthalene, respectively. In both cases for PEN, the glycol monomer is Ethylene Glycol. Solid-state polymerization (SSP) of the melt-produced resin pellets is the preferred process to upgrade the molecular weight of PEN.

Applications: Significant commercial markets have been developed for its application in textile and industrial fibres, films, and foamed articles, containers for carbonated beverages, water and other liquids, and thermoformed applications.

Benefits when compared to PET (Polyethylene Terephthalate): The two condensed aromatic rings of PEN confer on it improvements in strength and modulus, chemical and hydrolytic resistance, gaseous barrier, thermal and thermo-oxidative resistance and ultraviolet (UV) light barrier resistance compared to PET.

- PEN is also the medium for Advanced Photo System film.
- PEN is also used for manufacturing high performance fibers that have very high modulus and better dimensional stability than Polyester or Nylon fibers.
- PEN is used as the substrate for some LTO tape cartridges.
- PEN is being used as a substrate for flexible integrated circuits.
- It is prepared from ethylene glycol and one or more naphthalene dicarboxylic acids by condensation polymerization.

1.7 Objective of study

In view of the above mentioned requirements and limitations, the principal objective of this study is the separation of bicyclic aromatics (naphthalene) by solvent extraction method from model light cycle oil (p-xylene, iso-octane and naphthalene). Specific objectives of the work are:

- To investigate the feasibility of using furfural and NMP as solvents for the extraction of naphthalene.
- To optimize and understand the effect of important parameters like
    a. solvent to feed ratio,
    b. paraffin in feed,
    c. time,
    d. temperature

  on the naphthalene yield and selectivity during the extraction process, using Box-Behnken design.

2. LITERATURE REVIEW

This section has been divided into 3 sub-sections covering different aspects of extraction, relevant to this study.

2.1 Extraction of aromatic compounds

In past extraction has been used in a variety of cases to remove aromatics from the system. Table 2.1 provides a brief review of research work in this area. It can be observed that appreciable work has been carried out in the field of aromatic extraction. However, the system analysed are majorly naphtha reformate, lube oil etc. Kim et al., [2003] also examined the process of separation and recovery for dimethylnaphthalene (DMNA) mixture with 10 structural isomers in LCO using experimental results of the previous work and that of equilibrium re-extraction.

Pasadakis et al., [2011] carried out the liquid–liquid extraction of the Light Cycle Oils (LCO) fraction using acetonitrile and its mixtures with water and methanol at 40 °C and 1:1.5 solvent to feed ratio. The yield of raffinate was found to increase with increased water content in the solvent, while it was invariant in the presence of MeOH. Detailed compositional study of the LCO feed stock and its extraction products using FT-IR and GC–MS techniques, revealed characteristic distribution patterns of individual saturated and aromatic hydrocarbons in the raffinate and extract fractions. The developed analytical protocol provides detailed compositional information of the extraction products and can be used efficiently in future studies dealing with the upgrading of the LCO.

Supercritical extraction is also popular research area. Much of the work is done with CO_2, water and other compounds in supercritical state for extraction of poly-aromatics, which is limited to solid extraction.

Recently interest in ionic liquids has been brought up. Many Ionic liquids, [mebupy]BF4, [mebupy]CH3SO4, [bmim]BF4 (40 °C) and [emim] tosylate (75 °C) have been used. (Meindersma et al., 2005).Even though the solvents give high performance, economic constraints make them industrially inapplicable. (Wytze et al., 2005).

Table 2.1 Major research papers in the field of Aromatic Extraction

Author and year	System studied	Sovlent(s) used	Brief Description
Vishanyakova et al., 1971	high-boiling distillate petroleum products	diethyleneglycol	Alkylcarbamates was used as a selective solvent to obtain concentrates of the bicyclic aromatic hydrocarbons by the method of the liquid extraction of the gas oil from catalytic cracking. They devised that if extraction can be carried out at a lower temperature, with a lower solvent: crude material ratio and the aromatic hydrocarbons are extracted more completely.
Rogozkin et al., 1981	Aliphatic-aromatic mixture	dimethylacetamide (DMAA)	They carried out single-stage extraction of low weight aromatic hydrocarbons from blends with nonaromattc hydrocarbons by the use of DMAA with added water, ethylene glycol (EG), or diethyleneglyeol (DEG).
Jimmy et al., 2002	Water samples	β-cyclodextrin epichlorohydrin copolymer	12 aromatic compounds as model compounds and GC–MS and UV spectrophotometry for detection. It was found that The optimum pH range for the extraction of aromatic compounds is 2.5–5.0. The method has high extraction efficiency with the recoveries between 90 and 101% for aromatic compounds at 0.02–1.67 ppm levels,
Kim et al., 2003	Light Cycle Oil	furfural, DMF,DMSO sulpholane	Separation and recovery of valuable aroatic components (bicyclic aroamtics: carbon number 10-12) in LCO by solvent extraction was carried out. Effect of temperature and moissture content in solvent was studied.
Librando et al., 2003	Marine sediment	CO_2 in supercrital phase	Effect of Temperature (50 to 80°C), Pressure (230-600 bar) and three organig modifiers (methane, *n*-hexane and toluene), added at 5 %/vol on the extraction of polycyclic aromatics hydrocarbons was studied. Using methanol as a co-solvent increased yield and higher temperaures decreased yield.
Meindersma et al., 2005	Toluene/heptane mixture	Ionic liquids	Ionic liquids, [mebupy]BF4, [mebupy]CH3SO4, [bmim]BF4 (40 -C) and [emim] tosylate (75 -C) were employed for the extraction of toluene. Also extraction with [mebupy]BF4 for other aromatic/aliphatic combinations (benzene/n-hexane, ethylbenzene/n-octane and m-xylene/n-octane) was carried out.

Author and year	System studied	Sovlent(s) used	Brief Description
Gaile et al., 2006	Toluene Xylene fraction of Reforming Catalyzate	Toluene, Xylene	Seven-stage counterflow extraction of aromatic hydrocarbons with sulfolane and its mixtures with triethylene glycol was studied. Efficiencies of extraction of arenes from the toluene-xylene fraction with mixed TEG-sulfolane-water solvents of various compositions were compared
Hoseini et al., 2008	Lube oil	Furfural, *n*-hexane as co-solvent	The aromatics in lube oil were extracted at different temperatures (ranging from 323.15 to 343.15 K) and different co-solvent to feed volume ratios (ranging from 0.0 to 0.5). The extraction temperature and the amount of *n*-hexane in furfural were investigated systematically in order to determine their optimum values
Hoseini et al., 2008	Lube oil	Furfural, *n*-hexane as co-solvent	The aromatics in lube oil were extracted at different temperatures (ranging from 323.15 to 343.15 K) and different co-solvent to feed volume ratios (ranging from 0.0 to 0.5). The extraction temperature and the amount of *n*-hexane in furfural were investigated systematically in order to determine their optimum values
Mohsen Nia et al., 2010	*n*-heptane	Ethylene carbonate	Selectivity factors and partition coefficients of ethylene carbonate and the (ethylene carbonate + sulfolane) solvent mixture for the separation of benzene or toluene from (benzene or toluene + n-heptane) were obtained from the liquid + liquid equilibrium data for ternary mixtures and quaternary mixture.
Meng et al., 2010	Aqueous sample	Polymeric ionic liquid	Poly(1-4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl] imide(poly(VBHDIm+NTf2-)),was synthesized and shown to exhibit impressive selectivity towards the extraction of 12 polycyclic aromatic hydrocarbons (PAHs) from aqueous samples when used as a sorbent coating in direct-immersion solid-phase microextraction (SPME) coupled to gas chromatography
Gracia et al., 2010	z-methyl-N-butyl-pyridinium tetra-fluoroborate iso-mers (z = 2, 3, 4)	Ethylene carbonate	Selectivity factors and partition coefficients of ethylene carbonate and the (ethylene carbonate + sulfolane) solvent mixture for the separation of benzene or toluene from (benzene or toluene + n-heptane) were obtained from the liquid + liquid equilibrium data for ternary mixtures and quaternary mixture.

2.2 Development and improvement of extraction process for separation and purification of petroleum products

At present, more than 150 industrial installations for extraction of aromatic hydrocarbons with sulfolane from products formed in pyrolysis and catalytic reforming of gasoline fractions are in the use in the world. About 9 million tons of benzene, toluene, and xylene is annually produced by extractive rectification (Morphylane) and extraction (Morphylex) with N-formylmorpholine on 55 industrial installations. Mixtures of N-formylmorpholine and N-acetyl-morpholine are also used in the *morphysorb* process for absorption purification of natural gas and industrial gasses with high content of hydrogen sulphide and other sulphur-bearing compounds from hydrocarbon gasses and hydrogen. This process employs a mixed absorbent composed of a chemisorbent (diisopropanolamide), water and sulfolane as a physical solvent (Gaile, 2008).

In 2001, the first industrial extraction installation was put into operation in the United States for removal of sulphur-bearing compounds and aromatic hydrocarbons from the diesel fraction and for the production of an ecologically clean diesel fuel. Processes of extraction, extractive and azeotropic rectification, absorption, and extractive crystallization, which use selective solvents, are widely used in petroleum processing and petrochemistry. As far back as 1950s–1960s, effective agents were suggested for separation and purification of petroleum products: sulfolane, *N* formylmorpholine, and *N*-methylpyrrolidone.

Gmehling and co-workers [1194-2003] have made a major contribution to studies of the thermodynamics of solutions of hydrocarbons and other organic compounds in selective solvents. The following parameters have been determined: activity coefficients of hydrocarbons at infinite dilutions (by gas–liquid chromatography), selectivity of solvents toward aromatic and unsaturated hydrocarbons, and heats of mixing.

In recent years, numerous studies have been reported, devoted to the selectivity of ionic fluids and their use as separating agents in extractive rectification and extraction for isolation of aromatic hydrocarbons and extractive purification of diesel fuel and oil fractions. It has been found that some ionic fluids are more selective toward the hexane–benzene system, than sulfolane, which is the most

selective of the industrial extractive agents. These are, e.g., 1-ethyl and 1-butyl- 3-methylimidazolium tetrafluoroborate and 4- methyl-*N*-butylpyridinium tetrafluoroborate. It is noted that the latter ionic fluid makes it possible to extract toluene from a mixture with heptane by using a rotary-disc extractor at a lower ratio to the feed, compared with sulfolane. It is suggested to use ionic fluids for extraction of sulfur-containing compounds from diesel fractions (degree of recovery in a single stage, 10–30%) and for selective purification of oil fractions.

2.3 Extraction methodology for poly-cyclic aromatics

Polycyclic aromatic hydrocarbons (PAHs) represent an important class of hazardous organic chemicals consisting of two or more fused benzene rings in linear, angular or cluster arrangements Extraction can vary in degree of selectivity, speed and convenience.

It depends not only on the approach and conditions used but also on the configurations of the extraction phase. Several pretreatment methods such as liquid–liquid extraction (LLE), solid-phase extraction (SPE), solid-phase microextraction (SPME), headspace solvent microextraction (HSME), single drop microextraction (SDME), supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), microwave-assistedextraction (MAE) and cloud-point extraction (CPE) have been developed among the other extraction methods. LLE is time-consuming method and requires large amount of toxic solvents. Although SPE consumes much less time than LLE but a solvent evaporation step before final analysis is required. SPME is solvent-free, simple and fast, however, it is expensive, and its fiber is fragile. Further, it has limited life time and also sample carry-over can be a problem. HSME is inexpensive and very little solvent is used but it is suitable only for the extraction of volatile compounds. SDME is a cheap method and there is a minimal exposure to toxic organic solvents, however, some disadvantages of this method include: (a) fast stirring would tend to break up the organic drop; (b) air bubble formation reduces extraction rate; (c) extraction is time-consuming; (d) equilibrium could not be attained after a long time in most cases. CPE consumes surfactants as extraction solvent but the use of the surfactants often brings the problems into the analysis of the analytes by many instruments such as GC and HPLC. Also CPE is a time-consuming procedure. SFE, PLE and MAE have successfully been developed in

order to reduce the extraction time and the amount of solvent but they require a specialized and expensive apparatus to perform.

Tavakoli et al (2008) devised fast and effective preconcentration method for the extraction of polycyclic aromatic hydrocarbons (PAHs) using a homogeneous liquid–liquid extraction based on phase separation phenomenon in a ternary solvent (water/methanol/chloroform) system. The proposed method was successfully applied for the extraction and determination of the PAHs in waste water samples.

3 EXPERIMENTAL METHODOLOGY AND THEORY

In order to study the main variables as mentioned in the first objective, design of experiments concept was used. In consideration with the range of variation of variables, Box-Behnken seemed to be the appropriate design. In the following section, basic theory behind this statistical tool has been explained.

3.1 Box-Behnken design - Theory

In statistics, Box-Behnken design is experimental design to response surface methodology, devised by George Box and Donald Behnken in 1960, to achieve the following goals:

- Each factor, or independent variable, is placed at one of three equally spaced values. (At least three levels are needed for the following goal.)
- The design should be sufficient to fit a quadratic model, that is, one containing squared terms and products of two factors.
- The ratio of number of experimental points to the number of coefficients in the quadratic model should be reasonable (in fact, their design kept it in the range of 1.5 to 2.6)
- The estimation variance should more or less depend only on the distance from the centre (this is achieved exactly for the design with 4 and 7 factors and should nor vary too much inside the smallest (hyper) cube containing the experimental points.

The design with 7 factors was found first while looking for a design having the desired property concerning estimation variance, and then similar design were found for other numbers of factors.

Each design can be thought of as a combination of a two level (full or fractional) factorial design with an incomplete block design. In each block, a certain number of factors are put through all combinations for the factorial design, while the other factors are kept at the central values. For instance, the Box-Behnken design for 3 factors involves 3 blocks, in each of which 2 factors are varied through the 4 possible combinations of high and low. It is necessary to include centre points as

well (in which all factors are at their central values). In this table, *m* represents the number of factors which are varied in each of the blocks.

Table 3.1 Characteristics of Box-Behnken Design

Factors	*m*	No. of blocks	Factorial points per block	Total with 1 centre point	Typical total with extra centre points	No. of coefficients in quadratic model
3	2	3	4	13	15,17	10
4	2	6	4	25	27,29	15
5	2	10	4	41	46	21
6	3	6	8	49	54	28
7	3	7	8	57	62	36
8	4	14	8	113	120	45
9	3	15	8	121	130	55
10	4	10	16	161	170	66
11	5	11	16	177	188	78
12	4	12	16	193	204	91
16	4	24	16	385	396	153

The design for 8 factors was not in the original paper. Designs for other number of factors have also been invented (at least up to 21). A design for 16 factors exists having only 256 factorial points.

Most of these designs can be split into groups (blocks), for each of which the model will have a different constant term, in such a way that the block constants will be uncorrelated with other coefficients.

3.2 Design of experiments in this study

A 4 factor Box-Behnken design has been in the present study as the experimental design model. This model is orthogonal and rotable. A total of 29 experiments have been employed in this work to evaluate the indivisual and interactive effects of the four main ineependent parameters on the yield and selectivity of aromatics. Four process parameters, have been taken input parameters, namely

- Paraffin in Feed (P/F)
- Solvent to feed ratio (S/F)
- Temperature (T)
- Time (t)

For statistical calculations, the levels for the four main variables X_i {X_1 (P/F), X_2 (S/F), X_3 (T), X_4 (t)} were coded as according to the following relationship:

$$x_i = (X_i - X_0)/\delta X \qquad 3.1$$

Where X_0 is the value of the X_i at the centre point and δX represents the step change. The variables and levels of the design model are given in Table 3.3. The actual experimental design matrix is given in Table 3.2. A system with several variables is conducted primarily by some of the main effects and low order interactions and it may be assumed that the higher order interactions are small relative to the low order interactions.

A polynomial model with interaction terms was fitted to the experimental runs conducted. The results were analysed using the coefficient of determination (R^2) and Pareto analysis of variance (ANOVA).

Table 3.2 Process parameters and their levels for furfural

Variable, unit	Factors	Level		
	X	−1	0	1
Paraffin in feed , P/F	X_1	0.7	0.75	0.8
Solvent feed ratio, S/F	X_2	0.5	0.75	1.0
Temperature, T (°C)	X_3	20	30	40
Time, t (h)	X_4	1	2	3

Table 3.3 Box-Behnken experimental conditions for furfural

Run No.	Factor 1 A:P/F	Factor 2 B:S/F	Factor 3 C:T(°C)	Factor 4 D: t(h)
1	0.70	0.50	30.00	2.00
2	0.70	0.75	20.00	2.00
3	0.70	0.75	30.00	1.00
4	0.70	0.75	30.00	3.00
5	0.70	0.75	40.00	2.00
6	0.70	1.00	30.00	2.00
7	0.75	0.50	20.00	2.00
8	0.75	0.50	30.00	1.00
9	0.75	0.50	30.00	3.00
10	0.75	0.50	40.00	2.00
11	0.75	0.75	20.00	1.00
12	0.75	0.75	20.00	3.00
13	0.75	0.75	30.00	2.00
14	0.75	0.75	30.00	2.00
15	0.75	0.75	30.00	2.00
16	0.75	0.75	30.00	2.00
17	0.75	0.75	30.00	2.00
18	0.75	0.75	40.00	1.00
19	0.75	0.75	40.00	3.00
20	0.75	1.00	20.00	2.00
21	0.75	1.00	30.00	1.00
22	0.75	1.00	30.00	3.00
23	0.75	1.00	40.00	2.00
24	0.80	0.50	30.00	2.00
25	0.80	0.75	20.00	2.00
26	0.80	0.75	30.00	1.00
27	0.80	0.75	30.00	3.00
28	0.80	0.75	40.00	2.00
29	0.80	1.00	30.00	2.00

Table 3.4 Process parameters and their levels for NMP

Variable, unit	Factors	Level		
	x	−1	0	1
Paraffin in feed, P/F	X_1	0.7	0.75	0.8
Solvent feed ratio, S/F	X_2	0.5	0.75	1.0
Temperature, T (°C)	X_3	20	30	40
Time, t (h)	X_4	1	4	7

Table 3.5 Box-Behnken experimental conditions for NMP

Run No.	Factor 1 A:P/F	Factor 2 B:S/F	Factor 3 C:T(°C)	Factor 4 D: t(h)
1	0.70	0.50	30.00	4.00
2	0.70	0.75	20.00	4.00
3	0.70	0.75	30.00	1.00
4	0.70	0.75	30.00	7.00
5	0.70	0.75	40.00	4.00
6	0.70	1.00	30.00	4.00
7	0.75	0.50	20.00	4.00
8	0.75	0.50	30.00	1.00
9	0.75	0.50	30.00	7.00
10	0.75	0.50	40.00	4.00
11	0.75	0.75	20.00	1.00
12	0.75	0.75	20.00	7.00
13	0.75	0.75	30.00	4.00
14	0.75	0.75	30.00	4.00
15	0.75	0.75	30.00	4.00
16	0.75	0.75	30.00	4.00
17	0.75	0.75	30.00	4.00
18	0.75	0.75	40.00	1.00
19	0.75	0.75	40.00	7.00
20	0.75	1.00	20.00	4.00
21	0.75	1.00	30.00	1.00
22	0.75	1.00	30.00	7.00
23	0.75	1.00	40.00	4.00
24	0.80	0.50	30.00	4.00
25	0.80	0.75	20.00	4.00
26	0.80	0.75	30.00	1.00
27	0.80	0.75	30.00	7.00
28	0.80	0.75	40.00	4.00
29	0.80	1.00	30.00	4.00

3.3 Materials, Method and Experimental Procedure

3.3.1 Chemicals

Analytical grade compounds iso-octane, p-xylene and naphthalene were supplied by Rankem, India. Model oil used in the study was prepared by mixing required ratio of iso-octane and p-xylene to make 10 ml of solution in a 100ml conical flask. 0.2 g of naphthalene was added to the solution. Solvent was added to the solution in required amount (corresponding to S/F ratio for the particular experimental run). The solvents were tested in this study, namely furfural and NMP. The main properties of all the chemicals used have been given in Table 3.6.

Table 3.6 Properties of chemicals used

	Iso-octane	p-xylene	NMP	Furfural
IUPAC name	2,2,4-trimethylpentane	1,4-Dimethylbenzene	1-methyl-2-pyrrolidinone	Furan-2-Carbaldehyde
CAS number	540-84-1	106-42-3	872-50-4	98-01-1
Molecular formula	C_8H_{18}	$C_6H_4(CH_3)_2$	C_5H_9NO	$C_5H_4O_2$
Molar mass (g/mol)	114.23	106.16	99.13	96.08
Density (g/ml)	0.691	0.87	1.028	1.16
Melting Point (°C)	-107	12	-23.6	-36.5
Boiling Point (°C)	98	138	202	151.7

3.3.2 Procedure

The experiments were done in an orbital shaking incubator maintained at constant temperature (20, 30 or 40°C, as the case may be). The shaking incubator regulated by precision ±0.1 °C was agitated at a constant speed of 150 rpm for required time period. After agitating the solution in a shaking incubator, it was allowed to settle for 4 hours, in the same conical flask, maintained at same temperature. Samples from raffinate phase and extract phase were analysed for composition.

3.3.3 Analysis of samples

The sample analysis was performed using a gas chromatograph equipped with a flame ionization detector (FID). 0.2µl sample of solution taken from each phase was injected into the GC. The GC response-factors for each component in the sample mixtures were obtained by calibration (Standard mixtures were used as calibration solution). The conditions mentioned in the GC have been indicated in the Table 3.7.

Table 3.7 Conditions maintained in Gas Chromatogram

Oven		Detector	
Initial Temperature	80°C	Base Temperature	280°C
Final Temperature	280°C	Ignition threshold	0.5
Ramp (°C/min)	10.0	H_2	35
Inlet		Air	350
Temperature	280°C	Makeup N_2	30
		Detector type	FID
Split flow	25	Carrier Gas	N_2

The retention time of various compounds have been indicated below:

Iso-octane	4.5 min
Furfural	5.2 min
p-xylene	5.7 min
NMP	7.2 min
Naphthalene	9.5 min

A sample screenshot for peaks obtained in GC have been shown below:

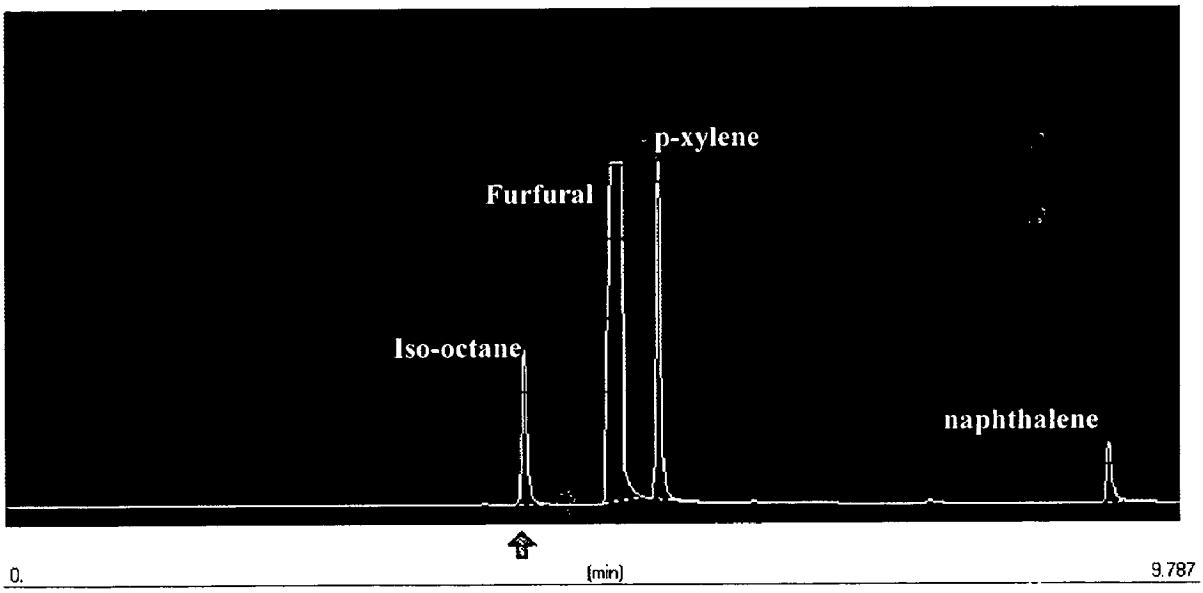

Figure 3.1 Screenshot of peaks obtained for various compounds with furfural as solvent

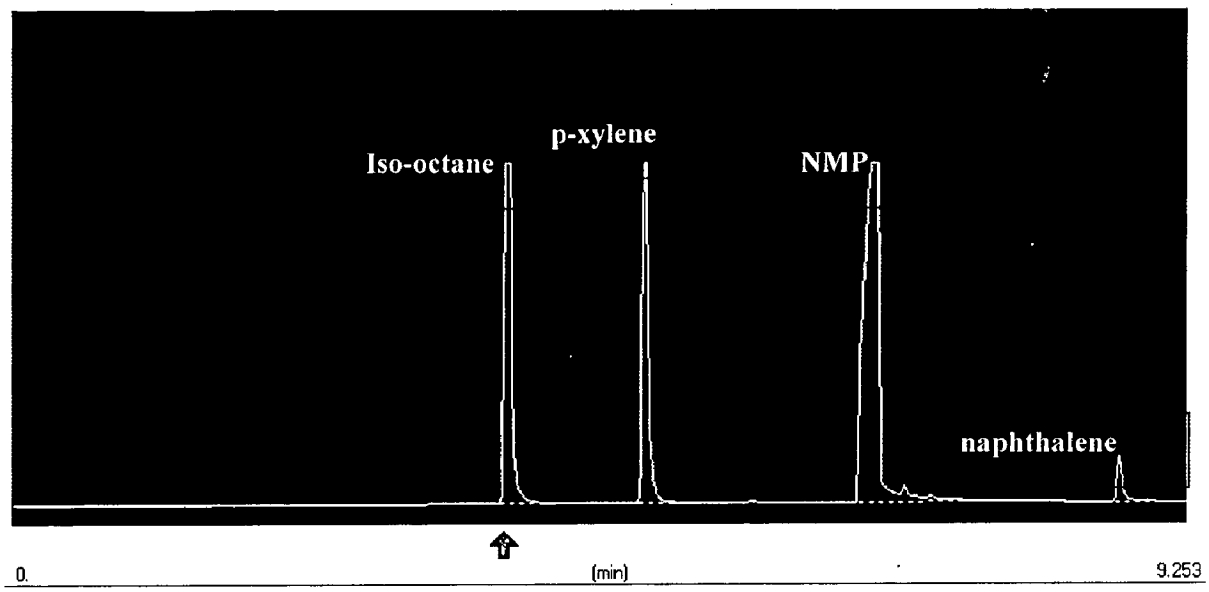

Figure 3.2 Screenshot of peaks obtained for various compounds with NMP as solvent

3.4 Theory – Yield & Selectivity

The main variables which can quantize extraction are yield and selectivity of the desired compound to be extracted. In following paragraphs both these concepts have been explained.

The distribution coefficient (m_i) which is the ratio of component i in extract phase to that in raffinate phase is defined as:

$$m_i = y_i/xi \qquad 3.2$$

where, y_i and x_i denote the mass fraction of component i in the extract and in the raffinate phase respectively

Yield if component i (Y_i) is defined as:

$$Y_i = Ey_i/R_o x_{i,o} \qquad 3.3$$

Where $x_{i,o}$ denotes the mass fraction of component i in the feed. E refers to the mass of the extract phase after a run and R_o denotes the mass of the feed.

Selectvity of component i ($\beta_{i,j}$) is the ratio of the distribution coefficient for component i (naphthalene in this study) to that for component j (p-xylene in this study). It was calculated by following expression:

$$\beta_{i,j} = m_i/m_j \qquad 3.4$$

Selectivity gives a measure of the ability of a solvent to differentiate between the alkanes and the aromatics. For an efficient separation, it is necessary that the aromatics content in solvent should be high and the alkane content should be less. In other words, selectivity should be high for efficient separation.

Mass balance of component i was checked by using following equation:

$$R_o x_{i,o} + E_o y_{i,o} = R x_i + E y_i \qquad 3.5$$

Where, E_o and R_o, respectively, denote the initial mass of extract phase and that of raffinate phase.

Selectivity: This is the first property ordinarily studied in deciding the applicability of a solvent. The solvent should be as selective as possible for the desired solute over impurities, so as to reduce or eliminate the need for scrubbing.

Yield : In addition to high selectivity, unless the solvent has the capacity to dissolve relatively large quantities of the preferentially extracted solute, it will likely be uneconomical to use because of the large quantities that must be circulated through the extraction system (Treybal, 1968). Therefore, high value of yield 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 by distillation.

4. RESULTS AND DISCUSSION

The experiments were performed as mentioned in section 3.3. Extraction operations resulted in an increase in the paraffin concentration of raffinate phase, and subsequently increase in the cetane number of raffinate phase. It appeared that it could be used as diesel oil. Since in this work the emphasis is on the extraction of bicyclic aromatics, the yield and selectivity of naphthalene in extract phase were of main concern. Box-Behnken experimental design was employed to determine the simple and combined effects of operating variables on naphthalene extraction. This process involves three major steps:

- performing the statistically designed experiments,
- estimating coefficients in the proposed model and
- predicting the nature of response and checking the validity of the model.

The yield (Y_N) and selectivity ($\beta_{N,I}$) were calculated for all set of experiments using the following formula:

$$Y_N = Ey_N / R_o x_{N,o} \qquad 4.1$$

$$\beta_{N,I} = m_N / m_I \qquad 4.2$$

$$where,\ m_N = y_N / x_N \qquad 4.3$$

$$m_I = y_I / x_I \qquad 4.4$$

y_N and x_N denote the concentration of naphthalene (g/ml) in the extract and in the raffinate phase respectively. $x_{N,o}$ represents concentration of naphthalene in feed.

y_I and x_I denote the concentration of iso-octane (ml/ml) in the extract and in the raffinate phase respectively.

E and R are the volume of extract and raffinate phase respectively. R_o represents volume of feed.

4.1 Extraction using furfural as solvent

Yield and selectivity of naphthalene at various experimental conditions have been recorded in Table 4.1. No aliases were found using quadratic model. Insignificant terms (as suggested by ANOVA) were removed through a standard modification algorithm namely stepwise.

4.1.1. Modeling of Data and Statistical Analysis

An empirical relationship expressed by modified quadratic equation was fitted between the response and input variables.

The final equation obtained in coded factors is given below.

$$\text{Yield} = 0.57 - 0.091\ A - 0.078\ B - 3.560\times10^{-3}\ C + 0.056\ D - 0.11\ AC + 0.067\ BC - 0.044\ BD - 0.086\ CD + 0.041\ A^2 + 0.091\ B^2 + 0.15\ C^2 + 0.11\ D^2 \quad 4.5$$

Modified quadratic model was found to be the best fit for the yield of naphthalene. ANOVA and the various statistical tests for this model for yield of naphthalene have been indicated in Table 4.2. The model gives coefficient of determination (R^2) value of 0.6865 and adjusted R^2 value of 0.4513.

For selectivity of naphthalene, Box-Cox plot suggested square root transformation. An empirical relationship expressed by modified quadratic equation was fitted between the response and input variables.

The final equation obtained in coded factors is given below.

$$\sqrt{Selectivity} = 4.83 - 3.30\ A - 1.60\ B + 2.31\ C + 0.75\ D - 3.34\ AC - 4.30\ AD + 4.10\ BC - 4.84\ CD + 2.47\ A^2 + 1.75\ B^2 + 3.61\ C^2 + 4.08\ D^2 \quad 4.6$$

ANOVA for selectivity of naphthalene has been indicated in Table 4.3. The model gives coefficient of determination (R^2) value of 0.6863 and adjusted R^2 value of 0.4510.

Table 4.1 Yield and selectivity of naphthalene from model oil with furfural

Run	Paraffin in Feed (P/F)	Solvent to feed (S/F)	Temperature (°C) (T)	Time (h) (t)	Naphthalene	
					Yield (Y)	Selectivity (β)
1	0.7	0.5	30	2	0.619471	10.05568
2	0.7	0.75	20	2	0.757336	10.13746
3	0.7	0.75	30	1	0.664272	9.705319
4	0.7	0.75	30	3	0.966781	26.97316
5	0.7	0.75	40	2	0.930447	15.96146
6	0.7	1	30	2	0.98667	9.675114
7	0.75	0.5	20	2	0.912868	16.53333
8	0.75	0.5	30	1	0.96672	12.18231
9	0.75	0.5	30	3	0.938045	13.92417
10	0.75	0.5	40	2	0.708956	10.86675
11	0.75	0.75	20	1	0.459837	2.591906
12	0.75	0.75	20	3	0.74627	7.407325
13	0.75	0.75	30	2	0.632176	4.698265
14	0.75	0.75	30	2	0.442377	5.466928
15	0.75	0.75	30	2	0.315189	1.152211
16	0.75	0.75	30	2	0.633644	9.171621
17	0.75	0.75	30	2	0.856232	3.646644
18	0.75	0.75	40	1	0.882236	25.27932
19	0.75	0.75	40	3	0.724433	10.72876
20	0.75	1	20	2	0.750052	5.660893
21	0.75	1	30	1	0.90773	7.013995
22	0.75	1	30	3	0.90291	6.642546
23	0.75	1	40	2	0.762469	15.53992
24	0.8	0.5	30	2	0.316719	6.692899
25	0.8	0.75	20	2	0.929716	11.08766
26	0.8	0.75	30	1	0.757057	7.891648
27	0.8	0.75	30	3	0.730663	7.941214
28	0.8	0.75	40	2	0.657328	3.559771
29	0.8	1	30	2	0.641035	5.708638

Table 4.2 ANOVA for yield of naphthalene (using furfural as solvent)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.537017	12	0.044751	2.919269	0.0239	Significant
A-P/F	0.099456	1	0.099456	6.487789	0.0215	
B-S/F	0.073727	1	0.073727	4.809466	0.0434	
C-TEMP	0.000152	1	0.000152	0.009922	0.9219	
D-TIME	0.037548	1	0.037548	2.449366	0.1371	
AC	0.049617	1	0.049617	3.236692	0.0909	
BC	0.018069	1	0.018069	1.178694	0.2937	
BD	0.007757	1	0.007757	0.506001	0.4871	
CD	0.029625	1	0.029625	1.9325	0.1835	
A^2	0.010814	1	0.010814	0.705455	0.4133	
B^2	0.054053	1	0.054053	3.526055	0.0788	
C^2	0.155485	1	0.155485	10.14273	0.0058	
D^2	0.08506	1	0.08506	5.548749	0.0316	
Residual	0.245275	16	0.01533			
Lack of Fit	0.196404	12	0.016367	1.339631	0.4212	not significant
Pure Error	0.04887	4	0.012218			
Cor Total	0.782291	28				

Table 4.3 ANOVA for selectivity of naphthalene (using furfural as solvent)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	685.6203	12	57.13503	2.917075	0.0240	significant
A-P/F	130.8541	1	130.8541	6.680861	0.0199	
B-S/F	30.58311	1	30.58311	1.561445	0.2294	
C-TEMP	63.75871	1	63.75871	3.255252	0.0901	
D-TIME	6.679208	1	6.679208	0.341012	0.5674	
AC	44.56825	1	44.56825	2.275468	0.1509	
AD	74.11724	1	74.11724	3.784116	0.0695	
BC	67.26035	1	67.26035	3.434032	0.0824	
CD	93.76026	1	93.76026	4.787006	0.0439	
A^2	39.65369	1	39.65369	2.024551	0.1740	
B^2	19.94834	1	19.94834	1.018479	0.3279	
C^2	84.57758	1	84.57758	4.318177	0.0542	
D^2	108.1863	1	108.1863	5.523539	0.0319	
Residual	313.3826	16	19.58641			
Lack of Fit	279.1834	12	23.26529	2.721155	0.1728	not significant
Pure Error	34.19913	4	8.549783			
Cor Total	999.0029	28				

4.1.2 Model diagnostic plots:

4.1.2.1 Predicted vs Actual plot

Figure 4.1 and 4.2 show actual response values (yield and selectivity) versus the predicted response values. The data points in both the plots are evenly spread by the 45 degree line.

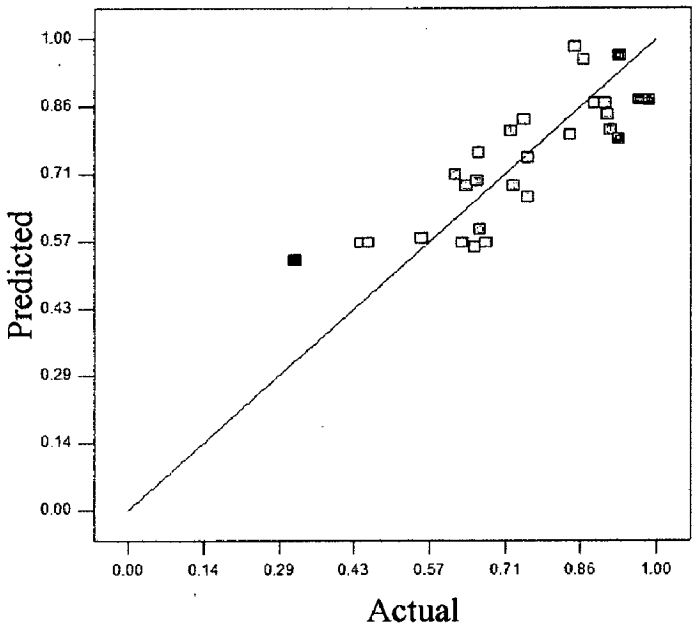

Figure 4.2 Predicted vs actual response for naphthalene yield

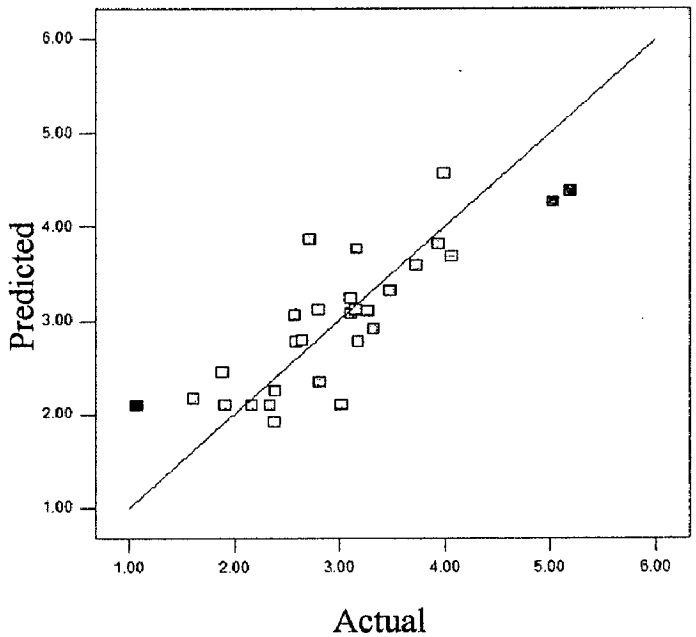

Figure 4.1 Predicted vs actual response for naphthalene selectivity

4.1.2.2 Normal Probability

The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. We can expect some scatter even with normal data. Figure 4.3 and 4.4 give normal probability plots for naphthalene yield and selectivity distributed along straight line.

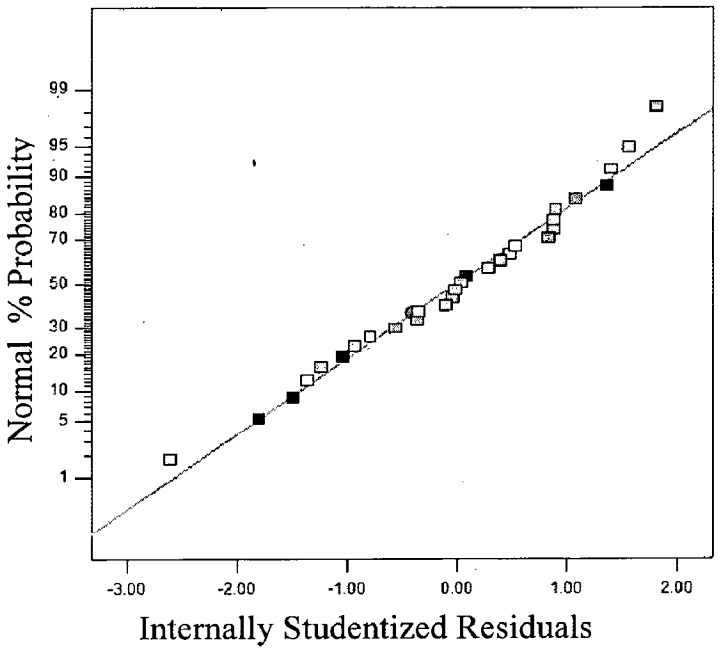

Figure 4.3 Normal plot of residuals for yield

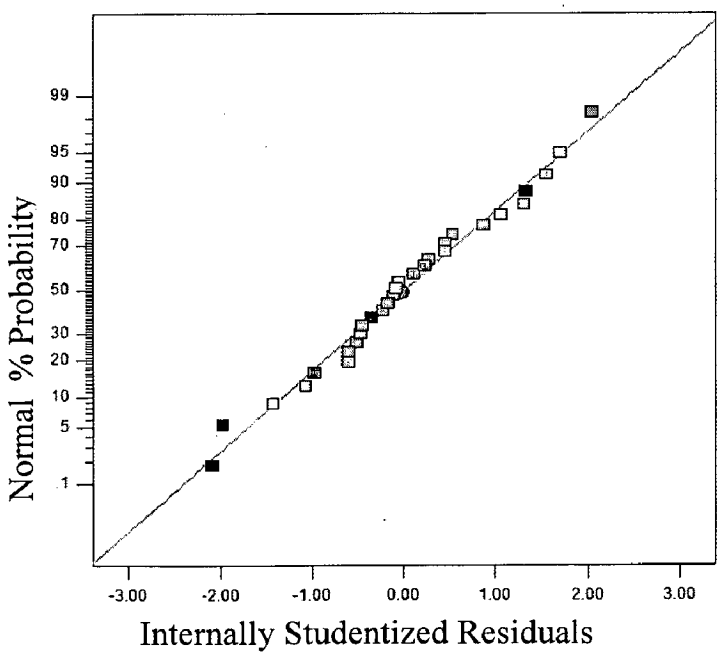

Figure 4.4 Normal plot of residuals for selectivity

4.1.2.3 Residuals vs Predicted

Figure 4.5 and 4.6 show is a plot of the residuals versus the ascending predicted response values. It tests the assumption of constant variance. The plot should be a random scatter (constant range of residuals across the graph.) Expanding variance ("megaphone pattern <") in this plot indicates the need for a transformation. We can see that in Figure 4.5, the plot is a random scatter. In Figure 4.6, the plot shows expanding variance, we require power transformation.

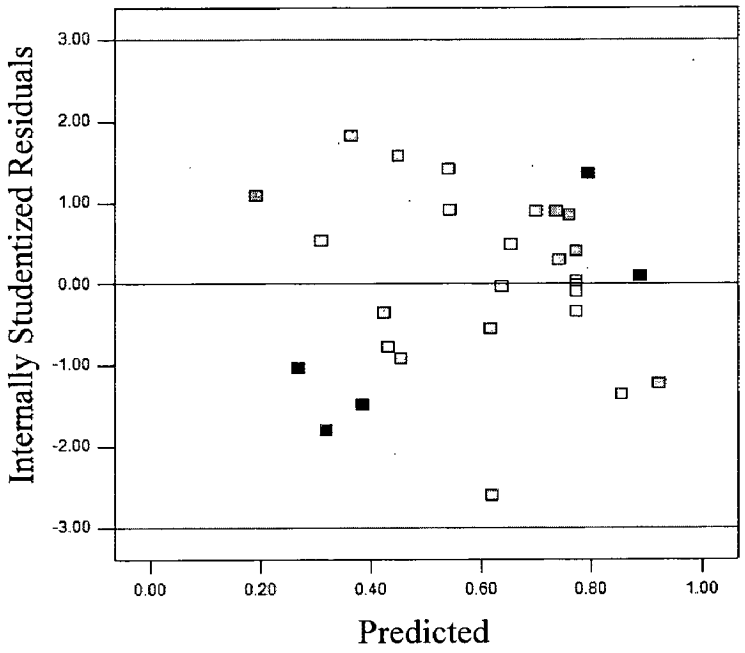

Figure 4.5 Residuals vs predicted for yield

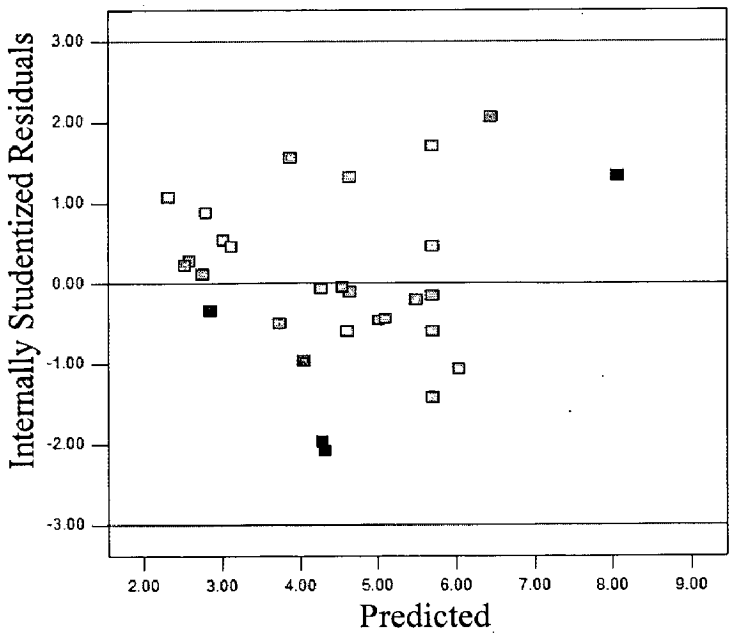

Figure 4.6 Residuals vs predicted for selectivity

4.1.2.4. Residuals vs Factors

It checks whether the variance not accounted for by the model is different for different levels of a factor. If all is okay, the plot should exhibit a random scatter. Pronounced curvature may indicate a systematic contribution of the independent factor that is not accounted for by the model.

In Figure 4.7 and 4.8, it can be observed that the points are scattered in all plots. Thus there are no specific correlation between the residuals and the factors. Thus, the model is flawless in this regard.

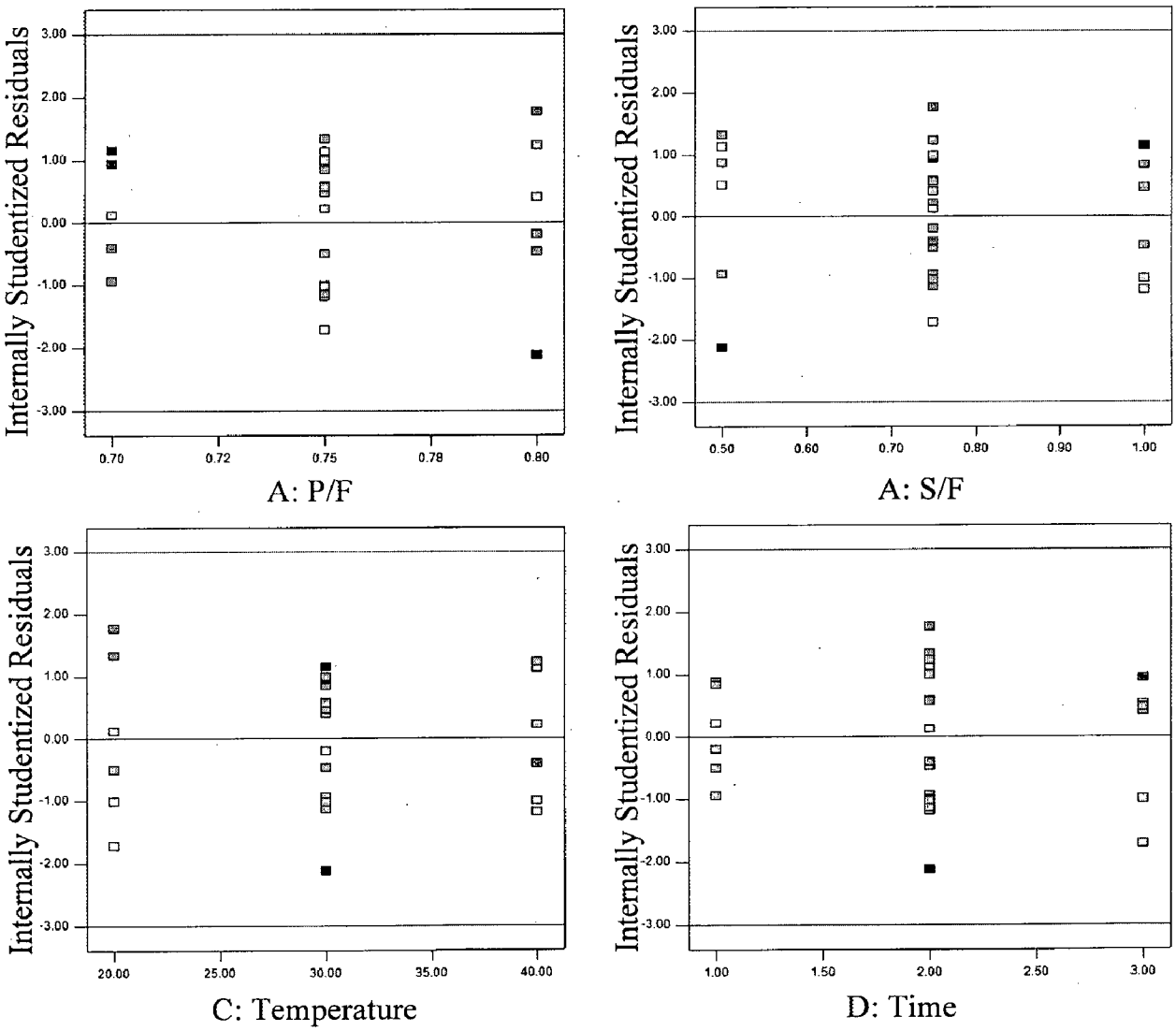

Figure 4.7 Plots between residuals in naphthalene yield and various factors

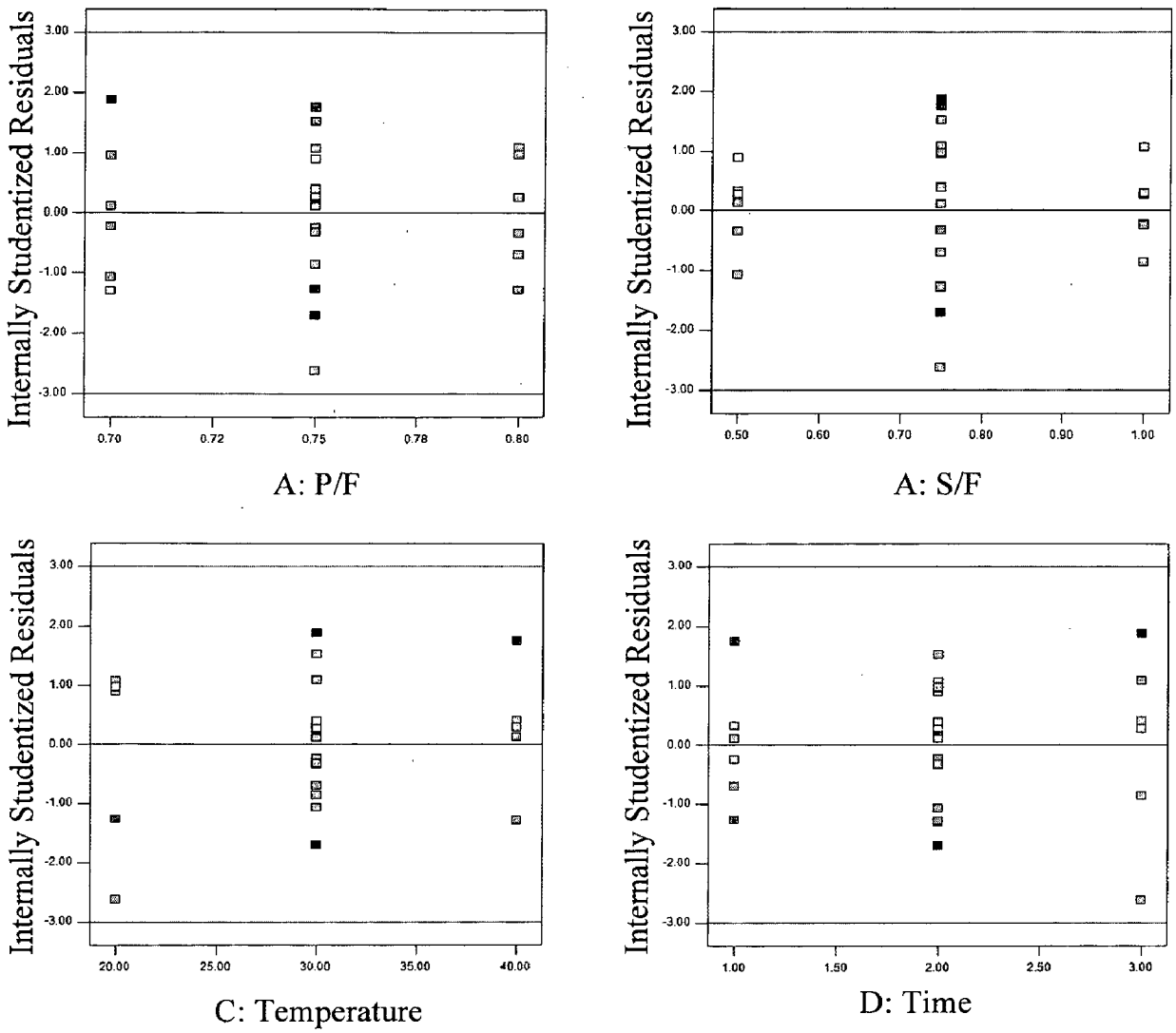

Figure 4.8 Plots between residuals in naphthalene selectivity and various factors

4.1.2.5. Box-Cox plots for power transforms

This plot provides a guideline for selecting the correct power law transformation. Most data transformation can be described by the power function:

$$\sigma = fn(\mu^{\alpha}), \qquad 4.7$$

where σ is standard deviation, μ is the mean, α is the power transform. λ (*Lambda*) is 1- α in all cases. The lowest point on the Box-Cox plot represents the value of lambda (λ) that results in the minimum residual sum of squares in the transformed model. The potential for improvement is greatest when the range of the maximum to minimum response value is greater than 3.

A recommended transformation is listed, based on the best lambda value, which is found at the minimum point of the curve generated by the natural log of the sum of squares of the residuals. If the 95% confidence interval around this lambda includes 1 then the software does not recommend a specific transformation. This plot is not displayed when either the logit or the arcsine square root transformation has been applied.

From Figure 4.9, we can see that the current transformation (indicated in blue line) lies in the appropriate region (i.e. region b/w 2 red lines). Thus the current transformation is right and no changes need to be effected on the model.

In Figure 4.10, λ=1 lies beyond the region b/w 2 red lines. Also does the software suggests square root transform ($\lambda = 0.5$) for the selectivity.

Recommended Transform: None

Lambda = 1

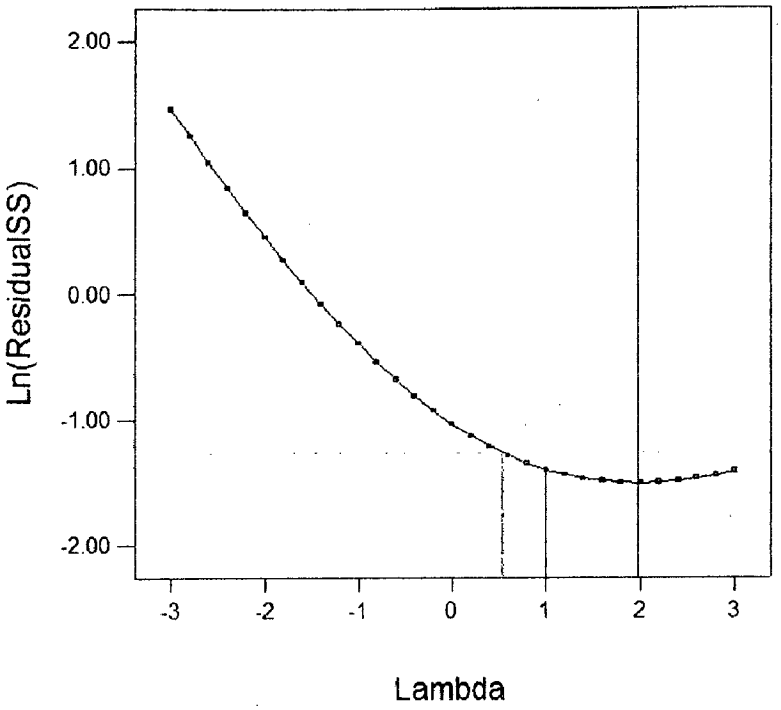

Figure 4.9 Box-Cox plot for yield of naphthalene

Recommended Transform: Square root

Lambda = 0.5

Lambda
Current = 0.5
Best = 0.46
Low C.I. = -0.01
High C.I. = 0.96

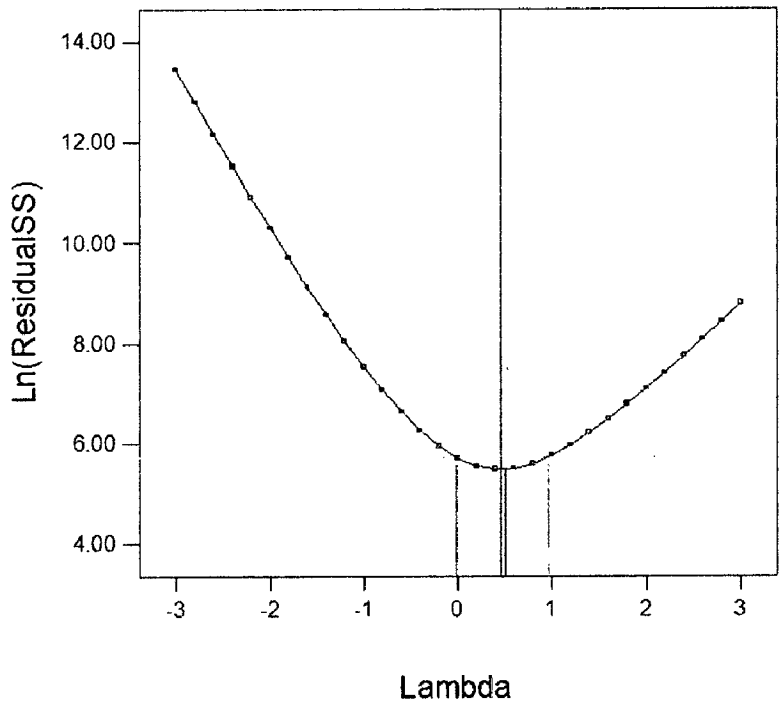

Figure 4.10 Box-Cox plot for selectivity of naphthalene

4.1.3 Effect of paraffin in feed (P/F) and solvent to feed ratio (S/F) on naphthalene yield

The effect of solvent to feed ratio on the extraction of aromatics is of prime importance, since it is this parameter that determines the capacity of an extraction unit (Treybal, 1968). Solvent extraction processes are energy controlled because large volumes of solvents are distilled and recirculated for each volume of feed. Increased costs of energy have directed refiners to re-examine their fuel consumption features, especially the solvent to feed ratio, in order to make the extraction process more economically effective (Gary and Handwerk, 1984). It is clear from the Figure 4.11, that on increasing S/F ratio from 0.5 to 1, there is an increase in naphthalene yield. An increase in amount of solvent increases the capacity to dissolve naphthalene from the model oil which in turn increases the naphthalene yield. This is observed for all P/F.

It can also be seen that, there is a general trend of reduction in the valve of yield with increment in paraffin content. The decreasing trend can be attributed to the fact that with an increase in paraffinic content, the total amount of alkane increase, and thus, more naphthalene tends to remain in aliphatic phase rather than getting transferred to solvent (furfural) phase. It can also be stated from the figure that the effect of P/F and S/F is comparable. Lower P/F and higher S/F give maximum yield of naphthalene.

4.1.4 Effect of temperature and time on naphthalene yield

As seen in the Figure 4.12, increasing extraction temperature from 20°C to 40°C, generally decreased the recovery of naphthalene form the samples. The effect of time at higher temperature (40°C) is negligible, whereas at lower temperature (20°C), there is a pronounced increment in the yield of naphthalene.

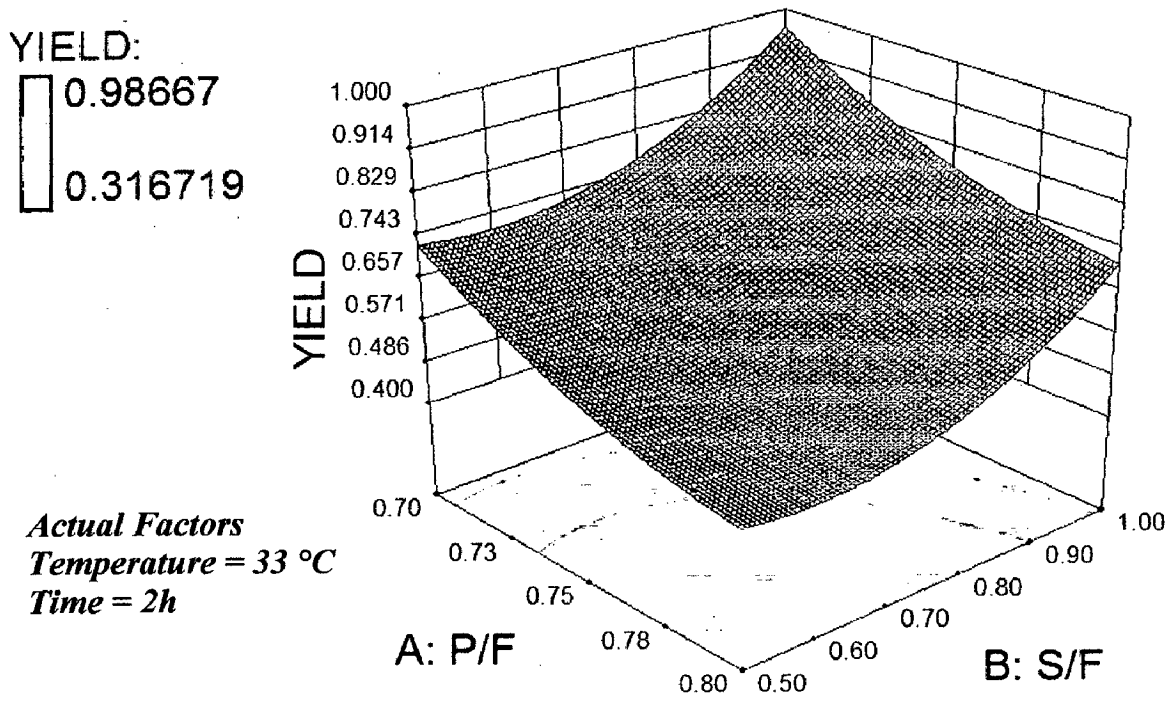

Figure 4.11Response surface graph showing effect of P/F and S/F on yield

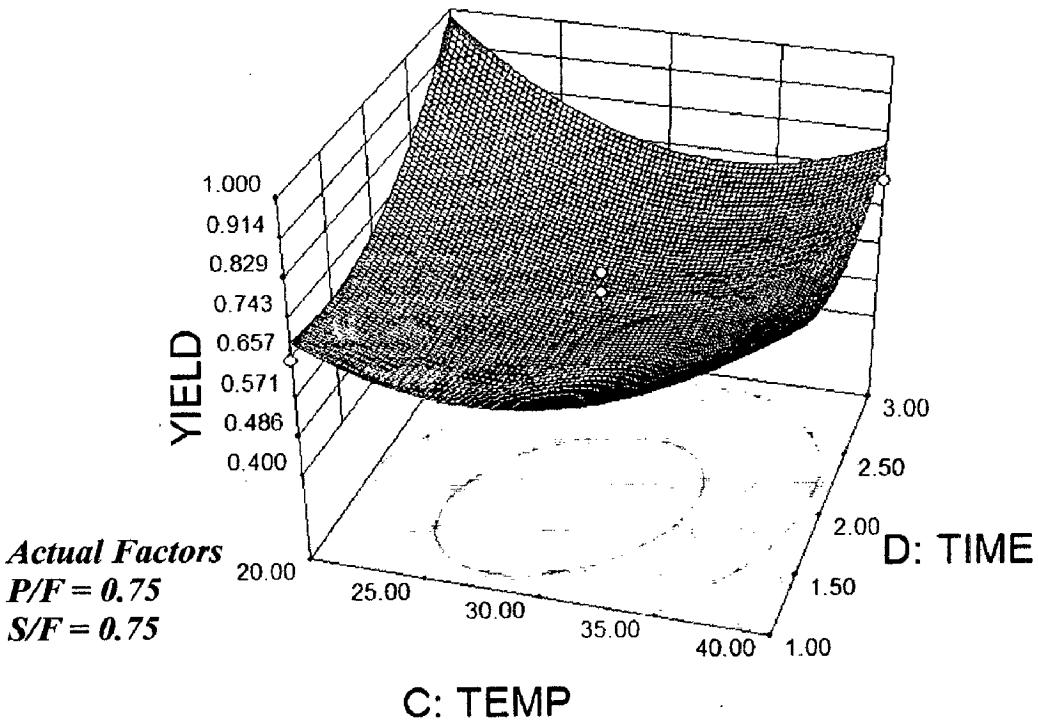

Figure 4.12 Response surface graphs showing effect of temperature and time on yield

4.1.5 Effect of paraffin in feed (P/F) and solvent to feed ratio (S/F) on naphthalene selectivity

The results illustrated in Figure 4.13 show the influence of solvent to feed ratio and paraffinic in feed on the selectivity of naphthalene. From this plot, it can be observed that with increase in paraffin content, selectivity decreases. It can also be observed that with P/F is higher (0.8), there is no appreciable change in selectivity with an increase in solvent to feed ratio. Thus, with addition of solvent, the total naphthalene dissolved increases but at the same time alkane dissolved increases proportionally at these conditions.

4.1.6 Effect of temperature and time on naphthalene selectivity

It is quite noticeable from the Figure 4.16, that contrary to yield, increase in temperature cause increase in selectivity of naphthalene. Which means that, at lower temperature (20 °C), more naphthalene dissolves in solvent, but the tendency of iso-octane (paraffin) to dissolve in solvent is even greater.

With increment in time, selectivity increases. At higher value of time, there is negligible change in selectivity with variation in temperature. Similarly, at higher values of temperature, there is slow variation in selectivity. This can be subjected to the slow mass transfer at lower temperature which requires more time to attain equilibrium as compared to that at higher temperatures where mass transfer due to diffusion is expected to be higher.

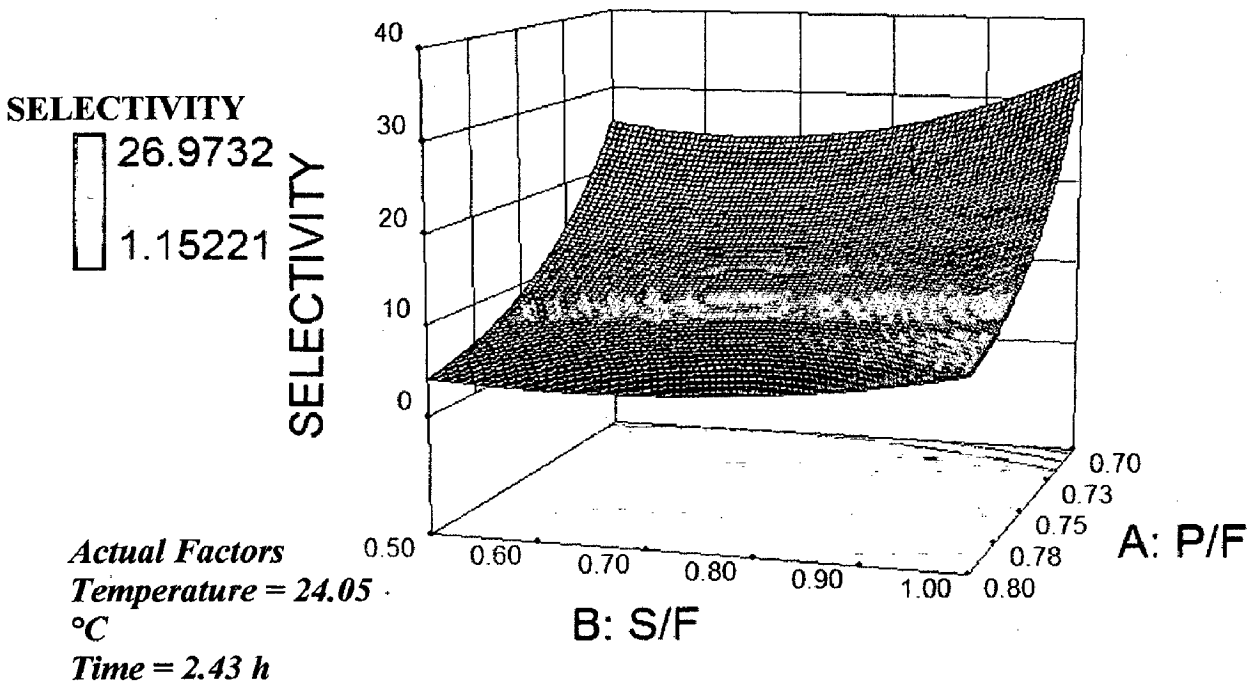

Figure 4.13 Response surface graph showing effect of P/F and S/F on naphthalene selectivity

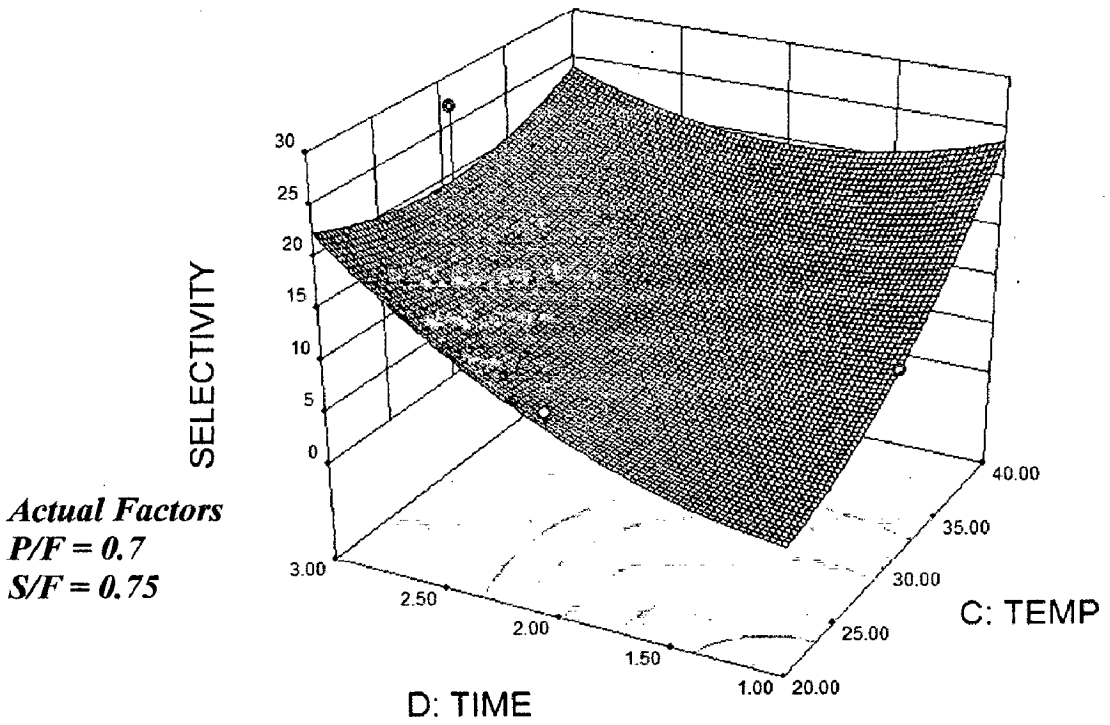

Figure 4.14 Response surface graph showing effect of temperature and time on naphthalene selectivity

4.2 Extraction using NMP (1-methyl-2-pyrrolidinone) as solvent

Yield and selectivity of naphthalene at various experimental conditions have been recorded in Table 4.4. No aliases were found using quadratic model. Insignificant terms (as suggested by ANOVA) were removed through a standard modification algorithm namely stepwise.

4.2.1. Modeling of Data and Statistical Analysis

Quadratic model was found to be the best model which could model the yield of naphthalene. Cubic and higher models were aliased. ANOVA and the various statistical tests for this model for yield of naphthalene has been indicated in Table 4.5. The model gives coefficient of determination (R^2) value of 0.8065 and adjusted R^2 value of 0.6130.

The final equation obtained in coded factors is given below.

$$\text{Yield} = 0.77 - 0.035\,A + 0.25\,B - 0.03\,C + 0.025\,D + 0.018\,AB - 0.044\,AC - 0.015\,AD + 0.078\,BC - 0.034\,BD - 0.069\,CD - 0.063\,A^2 - 0.088\,B^2 - 0.076\,C^2 - 0.018D^2 \qquad 4.1$$

For the selectivity of naphthalene modified/reduced quadratic model was found to be the best model. An empirical relationship expressed by modified quadratic equation was fitted between the response and input variables. ANOVA and the various statistical tests for this model for selectivity of naphthalene has been indicated in Table 4.6. The model gives coefficient of determination (R^2) value of 0.4989 and adjusted R^2 value of 0.2984.

The final equation obtained in coded factors is given below.

$$\text{Selectivity} = 5.71 + 0.27\,A + 0.88\,B - 0.65\,C - 0.13\,D - 0.63\,AC - 0.83\,BC - 0.81\,A^2 - 2.17\,D^2 \qquad 4.1$$

Table 4.4 Yield and selectivity of naphthalene from model oil with NMP

Run	Paraffin in Feed (P/F)	Solvent to feed (S/F)	Temperature (°C) (T)	Time (h) (t)	Naphthalene	
					Yield (Y)	Selectivity (β)
1	0.7	0.5	30	4	0.393759	3.034398
2	0.7	0.75	20	4	0.635523	4.519677
3	0.7	0.75	30	1	0.249705	2.97299
4	0.7	0.75	30	7	0.818148	3.777234
5	0.7	0.75	40	4	0.780648	3.92367
6	0.7	1	30	4	0.897599	5.197516
7	0.75	0.5	20	4	0.593799	6.172909
8	0.75	0.5	30	1	0.291895	4.036452
9	0.75	0.5	30	7	0.360507	2.865563
10	0.75	0.5	40	4	0.174471	4.487502
11	0.75	0.75	20	1	0.361908	1.386285
12	0.75	0.75	20	7	0.382408	2.69148
13	0.75	0.75	30	4	0.823923	3.480281
14	0.75	0.75	30	4	0.729876	4.781939
15	0.75	0.75	30	4	0.771985	5.450382
16	0.75	0.75	30	4	0.761674	6.425565
17	0.75	0.75	30	4	0.778113	8.391689
18	0.75	0.75	40	1	0.62678	3.787278
19	0.75	0.75	40	7	0.371827	2.920413
20	0.75	1	20	4	0.919612	9.606754
21	0.75	1	30	1	0.837494	4.493232
22	0.75	1	30	7	0.769173	4.183193
23	0.75	1	40	4	0.811089	4.593113
24	0.8	0.5	30	4	0.155868	1.507986
25	0.8	0.75	20	4	0.700818	8.800491
26	0.8	0.75	30	1	0.567067	3.752914
27	0.8	0.75	30	7	0.53098	2.397849
28	0.8	0.75	40	4	0.66998	5.675183
29	0.8	1	30	4	0.731216	4.537309

Table 4.5 ANOVA for yield of naphthalene (using NMP as solvent)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1.1668	14	0.083343	4.168062	0.0058	significant
A-P/F	0.014662	1	0.014662	0.733249	0.4063	
B-S/F	0.747943	1	0.747943	37.4054	< 0.0001	
C-TEMP	0.002114	1	0.002114	0.105722	0.7499	
D-TIME	0.00741	1	0.00741	0.370576	0.5524	
AB	0.001278	1	0.001278	0.063932	0.8041	
AC	0.007741	1	0.007741	0.387123	0.5438	
AD	0.091364	1	0.091364	4.569212	0.0507	
BC	0.02415	1	0.02415	1.207761	0.2903	
BD	0.004688	1	0.004688	0.234434	0.6357	
CD	0.018969	1	0.018969	0.948639	0.3466	
A^2	0.025871	1	0.025871	1.293851	0.2744	
B^2	0.049672	1	0.049672	2.484126	0.1373	
C^2	0.037427	1	0.037427	1.871765	0.1928	
D^2	0.21861	1	0.21861	10.9329	0.0052	
Residual	0.279938	14	0.019996			
Lack of Fit	0.27533	10	0.027533	23.89952	0.0039	significant
Pure Error	0.004608	4	0.001152			
Cor Total	1.446739	28				

Table 4.6 ANOVA for selectivity of naphthalene (using NMP as solvent)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	54.0418	8	6.755225	2.488636	0.0469	significant
A-P/F	0.878177	1	0.878177	0.323522	0.5758	
B-S/F	9.198544	1	9.198544	3.388758	0.0805	
C-TEMP	5.057574	1	5.057574	1.863219	0.1874	
D-TIME	0.211582	1	0.211582	0.077947	0.7830	
AC	1.599341	1	1.599341	0.5892	0.4517	
BC	2.769285	1	2.769285	1.020209	0.3245	
A^2	4.576074	1	4.576074	1.685833	0.2089	
D^2	32.44964	1	32.44964	11.9545	0.0025	
Residual	54.28858	20	2.714429			
Lack of Fit	40.68482	16	2.542801	0.747677	0.7011	not significant
Pure Error	13.60375	4	3.400938			
Cor Total	108.3304	28				

4.2.2 Model diagnostic plots:

4.2.2.1 Predicted vs Actual plot

Figure 4.15 and 4.16 show actual response values (yield and selectivity) versus the predicted response values. The data points in both the plots are evenly spread by the 45 degree line.

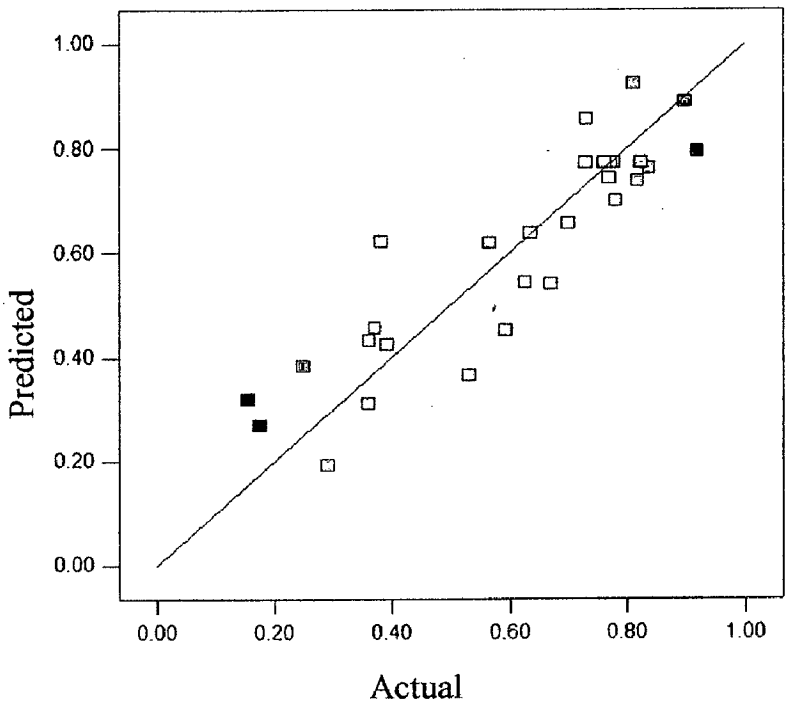

Figure 4.16 Predicted vs actual response for naphthalene yield

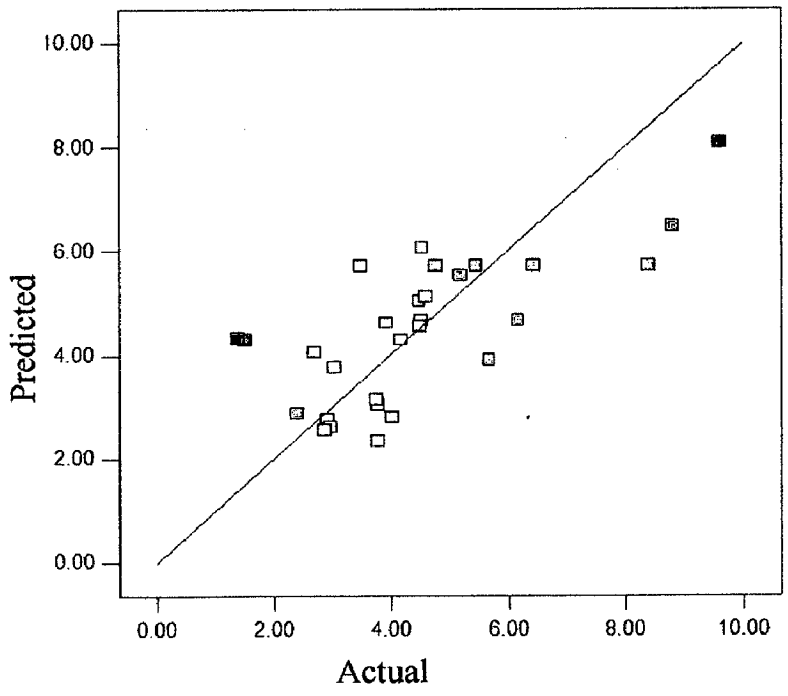

Figure 4.15 Predicted vs actual response for naphthalene selectivity

4.2.2.2 Normal Probability

The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. We can expect some scatter even with normal data. Figure 4.17 and 4.18 give normal probability plots for naphthalene yield and selectivity distributed along straight line.

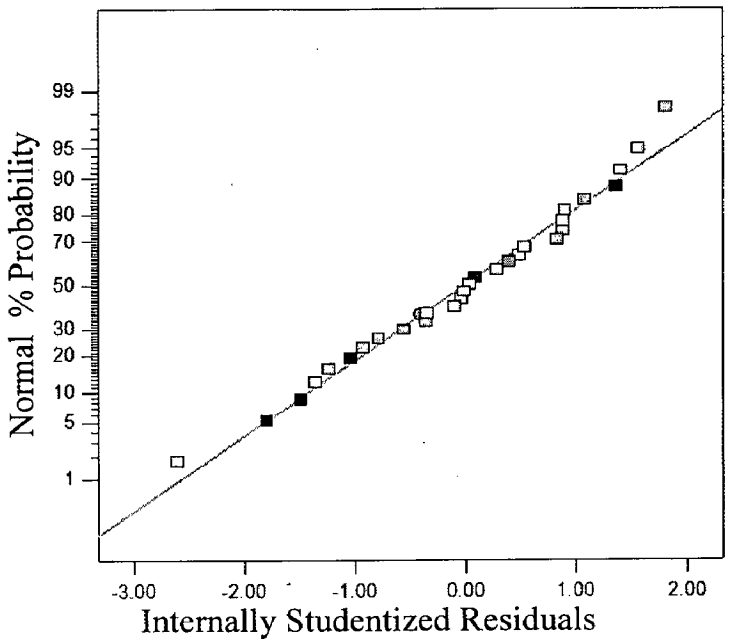

Figure 4.17 Normal plot of residuals for yield

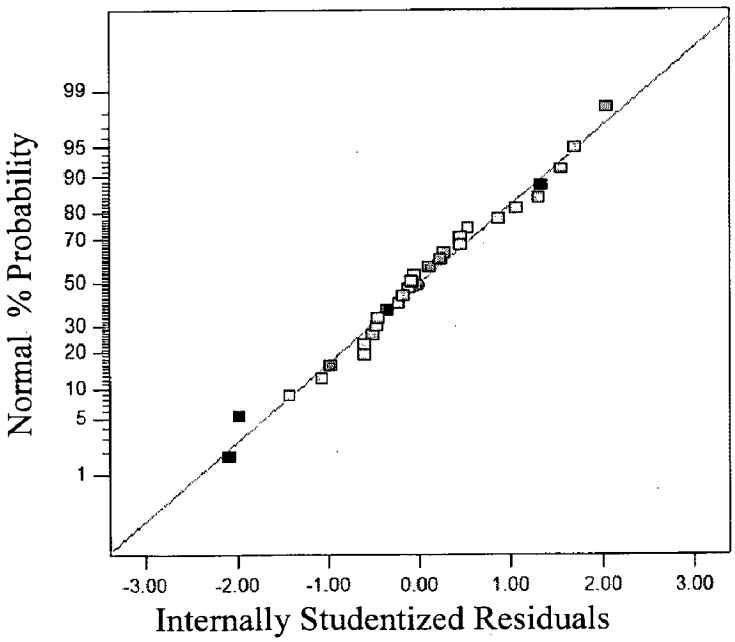

Figure 4.18 Normal plot of residuals for selectivity

4.2.2.3 Residuals vs Predicted

Figure 4.19 and 4.20 show is a plot of the residuals versus the ascending predicted response values. We can see that in both the figures, the plot is a random scatter. Hence, no transformation is required.

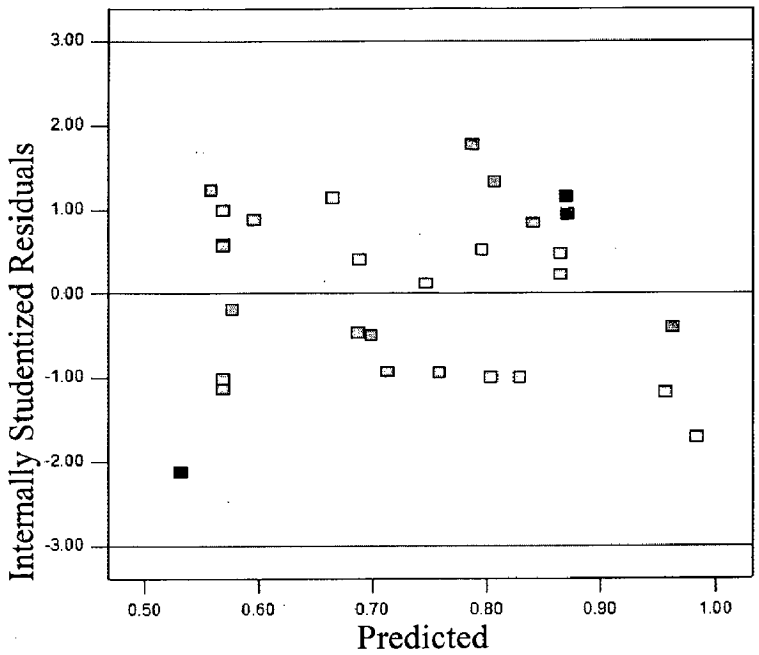

Figure 4.19 Residuals vs predicted for yield

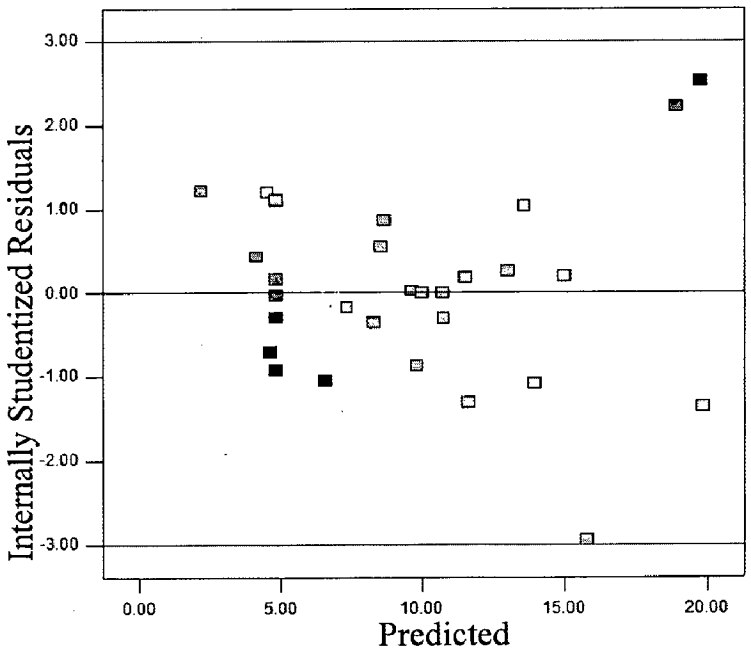

Figure 4.20 Residuals vs predicted for selectivity

4.1.2.4. Residuals vs Factors

It checks whether the variance not accounted for by the model is different for different levels of a factor. If all is okay, the plot should exhibit a random scatter. Pronounced curvature may indicate a systematic contribution of the independent factor that is not accounted for by the model.

In Figures 4.21 and 4.22, it can be observed that the points are scattered in all plots. Thus there are no specific correlation between the residuals and the factors. Thus, the model is flawless in this regard.

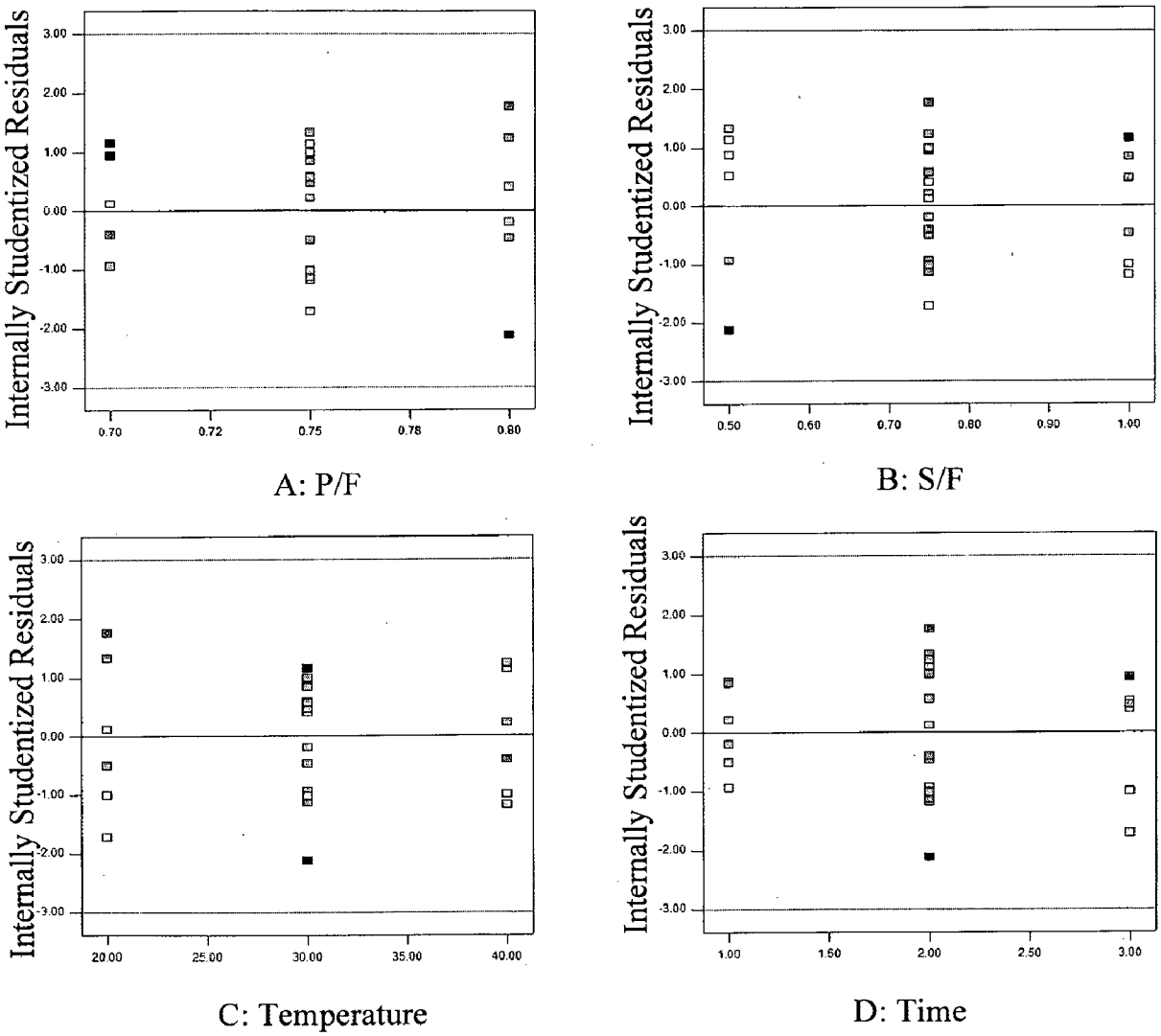

Figure 4.21Residuals in yield vs various factors

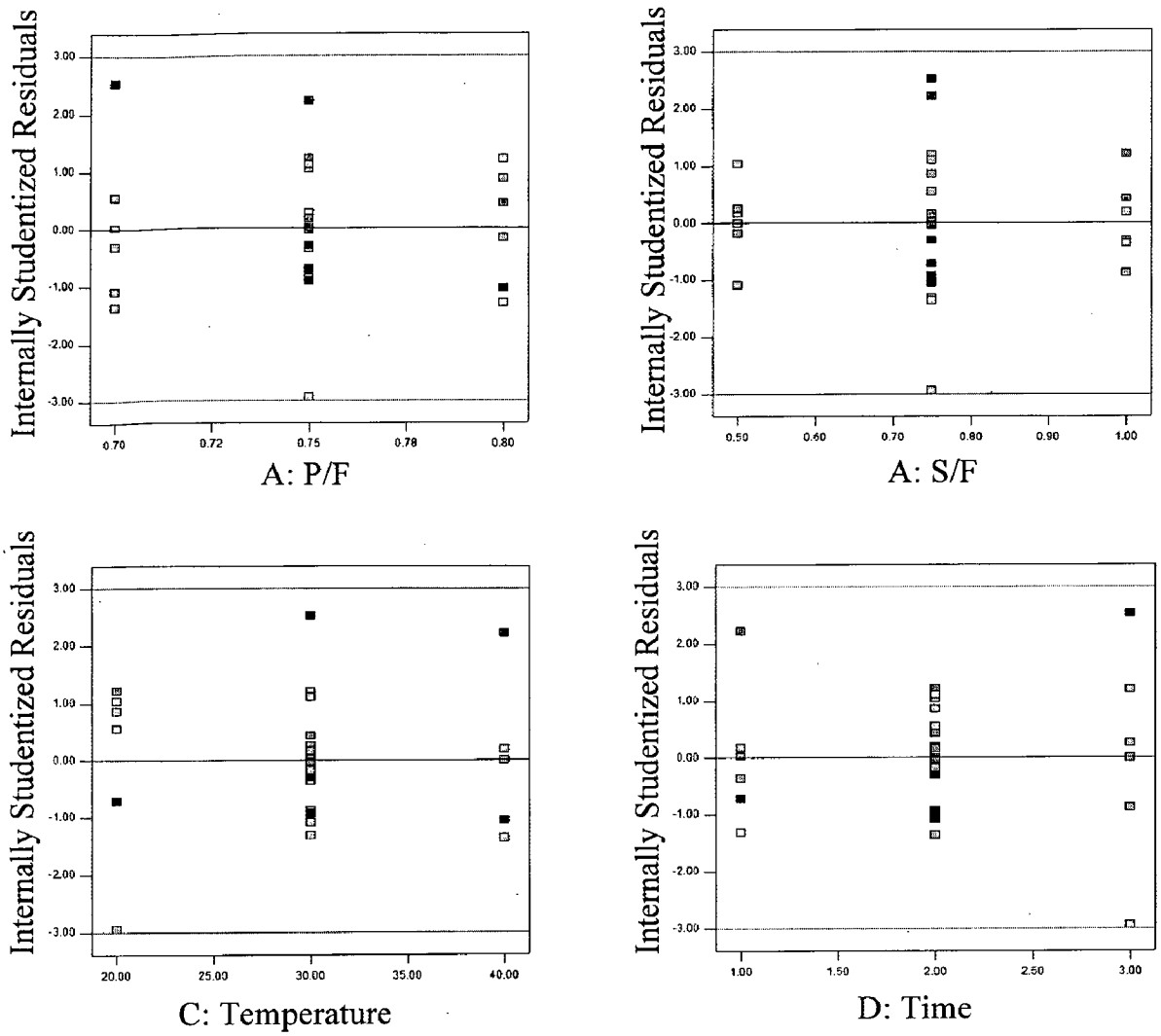

Figure 4.22 Residuals in selectivity vs various factors

4.1.2.5. Box-Cox plots for power transforms

From Figures 4.23 and 4.24, we can see that the current transformation (indicated in blue line) lies in the appropriate region (i.e. region b/w 2 red lines). Thus the current transformation is right and no changes need to be effected on the model.

Recommended
Transform: None

Lambda = 1

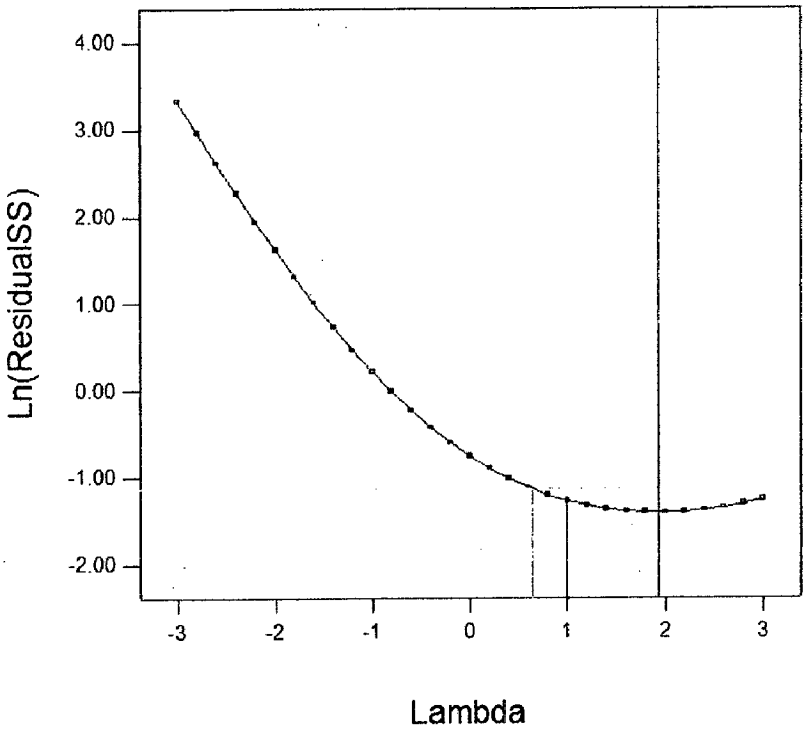

Figure 4.23 Box-Cox plot for yield of naphthalene

Recommended
Transform: None

Lambda = 1

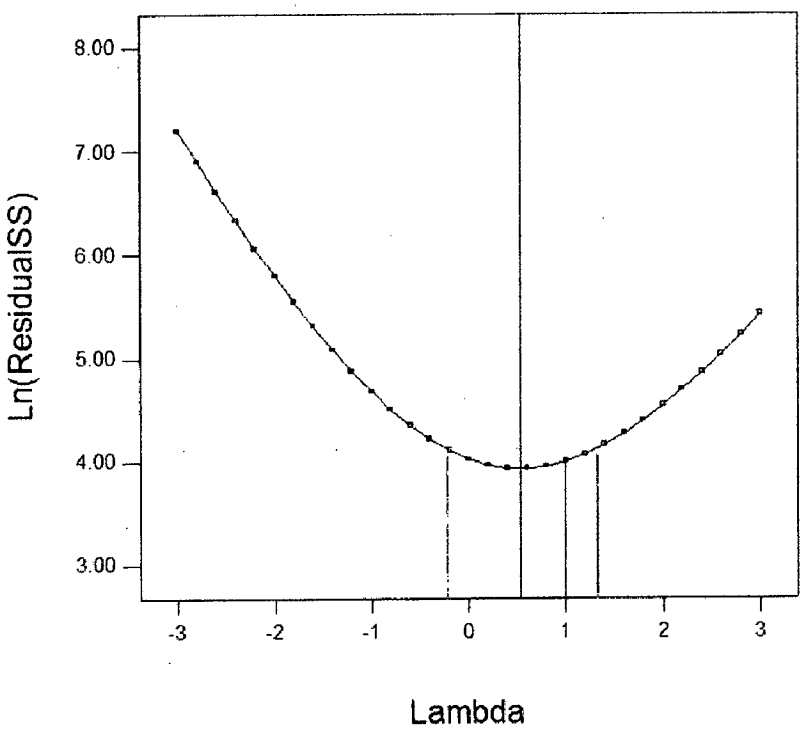

Figure 4.24 Box-Cox plot for selectivity of naphthalene

4.2.3 Effect of paraffin in feed (P/F) and solvent to feed ratio (S/F) on naphthalene yield

The trend observed for the effect of P/F and S/F on yield is shown in Figure 4.25. It can be observed that with increase in S/F ratio, the yield of naphthalene in extract phase increases. This trend may be subjected to the same reason as mentioned for furfural as solvent (section 4.1.3). Contrary to trend observed for furfural, there is a gradual increase in naphthalene yield with increase in the value of P/F. Greater P/F means less amount of p-xylene is present in feed. This implies more leverage for naphthalene to dissolve in NMP.

4.2.4 Effect of temperature and time on naphthalene yield

Figure 4.26 illustrates the effect of temperature (20 – 40 °C) and time (1 – 7 h) on the yield of naphthalene. It is observed that at 20°C, yield increases appreciably with time close to 5 hours, and then remains almost constant. At higher values of temperature, there is slow variation in selectivity. This can be subjected to the slow mass transfer at lower temperature which requires more time to attain equilibrium as compared to that at higher temperatures where mass transfer due to diffusion is expected to be higher. Temperature does not show appreciable change in the value of selectivity.

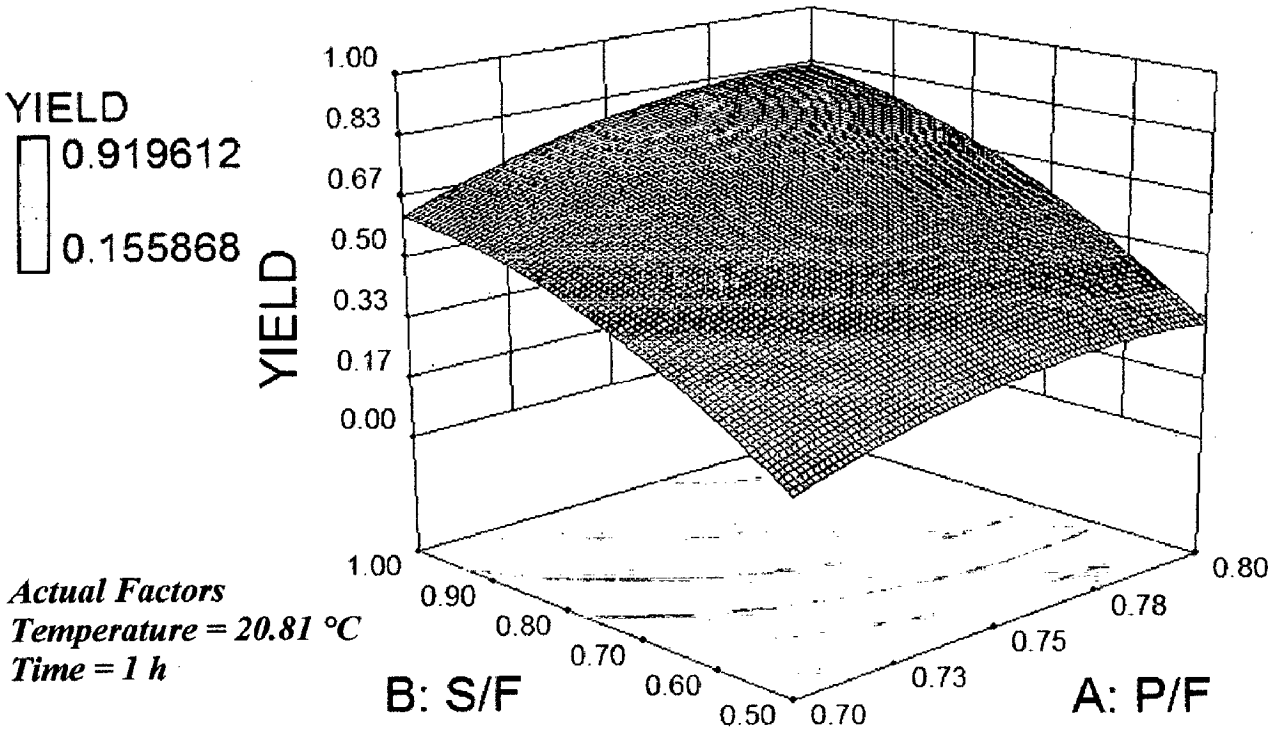

Figure 4.25 Response surface graph showing effect of P/F and S/F on yield

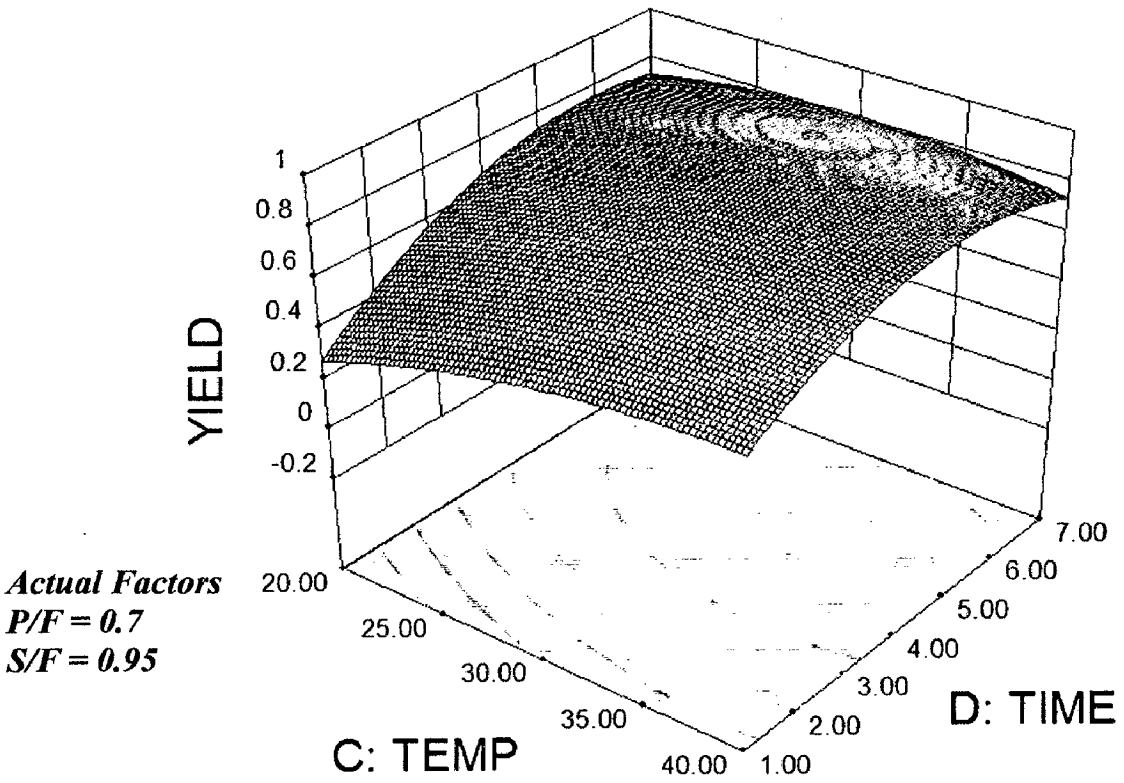

Figure 4.26 Response surface graph showing effect of temperature and time of yield

4.2.5 Effect of initial paraffin content (P/F) and solvent to feed ratio (S/F) on naphthalene selectivity

Figure 4.27 illustrates the effect of P/F and S/F on selectivity of naphthalene. With increase in the value of P/F from 0.7 to 0.75, there is significant increase naphthalene selectivity, after which it becomes constant. It can also be observed that with increase in the value of S/F, there is a steady increment in selectivity.

4.2.6 Effect of temperature and time on naphthalene selectivity

It can be observed from Figure 4.28 that with increase in temperature, selectivity of naphthalene decreases, contrary to yield. At high temperatures, although more amount of naphthalene gets dissolves in NMP, but even greater amount of iso-octane dissolves in NMP. It is quite an interesting result that with increase in time, selectivity of naphthalene decreases. It may be subjected to the reason that, although the naphthalene yield remains constant after a certain period of time, iso-octane keeps on dissolving with solvent, hence decreasing the selectivity of naphthalene.

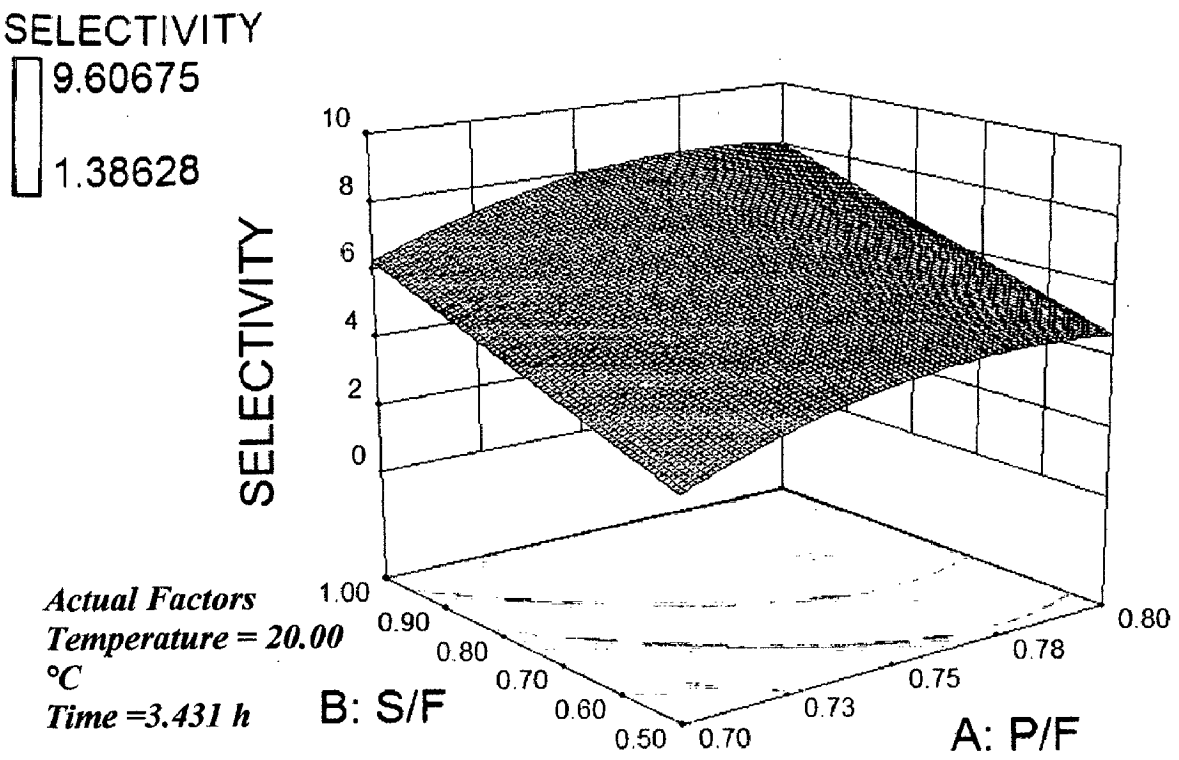

Figure 4.27 Response surface graph showing effect of P/F and S/F on selectivity

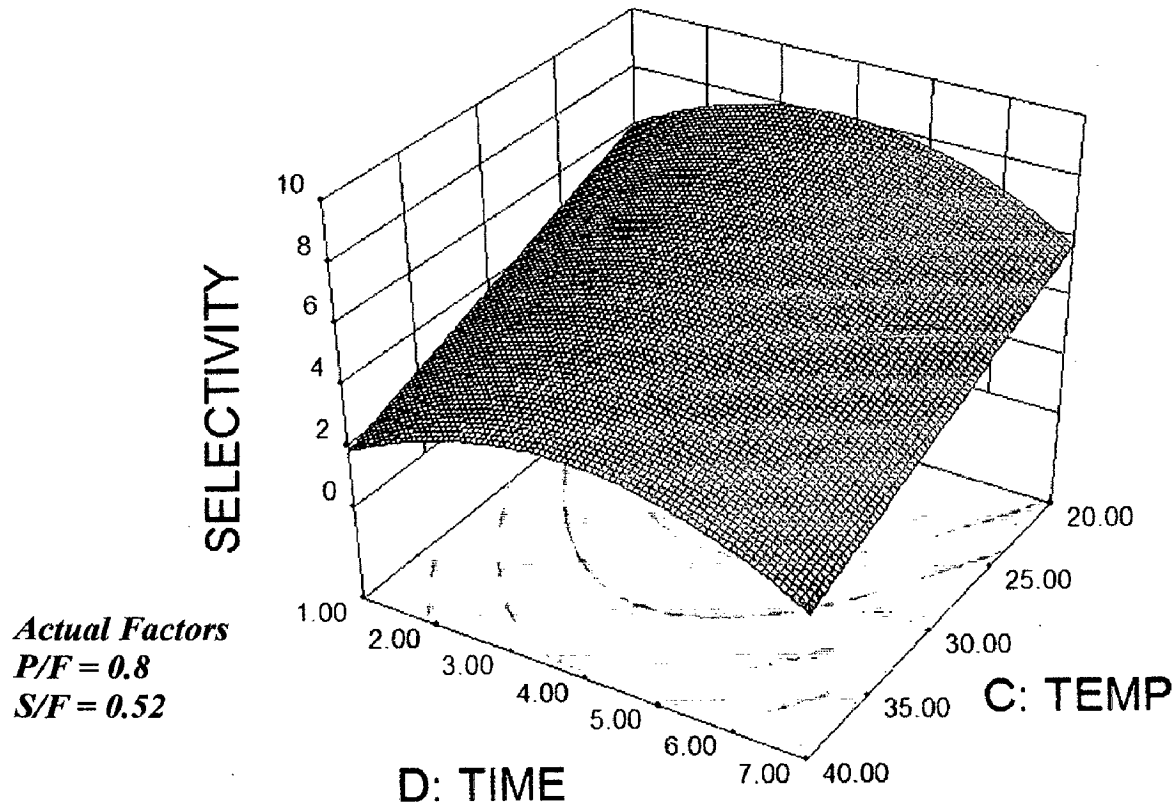

Figure 4.28 Response surface graph showing effect of temperature and time on selectivity

4.3 Selection of optimal levels and estimation of optimum response characteristics

The aim of this work is to extract maximum of naphthalene with lowest possible amount of solvent. Table 4.7 summarizes the optimal level of various parameters obtained after examining the response curves for furfural and NMP as solvents. Three confirmation experiments were conducted at selected optimal levels of the process parameters for both the system. The average values of the yield and selectivity obtained are compared with the predicted values.

Table 4.7 Optimum and confirmation values of process parameters for maximum naphthalene extraction

Optimal levels of process parameters	Predicted optimal value with 95% confidence intervals		Average of confirmation experiments	
	Yield	Selectivity	Yield	Selectivity
Furfural P/F = 0.7 S/F = 0.5 Temp = 24.41°C Time = 2.98	0.733<0.987<1.240	15.85<28.6<45.05	0.863	19.57
NMP P/F = 0.76 S/F = 0.76 Temp = 21.93°C Time = 4.07	0.603<0.738<0.872	5.09<6.44<7.79	0.694	5.35

It may be noted that that these optimal values are valid within the specified range of process parameters. Any extrapolation/ interpolation should be confirmed through additional experiments.

It was observed that the results of confirmation model lies within 95% confidence interval. Hence, the model correctly predicted the effect of various operating parameters on the responses.

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5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

On the basis of present investigation, following conclusions are drawn:

(1) The process of aromatic extraction from model oil similar to LCO was studied using two solvents – furfural and NMP (1-methyl-2-pyrrolidinone). Furfural was found to be a better solvent, giving higher yield and selectivity in relatively less time.

(2) The effect of solvent to feed (S/F), paraffin content (P/F), time and temperature on the process of liquid-liquid extraction was evaluated.

(3) For both the solvents, with increase in S/F, extraction (yield and selectivity) of naphthalene increased.

(4) Paraffin content (P/F) had different effects on both the solvents. Whereas, increase in P/F decreased the yield and selectivity in case of furfural, it enhanced the extraction in case of NMP.

(5) Temperature had different effect on different system.

   i) Furfural as solvent: yield increased with reducing temperature but at the cost of selectivity.

   ii) NMP as solvent: yield increased and selectivity decreased with increase in temperature.

(6) In case of NMP, with increase in time up to 5 h, yield and selectivity increased significantly after which they remained almost constant. For furfural, there was observed increase in extraction with increase in time, which suggests improved extraction at even more time.

(7) Response surface methodology by the Box–Behnken model was used to examine the role of four process factors on naphthalene extraction. It was shown that a quadratic or modified quadratic model could properly interpret the experimental data.

(8) The confirmation experiments were carried out at optimum conditions and results were found to be within the confidence interval of predicted responses.

(9) This study shows that the Box–Behnken model is suitable to optimize the experiments extraction of naphthalene from iso-octane, p-xylene, naphthalene and furfural/NMP containing system.

5.2 Recommendations

(1) Studies are required for evaluating mass transfer coefficients during aromatic extraction

(2) The process of recovery of solvent after extraction needs more studies.

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