MAJOR PROJECT

RECOVERY OF VALUABLE OLEFINS FROM "COKER KERO STREAM" USING UREA ADDUCTION PROCESS

A Major Project Report submitted in partial fulfillment for the award of the degree of

MASTER OF TECHNOLOGY (M. Tech.)

In

POLYMER TECHNOLOGY

Submitted by

VIVEK CHAMOLI
[2K12/PTE/18]

Under the supervision of
Dr. Ram Singh
Department of Applied Chemistry and Polymer Technology
Delhi Technological University, Delhi-110042
&

Dr. G.S. Kapur
Deputy General Manager (DGM)
Petrochemical & Polymer Department
Indian Oil Corporation Ltd., R&D Centre, Faridabad-121007
July 2014

DECLARATION

I, **Vivek Chamoli**, hereby certify that the work which is being submitted in this major project report entitled "***Recovery of Valuable Olefins from "Coker Kero Stream" Using Urea Adduction Process"*** in the partial fulfillment for the award of the degree of Master of Technology (Polymer Technology) at **Delhi Technological University** is an authentic record of my own work carried out by me under the supervision of **Dr. Ram Singh** (Assistant Professor, Department of Applied Chemistry and Polymer Technology, DTU) and **Dr. G. S Kapur** (DGM, Petrochemical and Polymer Department, IOCL-R&D).

I, further declare that the project report has not been submitted to any other Institute/University for the award of any degree or diploma or any other purpose whatsoever. Also it has not been directly copied from any source without giving its proper reference.

Vivek Chamoli
2K12/PTE/18
Master of Technology (Polymer Technology)
Department of Applied Chemistry and Polymer Technology
Delhi Technological University
Delhi, India.

CERTIFICATE

This is to certify that the M.Tech major project entitled **“*Recovery of Valuable Olefins from Coker Kero Stream Using Urea Adduction Process*”**, submitted by **Vivek Chamoli**, Roll number 2K12/PTE/18, for the award of the degree of **“Master of Technology in Polymer Technology”** is a record of bonafide work carried out by him. Vivek Chamoli has worked under our guidance and supervision and has fulfilled the requirements for the submission of the project report.

To the best of our knowledge and belief the content therein is his own original work and has not been submitted to any other university or institute for the award of any degree or diploma.

Dr. G.S. Kapur
Deputy General Manager
Petrochemical & Polymer Department
Indian Oil Corporation Limited
R & D Centre,
Faridabad-121007

Dr. Ram Singh
Assistant Professor
Department of Applied Chemistry &
Polymer Technology
Delhi Technological University
Delhi - 110042

Prof. (Dr.) D. Kumar
Head of Department
Department of Applied Chemistry &
Polymer Technology
Delhi Technological University
Delhi - 110042

ACKNOWLEDGEMENT

To start with, I would like to pay my heartiest thanks to my institutional guide **Dr. Ram Singh** (Assistant Professor, Department of Applied Chemistry & Polymer Technology, Delhi Technological University) for his continuous motivation, healthy scrutiny and his coordination with IOCL authorities without which this feat would not have been possible. I would also like to express my deep gratitude to my external guide **Dr. G.S. Kapur** (Deputy General Manager, Petrochemicals & Polymer Department, IOCL-R&D) for his indispensable supervision & valuable suggestions at each phase of the project.

I am also grateful to **Prof. (Dr.) D. Kumar**, Head of the Department, Department of Applied Chemistry & Polymer Technology, Delhi Technological University, for providing me the constant support to the best heights for this project work.

I would also like to thank the faculty members Prof. G.L.Verma, Prof. A.P. Gupta, Prof. R.C. Sharma, Dr. Archna Rani, Mr. S. G. Warkar, Dr. Richa Srivastava, Dr. D. Santhya, Dr. Anil Kumar, Dr. Roli Purwar, Dr. Raminder Kaur and Dr. Saurabh Mehta, for their support and encouragement throughout the course of this project.

I would extend my thanks to the management of IOCL R&D Centre-Faridabad, for giving me the opportunity to carry out this project work at their prestigious research facility.

I would also like to convey my sincere regards to Dr. Shashikant (General Manager, Petrochemical & Polymer Department, IOCL-R&D) for his kind attention, humbleness & precious time.

At the same time I would like to thank my immediate guides Dr. Gurmeet Singh (Deputy Manager Research, Petrochemicals & Polymer Department, IOCL-R&D) and Dr. Sukhdeep Kaur (Senior Research Officer, Petrochemicals & Polymer Department, IOCL-R&D) for their precious guidance, perseverance & patience throughout the tenure of the project.

I would like to continue by thanking Sh. M.S Negi, Dr. Naresh Kumar, Dr. Bhasker Bantu & Mr. Mohasin Momin for their massive help in making me understand the basic concepts & patiently responding to my incessant doubts.

Vivek Chamoli

Contents

LIST OF FIGURES

.

LIST OF TABLES

.

ABSTRACT

Crude oil is distilled in petroleum refineries to get the useful fraction out of it. The aim of refineries is to get the useful possible product out from the last left drop of crude oil. For this the oil first fed to atmosphere distillation followed by vacuum distillation, the residue from vacuum distillation process is then fed for cracking. One such cracking is called coking as the final residue from it is coke. The kerosene obtain from this coking is called ‘Coker Kero’.

This project is meant to recover linear olefins (C10-C14) out of this coker kero. For this we used urea adduction process. The urea adduction process is a well known clatheration phenomenon of tunnel like structure formation of urea due to their intermolecular hydrogen bonding behavior.

The structure forms a helical in presence of hydrocarbon and captures linear olefins and paraffins due to its dimensional constrain. The branched and substituted hydrocarbon will be washed off by subsequent washing with petroleum ether. The linear olefin obtain from this method can be used in many applications like making surfactant, plasticizer, synthetic lubricant etc and one of such application is to polymerize it to form ultra high molecular weight drag reducing agent used for pipeline transportation of crude/ petroleum product.

OBJECTIVES

Recovery of Valuable Olefins from "Coker Kero Stream" using Urea Adduction Process

To achieve this aim, following **objectives** need to be met

(i) To make urea adduct

(ii) Decompose urea adduct to obtain linear olefins & paraffins

CHAPTER 1

INTRODUCTION

1.1 CRUDE OIL

Petroleum is naturally occurring, yellow to black coloured liquid found beneath the earth surface. A fossil fuel, petroleum is formed when large quantity of dead animal and plant buried underneath the sedimentary rock under intense heat and pressure environment. Thus petroleum contains hydrocarbons of various molecular weights and some light weight organic compound.

Petroleum contains a mixture of a very large number of varied hydrocarbons, the most commonly found molecules are alkanes (paraffins), cycloalkanes (naphthenes), aromatic hydrocarbons, or more complicated chemicals like asphaltenes. Each petroleum variety varies in the mixture of molecules and has a unique mix of it depending upon the environment and method of recovery, which define its chemical and physical properties, like color and viscosity.

The alkanes, also termed as paraffins, are saturated hydrocarbons with straight or branched chains which contain only hydrogen and carbon and have the general formula C_nH_{2n+2}. They generally have from 5 to 40 carbon atoms per molecule, although trace amounts of shorter or longer molecules may be present in the mixture.

The alkanes from pentane (C_5H_{12}) to octane (C_8H_{18}), after refinery processes goes into petrol, the ones from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) into kerosene, diesel fuel and jet fuel. Alkanes with carbon atoms 16 or more can be refined into fuel oil and lubricating oil. At the heavier end of the range, paraffin wax is an alkane with approximately 25 carbon atoms, while asphalt has 35 and above, although these are usually cracked by refineries into more valuable products. The shortest molecules, those with four or fewer carbon atoms, are in a gaseous state at room temperature. They are the petroleum gases also sold as liquefied petroleum gas under high pressure condition (EIA reserve).

The cycloalkanes, also known as naphthenes, are saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula C_nH_{2n}. Cycloalkanes have similar properties to alkanes but have higher boiling points.

The aromatic hydrocarbons are unsaturated hydrocarbons which have one or more six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula C_nH_n They tend to burn with a sooty flame, and many have a sweet aroma. Some are carcinogenic. These different molecules are separated by fractional distillation at an oil refinery to produce petrol, jet fuel, kerosene, and other hydrocarbons. The Table 1.1 below shows the most common distillation fraction of petroleum also called fuel.

Table 1.1: Most common distillation fraction of petroleum [Speight (1999)]

Fractions	**Boiling range (°C)**
Liquefied petroleum gas (LPG)	−40
Butane	−12 to −1
Petrol	−1 to 110
Jet fuel	150 to 205
Kerosene	205 to 260
Fuel oil	205 to 290
Diesel fuel	260 to 315

Since crude oil is drilled out from beneath the earth surface so along with hydrocarbon it may also contain trace amount of metal and sulphur impurities. The metal and sulphur content although vary from formation to formation but the most common range found is coated in Table1.2 below.

Table 1.2: Composition of element in crude oil by weight [Speight (1999)]

Element	Percent range
Carbon	83 to 85%
Hydrogen	10 to 14%
Nitrogen	0.1 to 2%
Oxygen	0.05 to 1.5%
Sulfur	0.05 to 6.0%
Metals	< 0.1%

1.2 COKER KERO

Delayed coking is a thermal cracking process used in petroleum refineries to upgrade and convert petroleum residuum (bottoms from atmospheric and vacuum distillation of crude oil) into liquid and gas product streams leaving behind a solid concentrated carbon material called petroleum coke or simply “coke”. A fired heater with horizontal tubes is used in the process to reach thermal cracking temperatures of 480 to 500°C (Ellis et al, 1998). The cracking process is done in this heater and sending the residue to another drum called coke drum where the cracking process is completed by providing adequate residence time (Figure 1.1). With short residence time in the heater, coking of the feed material is thereby “delayed” until it reaches large coking drums downstream of the heater thus called the delayed coking process. The vapors from the coke drums are sent to the fractionators to be fractionated into gas and liquid product streams, while coke product is removed from the coke drum and sent to coke handling facilities. Products obtained from this coking unit are:

Light Naphtha

Heavy Coker Naphtha

Kerosene

Diesel

Gas Oil

Coke

The kerosene obtain by this process is called coker kerosene or simply “coker kero”.

So, the objective of the coking unit is to convert the bottom of the barrel residue to higher value products as well as processing the entire refinery oil. Thus delayed coking is a thermal cracking process which upgrades the heavy residues into valuable distillate products.

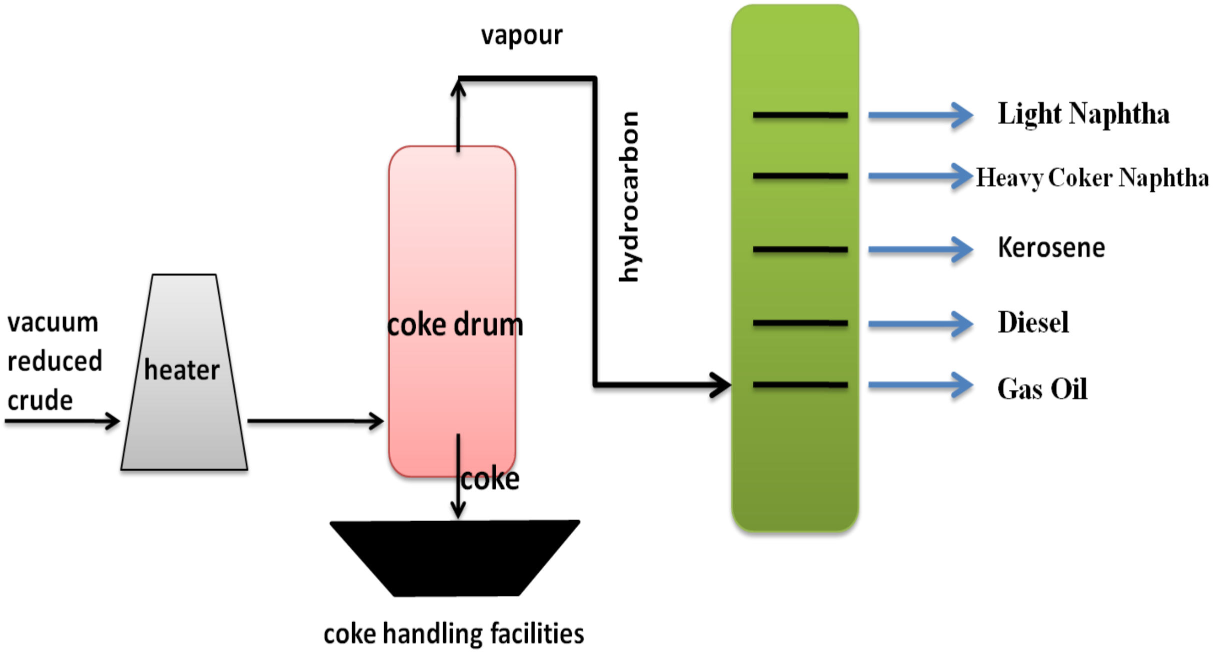


Figure 1.1: Flow diagram showing delayed coking operation

1.2.1 DELAYED COKING UNIT IN REFINING

To understand the delayed coking process, one must understand how the delayed coker is integrated with the rest of the refinery. Delayed coker feed originates from the crude oil supplied to the refinery. Therefore, brief descriptions of each of the processing steps preceding the delayed coking unit are provided below.

1.2.2 CRUDE OIL DESALTING

Crude oil contains around 0.2% water in which is mixed soluble salts such as sodium chloride and other metals which are on the edge of the sphere of water. In desalting, crude oil is washed with around 5% water to remove the salts and dirt from the crude oil. The water, being heavier than the oil, drops out of the bottom, and the cleaned oil flows overhead with around 0.1% water.

1.2.3 ATMOSPHERIC DISTILLATION

The desalted crude oil is heated in a tube furnace to over 380°C , just below the temperature at which cracking of the oil can occur, and then flashed into a distillation column (Ellis et al, 1998). The primary products are straight run gasoline, kerosene, jet fuel, diesel, atmospheric gas oil (AGO) and atmospheric reduced crude.

1.2.4 VACUUM DISTILLATION

The atmospheric reduced crude (ARC) is then heated to around 400°C and flashed into a vacuum distillation column that is operated at low pressures, 10 mm Hg absolute desired but more common 25 to 100 mm Hg absolute (Ellis et al, 1998). The desired aim is to lift the maximum amount of oil boiling below 565°C into heavy vacuum gas oil (HVGO) reducing the production of vacuum reduced crude (VRC) (which is the main feedstock to the delayed coker). The HVGO and the AGO are the principal feedstocks to a fluid catalytic cracking unit (FCCU) for the production of gasoline and diesel. Improving vacuum distillation is one of the best methods for increasing gas oil yield in a refinery while at the same time reducing the amount of vacuum reduced crude (coker feed). This enables higher refinery throughput rates to be achieved. The vacuum reduced crude (VRC) whatsoever left is fed to delayed coking process.

1.2.5 REACTION MECHANISM OF COKER CRACKING

The first step in cracking is the thermal decomposition of hydrocarbon molecules to two free radical fragments. This initiation step can occur by a homolytic carbon-carbon bond scission at any position along the hydrocarbon chain. The following represents the initiation reaction:

$$RCH_2CH_2CH_2R' \rightarrow RCH_2\dot{C}H_2 + R'\dot{C}H_2$$

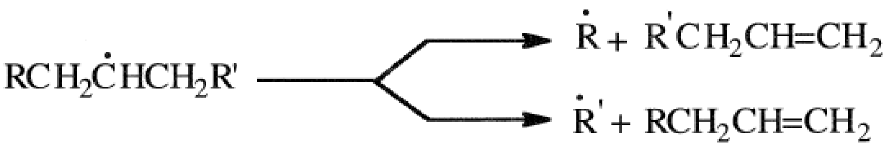
The radicals may further crack, yielding an olefin and a new free radical. Cracking usually occurs at a bond beta to the carbon carrying the unpaired electron (Matar et al, 2000).

$$RCH_2\dot{C}H_2 \rightarrow \dot{R} + CH_2{=}CH_2$$

Further β bond scission of the new free radical $R^{\cdot}$ can continue to produce ethylene until the radical is terminated. Free radicals may also react with a hydrocarbon molecule from the feed by abstracting a hydrogen atom. In this case the attacking radical is terminated, and a new free radical is formed. Abstraction of a hydrogen atom can occur at any position along the chain. However, the rate of hydrogen abstraction is faster from a tertiary position than from a secondary, which is faster than from a primary position.

$$\dot{R} + RCH_2CH_2CH_2R' \rightarrow RCH_2\dot{C}HCH_2R' + RH$$

The secondary free radical can crack on either side of the carbon carrying the unpaired electron according to the beta scission rule, and a terminal olefin is produced.



So the stream obtained after thermal cracking contains many terminal substituted and unsubstituted olefins which need to be removed from the fractions. So that the fraction obtained after cracking become more useful and the olefins recovered from it can be utilize in other wide range of applications. On the other hand the coke residue obtained from coking drum was further process and utilize in other applications. The type of coke also varies depending on its composition which is discussed below.

1.3 TYPES OF COKE

There are three type of coke formed during delayed coking process (Matar et al, 2000).

Shot Coke:

The production of shot coke in a delayed coker requires high concentrations of asphaltenes in the feedstock, dynamics (velocity and/or turbulence) in the coke drum, and high coke drum temperatures.

Sponge Coke:

Sponge coke is named for its sponge-like appearance and is produced from VRC with a low to moderate asphaltene concentration.

Needle Coke:

Needle coke, named for its needle-like structure, is produced from feedstocks without asphaltenes present, normally Fluid catalytic cracking unit decant oils. Needle coke is the premier coke, used in graphite electrode manufacturing.

1.4 UREA ADDUCTION

1.4.1 CLATHERATE

Clatherates are the host guest systems which are also known as inclusion compounds they can be considered as systems in which one species called the guest, is confined within another, the host, species. Inclusion compounds can majorly be divided into two classes that are whether the host structure consists of tunnels or cages (Takemoto et al, 1984). In order for a guest to be included within the host tunnels or cages, the guest must be of a suitable size and shape. Hence, inclusion compounds have applications in the separation and purification of molecules. It is also possible to stabilize molecules which are sensitive and labile by encapsulating it into a suitable host structure. Many clatherates and clatherate hydrates were studied; the most common among them are urea, thiourea and chitosan clatherates.

1.4.2 UREA

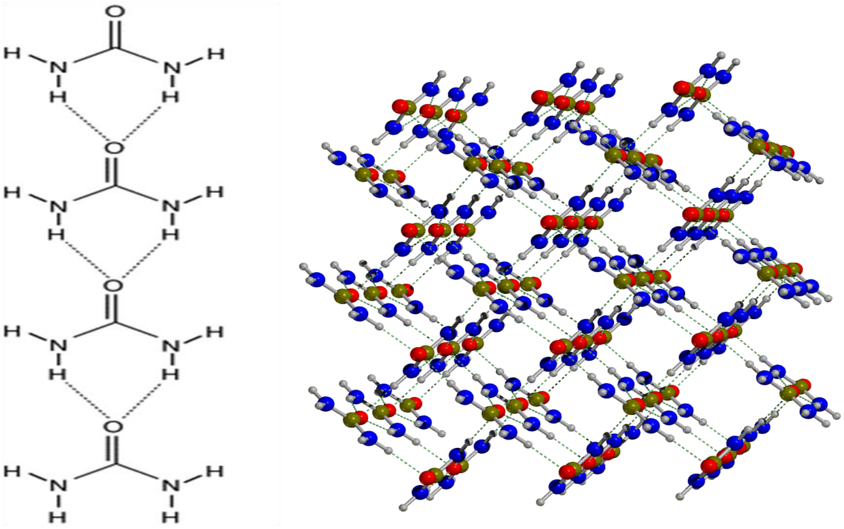
Urea or carbamide is an organic compound with the chemical formula $CO(NH_2)_2$. The molecule has two NH_2 groups joined by a carbonyl (C=O) functional group. Urea serves an important role in nitrogen metabolism in plant as well as in animal. It is a colorless, odorless solid, highly soluble in water and practically nontoxic. It behaves neither acidic nor basic when dissolve in water. Urea is widely used in fertilizers as a convenient source of nitrogen. Urea is also an important raw material for the chemical industry. Apart from natural sources urea can be synthesis artificially in laboratory where it exist as crystalline solid with two major forms as granules and prilled. The granular one is strong and difficult to dissolve easily as compare to prilled one.

1.4.3 UREA INCLUSION COMPOUND

Urea inclusion compounds also known as urea adducts or clatherates were discovered accidentally by Bengen in 1940 (Atwood et al, 1984) while studying the effects of urea on proteins in pasteurized milk. Its structure was first reviled by Smith while studying the X- ray diffraction on hexadecane- urea inclusion compound and there after the structure of other urea inclusion compounds are seems to be considering the same as hexadecane-urea inclusion compound (Yang, 2007).

The urea in its pure form is a tetragonal crystal structure which is considered to be rather so loose structure with neighbouring molecule that in presence of hydrophilic solvent and organic compound like long chain olefins and paraffin the structure starts changing and the urea molecule are so linked by hydrogen bonding with neighboring compound that it forms a helical like tunnel structure with hexagonal like walls of that helix tunnel. With great stability of hydrogen bonds and additional van der waal interaction of hydrocarbons make this helical form more stable than the corresponding tetragonal form.

In tetragonal urea each oxygen is tethered to four hydrogen (Hollingsworth et al, 1994). The carbonyl oxygen is tethered to both of the hydrogen of an adjacent molecule as shown in figure 1.2. The distance between the nitrogen and oxygen atoms in the $N-H \ldots O$ hydrogen bonds are nearly identical in the hexagonal and tetragonal structures. The urea molecule rotate to each other by and angle of 149°.

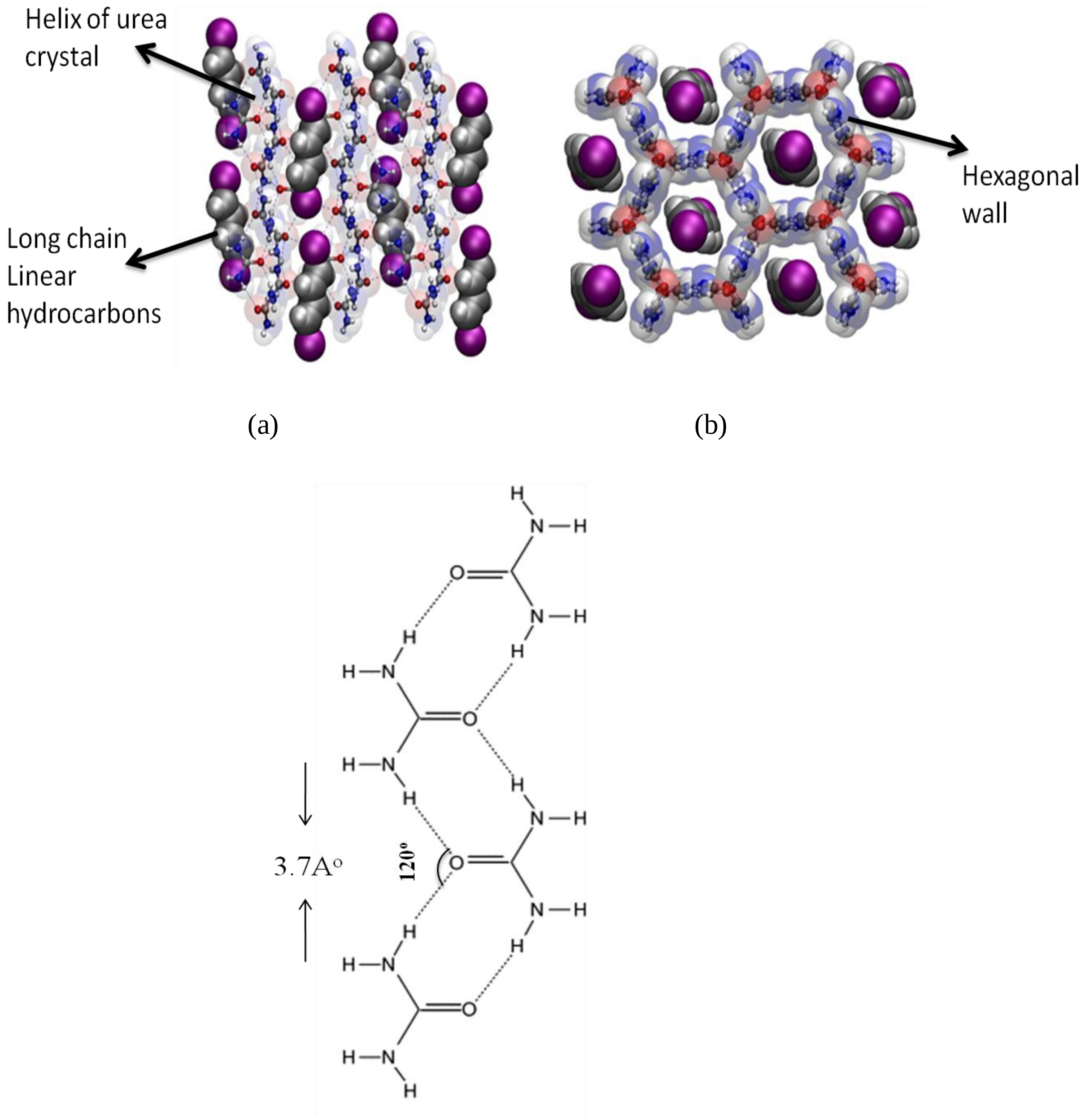


(a) (b)

Figure 1.2: (a) The bonding pattern in tetragonal urea (b) the crystal packing in tetragonal urea (Theochem)

The structure of urea adduct or the hexagonal urea is such that, three long running spirals are linked by hydrogen bonds to molecules and form a channel. These spirals thus form a hexagonal type of structure at the wall of the channel. These spirals could be right handed or left handed which is randomly decided on the basis of interaction with long chain hydrocarbons. Each oxygen in urea clatherate is linked by hydrogen bond to four nitrogen atom and thus each nitrogen is linked to two oxygen atom through hydrogen bonding. The hydrogen bond in adducted urea is generally divided into two types, shorter bond close to 2.9 to 3A° long and longer bond close to 3.04A^{o} long. In hexagonal urea each hydrogen is bonded to a different carbonyl and urea molecule rotated to each other by an angle of 120° forming a spiral figure (Bhatnagar, 1967) as shown in Figure 1.3.

The dimensions of the helix in adducted urea is falls around 5A° which is corresponding to the radii of the linear paraffins and olefins so only they can enter the helix surroundings and not the other branched molecules (Atwood et al, 1996). The strong host-host interactions, along with the relatively smooth features of the channel wall, give rise to a system in which the guest molecules are held only loosely, and undergo substantial torsions, librations and translations, as well as reorientations about the channel axis. Due to these structural features, urea adducted compounds are frequently nonstoichiometric (host-guest interaction are not specific, only depends on dimension), with the guest molecules normally packing within van der Waals contact of each other.



(a) (b)

(c)

Figure 1.3: Adducted urea structure (a) spiral (b) hexagonal wall (c) bonding pattern of urea (Somewhereville)

Urea inclusion compounds can either be incommensurate, i.e. the size of the host and guest structures cannot be related by a small integer, or commensurate when dimensions of host and guest are related by small integer.

1.5 APPLICATIONS OF LINEAR ALPHA OLEFINS

The linear alpha olefins obtained from urea adduction method can be used in wide range of applications which are discussed below.

1. The lower carbon numbers, 1-butene, 1-hexene and 1-octene are extremely used as co-monomers in production of polyethylene.
2. C_4-C_8 linear alpha olefins are use for making aldehyde and later carboxylic acid for plasticizer application.
3. 1-decene is used in making polyalphaolefin synthetic lubricant basestock and surfactant in a blend with higher olefins
4. C_{10}-C_{14} linear alpha olefins are used in making surfactants for aqueous detergent formulations.
5. C_{14} has other applications such as being converted into chloroparaffins.
6. A recent application of C_{14} is as on-land drilling fluid base stock replacing diesel of kerosene in that application
7. Linear alpha olefins of higher carbon number can be polymerized and used as drag reducing agent.

1.5.1 DRAG REDUCTION

Flow of the hydrocarbon fuel through pipelines often encountered with drag and frictional losses. To streamline the flow of liquid hydrocarbon fuels, such as gasoline, diesel and jet fuels in distribution pipelines, calculated amounts of a polymer based Drag Reducing Agent (DRA) is often injected into the pipelines at the pump stations. The mixing of the polymer based DRA with the hydrocarbon fuel has the effect of decreasing the friction between the turbulent flow of the fuel and the walls of the pipelines, and in turn, leads to considerable reduction in the pipeline shipping costs.

CHAPTER 2

EXPERIMENTAL

2.1 EXPERIMENTAL TECHNIQUES

The crude oil as isolated from beneath the earth surface, so the coker kero stream is expected to contain some metal impurities although all due care have been taken during processing. Hence it becomes necessary to analyze for the presence of metal impurities as metal may prove to be a hindrance on further applications of recovered olefin product. The metal analysis was performed with the help of iCAP analysis technique (Inductively coupled plasma atomic emission spectroscopy).

To check the different type of hydrocarbon content in coker kero stream from three different refineries, the samples were undergone proton NMR analysis. So the introduction and principle of these two techniques are discussed below.

2.1.1 Inductively coupled plasma atomic emission spectroscopy

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element (Stefánsson et al, 2007). The intensity of this emission is directly related to the concentration of the element within the sample. The ICP-AES is composed of an ICP torch which consists of 3 concentric quartz glass tubes. The torch unit of an ICP is used to create and sustain plasma (plasma is an electrically conducting gaseous mixture containing enough cations and electrons, though the plasma has a neutral charge overall to maintain the conductance). This torch is surrounded to the outer surface by a coil which is ultimately connected to a radio frequency generator which starts from 200W and finally ends till 1250W and thus generating radio frequency in the range of 21-41MHz.

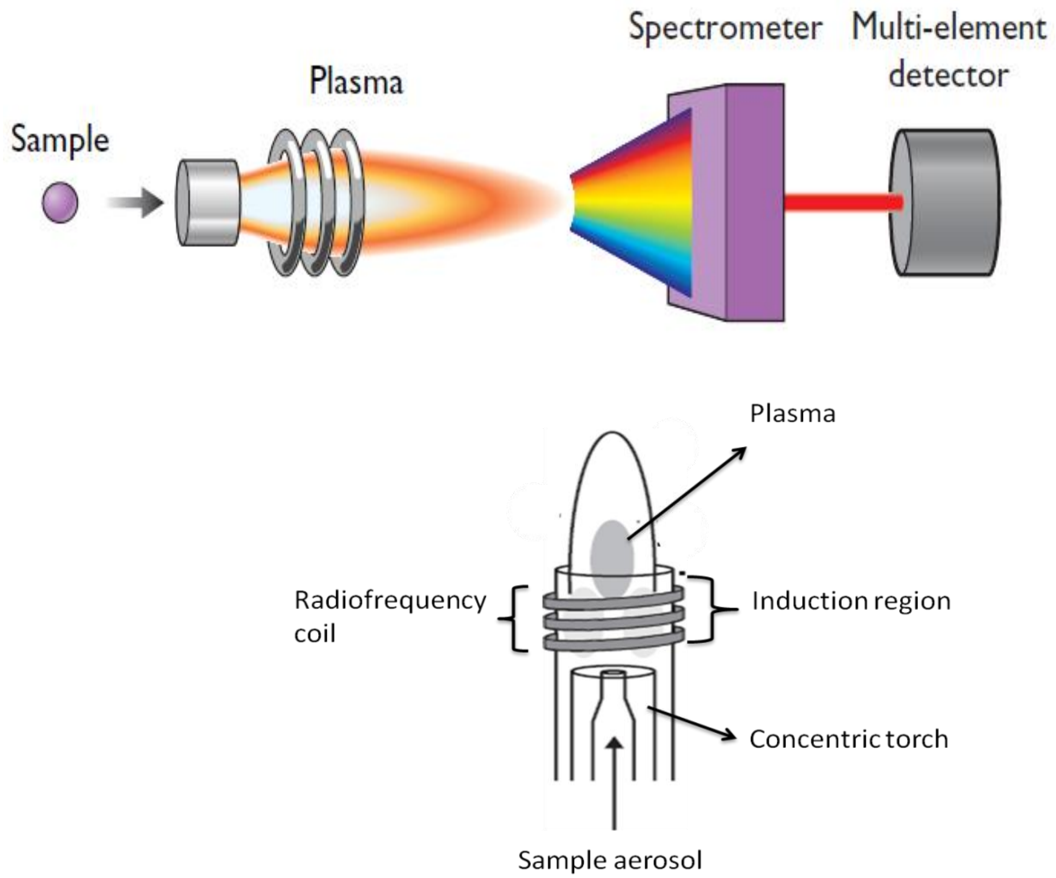


Figure 2.1: Schematic diagram of ICAP assembly (Xiandeng et al, 2000)

The plasma is created typically with argon gas. When the torch is turned on, an intense electromagnetic field is created within the coil by the high power radio frequency signal flowing in the coil. The argon gas flowing through the torch is ignited with a Tesla unit that creates a brief discharge arc through the argon flow to initiate the ionization process. Once the plasma is ignited, the Tesla unit is turned off.

The argon gas is ionized in the intense electromagnetic field and flows in a particular rotationally symmetrical pattern towards the magnetic field of the radio frequency coil. Stable, high temperature plasma of about 7000 K is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles.

The sample of interest is then send to a nebulizer where it is converted into an aerosol, or very fine mist of liquid droplets. The aerosol is carried into the center of the plasma by the argon gas flow. Upon entering the plasma, the droplets undergo three processes. The first step is desolvation, or the removal of the solvent from the droplets, resulting in microscopic solid particulates, or a dry aerosol. The second step is vaporization, or the decomposition of the particles into gaseous state molecules. The third step is atomization, or the breaking of the gaseous molecules into atoms. Finally, excitation and ionization of the atoms occur, followed by the emission of radiation from these excited species.

2.1.2 PROTON NMR

The NMR of the crude coker kero sample and the recovered product was performed in AGILENT NMR 500 with an operating frequency of 500 MHz, small amount of the sample is taken and final volume is made to 700µL with TMS/$CDCl_3$ (0.03 v/v %)

Principle of NMR

Nuclei have positive charges. Many nuclei which contains odd number of neutron or proton or both will behave as though they were spinning. Any charged particle which moves has a magnetic moment and produces a magnetic field. Therefore, a spinning nucleus acts as a tiny bar magnet oriented along the spin rotation axis (Thomas, 1998). This tiny magnet is often called a nuclear spin. If we put this small magnet in the field of a much larger magnet, it orientates itself in a most probable orientation. The most favorable orientation would be the low-energy state and the less favorable orientation, the high-energy state. Now if we apply a field energy equal to the energy difference between these two state then the lower energy state will absorb energy and move to higher state this absorb energy by nuclei is recorded as voltage change in turn coil. The applied frequency depends on the magnetic field in which nuclei is placed and is given by the following equations

$$\Delta E = \gamma h B_o / 2\pi$$

Where h is planks constant and replacing $\Delta E = h\vartheta$

$$\vartheta = \gamma B o / 2\pi$$

The gyromagnetic ratio γ is a constant for any particular type of nucleus and is directly proportional to the strength of the tiny nuclear magnet.

The NMR can be performed for all these nuclei ^1H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P because the most common isotopes of carbon, nitrogen and oxygen do not have nuclear spin.

Chemical Shift

The nuclei of the same type can achieve the resonance condition at different frequencies. This can occur if the local magnetic field experienced by a nucleus is slightly different from that of another similar nucleus. If a molecule containing the nucleus of interest is put in a magnetic field, the electron surrounding the nuclei also influence by magnetic field and produce an electronic current in the plane perpendicular to the applied magnetic field. These induced currents will then produce a small magnetic field opposed to the applied field that acts to partially cancel the applied field, thus shielding the nucleus. So the frequency require for transition will be different for different nuclei this frequency is denoted with reference to a reference sample like tetra methyl silane. The difference between the position of the signal of interest and that of the reference is termed the chemical shift which is denoted as ppm.

$$\delta = \frac{(\vartheta\text{sample-}\vartheta\text{reference})}{\vartheta\text{applied}} \times 10^{6}$$

as the peak positions are now denoted in ppm with the reference sample so this positions for specific nuclei will come in same position whatever be the applied frequency. The possible range for proton at different surrounding is given in Table 2.1 below-

Table 2.1: Chemical shift range for proton NMR (Silva et al, 2006)

Type of hydrogen	**Chemical shift (ppm)**
CH_3 aliphatic	0.6-1
CH_2 aliphatic	1- 1.5
CH aliphatic	1.5-2
CH_2 branched terminal olefin	4.5-4.8
CH_2 linear terminal olefin	4.8-5.05
CH branched internal olefin	5.05-5.3
CH from Z/E olefin	5.3-5.55
CH from linear terminal olefins	5.55-6.6
Aromatic ring	6.6-8

2.2 MATERIALS

Beakers (250 mL) – For weighing urea and petroleum ether.

Reagent bottle (250 mL) – For weighing coker kero

Four necked kettle

This reactor is from Riviera and was used for making urea adduct. The temperature of the reactor was maintained using a hot oil bath.

Hot plate magnetic stirrer

'Heidolph MR HEI End' hot plate stirrer is use for constant stirring of the reactor along with heating at 90°C so that the reactor temperature reaches approximately to 60ºC. The stirrer works using a rotating electromagnetic field.

Vacuum pump

A vacuum pump from ULVAC (Kiko Inc.) is used during washing of urea adduct with petroleum ether. The pump has a pumping speed of 40L/min with ultimate pressure of 1 X 10^3 Pa. This pump is based on membrane rotary pump system where a rotating membrane produce a chamber of high volume due to which the air in the flask sucked inside the rotary chamber.

Sintered G-4 filtration funnel

These crucible are made of Pyrex glass and are fitted with a porous (sintered) disc. The urea adduct was filtered in these crucible. The numbering of crucible is done depending on pore size.

Separating funnel

250 and 500 mL separating funnels are used to first decompose urea adduct with hot water and then separate olefin/paraffin from water soluble urea under the action of gravity.

Coker kero

Coker kero is petroleum stream obtained from different refineries after cracking process and is the source from where we have separated olefins. We used coker kero from three different refineries and compared the recovery yield of two of them.

Urea

Urea in its most pure crystal form is used from Merck Company (Melting point 132-134^{o}C, Batch number QH1Q610440) for adduction process.

Petroleum ether

Petroleum ether of boiling range 40-60°C and density at 20°C, 0.63-0.65g/ml was from RFCL RANKEM to use it as a solvent for organic content in petroleum stream.

Methanol

Methanol obtained from AVANTOR RANKEM is used as a supporting solvent for clatheration phenomenon for urea adduction to take place.

Acetone

Acetone obtained from RANKEM RFCL is used for a final washing of urea adduct before its decomposition to obtain olefins from it.

2.3 METHOD

Urea adduction process

1. In urea adduction process, 64g of petroleum stream was charged in a reactor fitted just above a hot oil bath.
2. 112g of urea was then added followed by 46g petroleum ether and 96g methanol.
3. The content was stirred at 60^{o}C for 5 hours in a four necked reaction kettle.
4. The urea adduct was then separated with G-4 filtration funnel along with vacuum and washed thoroughly with 100mL petroleum ether 7-8 times and a final wash with acetone to get a white urea adduct.
5. Adduct was then dried at room temperature overnight.
6. The urea adduct thus obtained was decomposed with hot water (60-70ºC) in a separating funnel and left it undisturbed overnight.
7. The next day, clear water soluble urea was drained out from bottom valve and was given a final wash with hot water.
8. The organic layer at the top was collected with a washing of pentane
9. The pentane is evaporated from the beaker using nitrogen blow till the weight of the beaker become constant.
10. Finally left product is weighed and given for analysis

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Results & Discussion

3.1.1 Sample characterization

The crude oil (coker kero) from three different refineries was analyzed for metal content using ICAP analysis (Inductively coupled plasma atomic emission spectroscopy). The analyzed result is reported in tabular form below (Table 3.1). The result clearly depicts that except Si there is no other metal whose amount exceed above 0.1 ppm. This clearly shows that the olefins extracted from these coker keros can be used as raw material for synthesis of copolymers, surfactants, lubricant additives and also for polymerization as there is no such metal to act as poison for polymerization.

Table 3.1: Metal content in coker kero sample using ICAP Analysis

	Samples		**ICAP Analysis(ppm)**											
S No	**Internal Id**	**Description**	**Ca**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Na**	**Ni**	**Pb**	**Si**	**V**	**Zn**
1	**PNP/13/GS/1084**	**Kero coker 1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**0.2**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**3.2**	**<0.1**	**<0.1**
2	**PNP/13/GS/1085**	**Kero coker 2**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**3.2**	**<0.1**	**<0.1**
3	**PNP/13/GS/1086**	**Kero coker 3**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**0.7**	**<0.1**	**<0.1**

Next the samples were analyzed using proton NMR for the presence of different type of hydrocarbons. AGILENT NMR 500 was used with an operating frequency of 500 MHz, small amount of the sample is taken and final volume is made to 700µL with TMS/$CDCl_3$ (0.03%v/v). By referring the Table 2.1, the ^{1}H NMR of coker kero samples below clearly shows the presence of aromatics (6.6-8 ppm), olefins (4-6 ppm) and paraffins (cyclo + normal) in the ranges of 0.5- 2 ppm (Figure 3.1-3.3). It can further be seen that there are different types of olefins present in these coker kero samples i.e, α- olefins, internal olefins and substituted α- olefins present in various proportions.

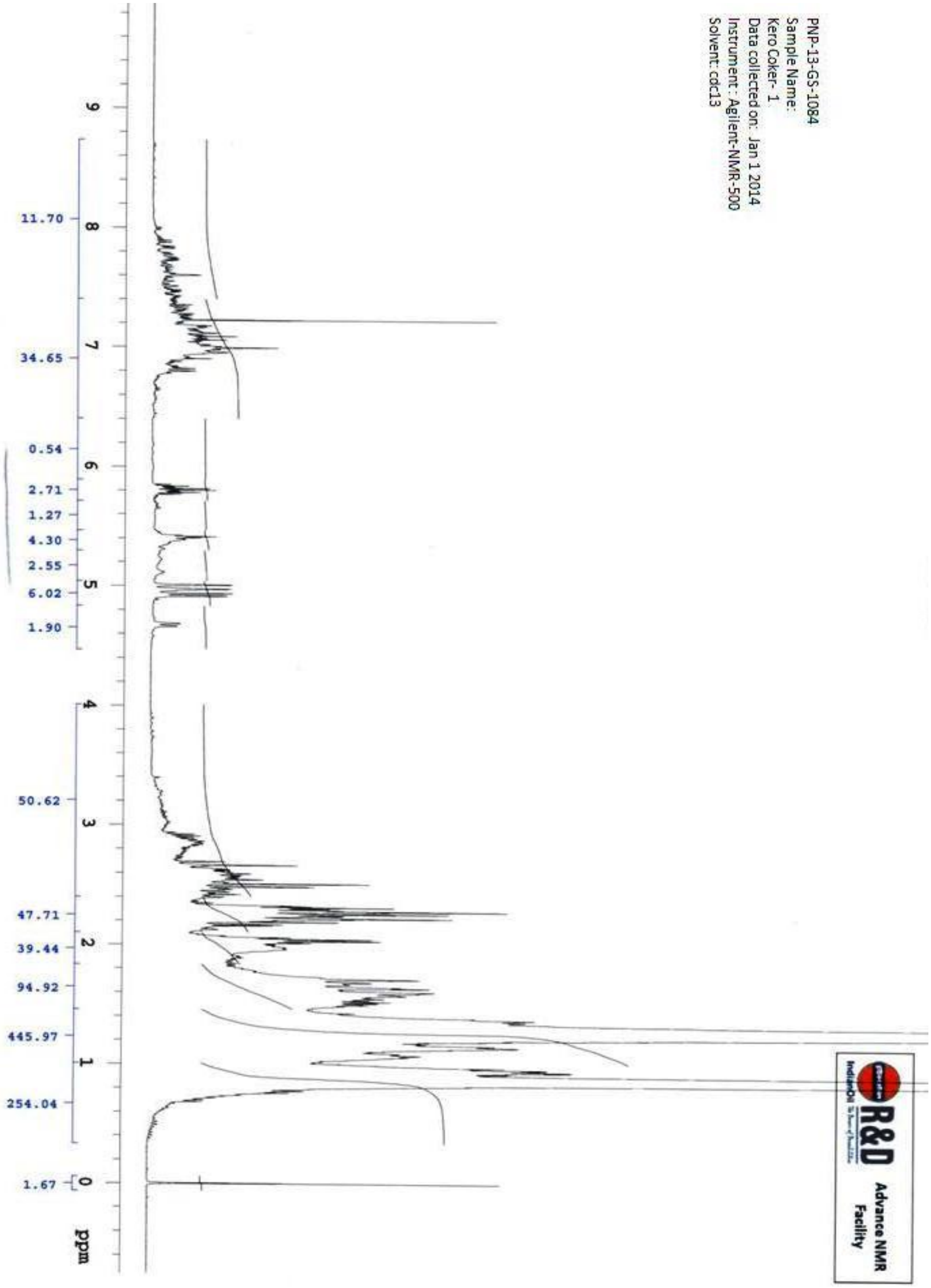


Figure 3.1: Proton NMR of coker kero sample 1

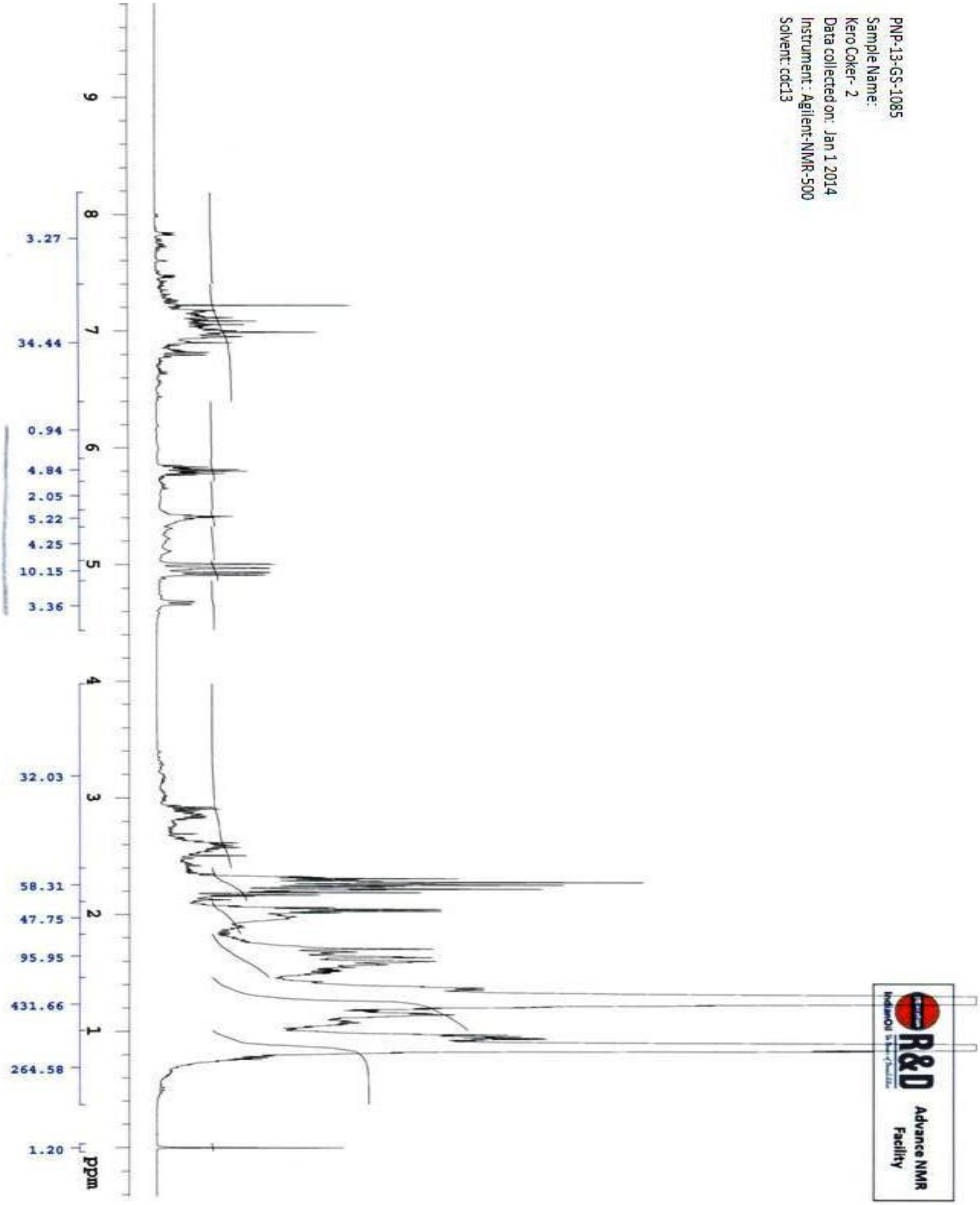


Figure 3.2: Proton NMR of coker kero sample 2

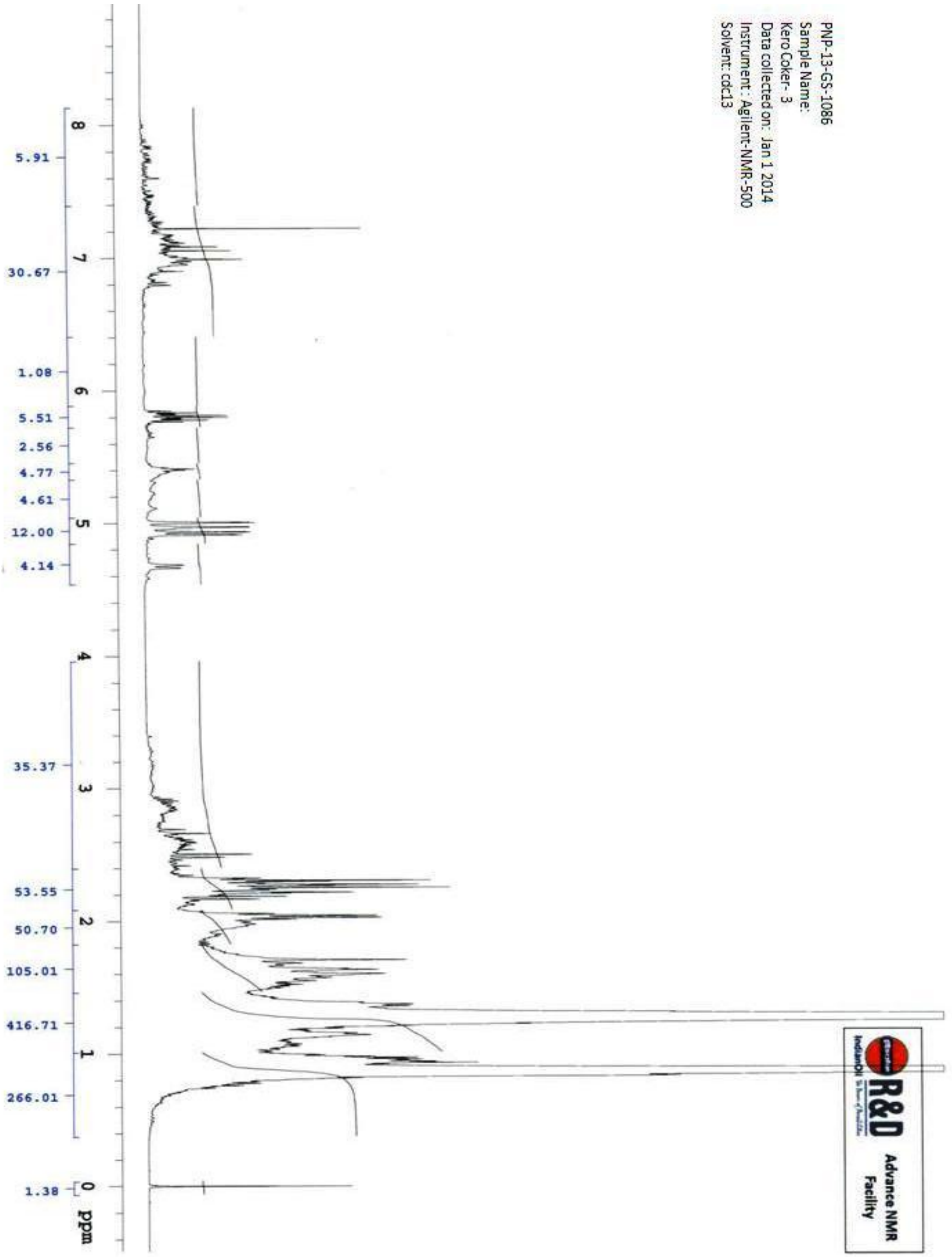


Figure 3.3 : Proton NMR of coker kero sample 3

The weight % of aromatics and olefins (different types) have been calculated using the in-house method of IOCL R&D Centre. It can be seen that the weight% of total olefin (Table 3.2 and Annexure 1) varies from 19.4 to 39% from coker kero 1 to coker kero 3. Further out of total olefins, the weight % of α-olefins and unsubstituted internal olefins, which are of interest to this work, also varies from 63-69%.

Table 3.2: Quantitative proton NMR analysis of coker kero samples

Sample	**Total Olefin Content (wt %)**	**Distribution of Olefin (wt%)**					**Aromatics**
		α-Unsubstituted	**α-Substituted**	**Internal Unsubstituted**	**Internal Substituted**	**Others**	
Coker Kero-1	19.4	6.8	1.8	6.6	4.2	-	25.4
Coker Kero-2	33.2	12.8	3.6	10.0	6.8	-	20.6
Coker Kero-3	39.0	14.5	4.8	10.4	7.5	~1.8	20.5

Coker kero from two different refineries (sample 1 and sample 3) were actually used to carry out urea adduction process and compare the yield. It has been stated in previous studies that urea crystals changes its structure from tetragonal to hexagonal tunnel which entraps linear olefins and paraffin. We investigate this by studying the surface morphology of both urea as well the adduct derive from both of the reactions. The change in surface morphology of urea crystal before and after adduction was studied with the help of scanning electron microscope.

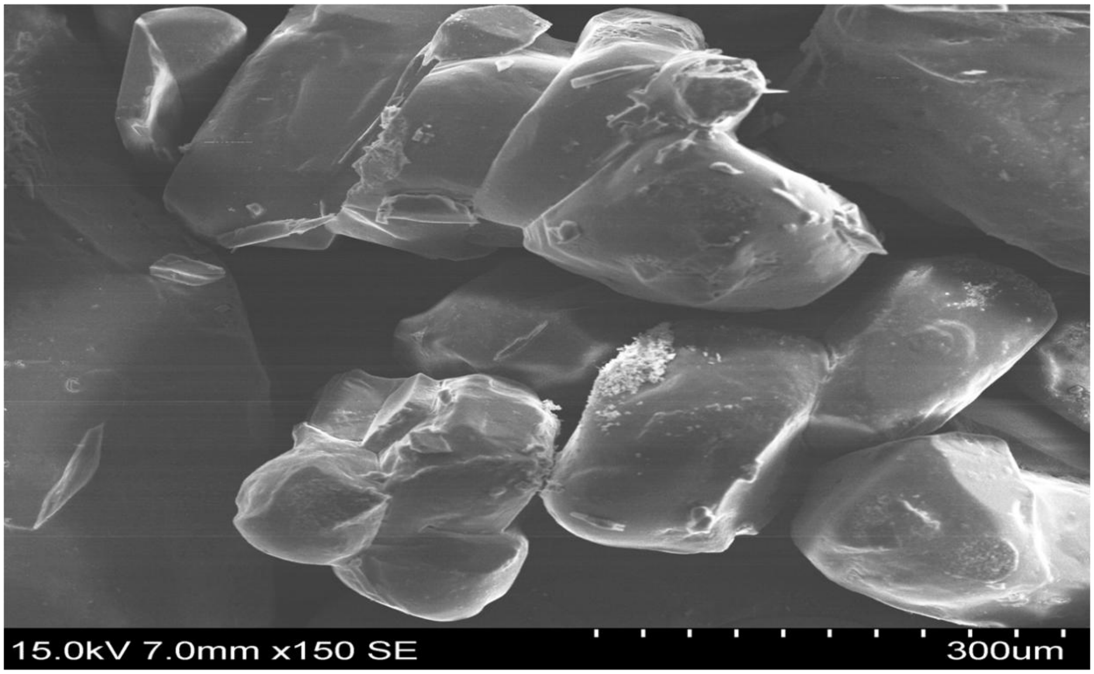


Figure 3.4: SEM image of urea crystal

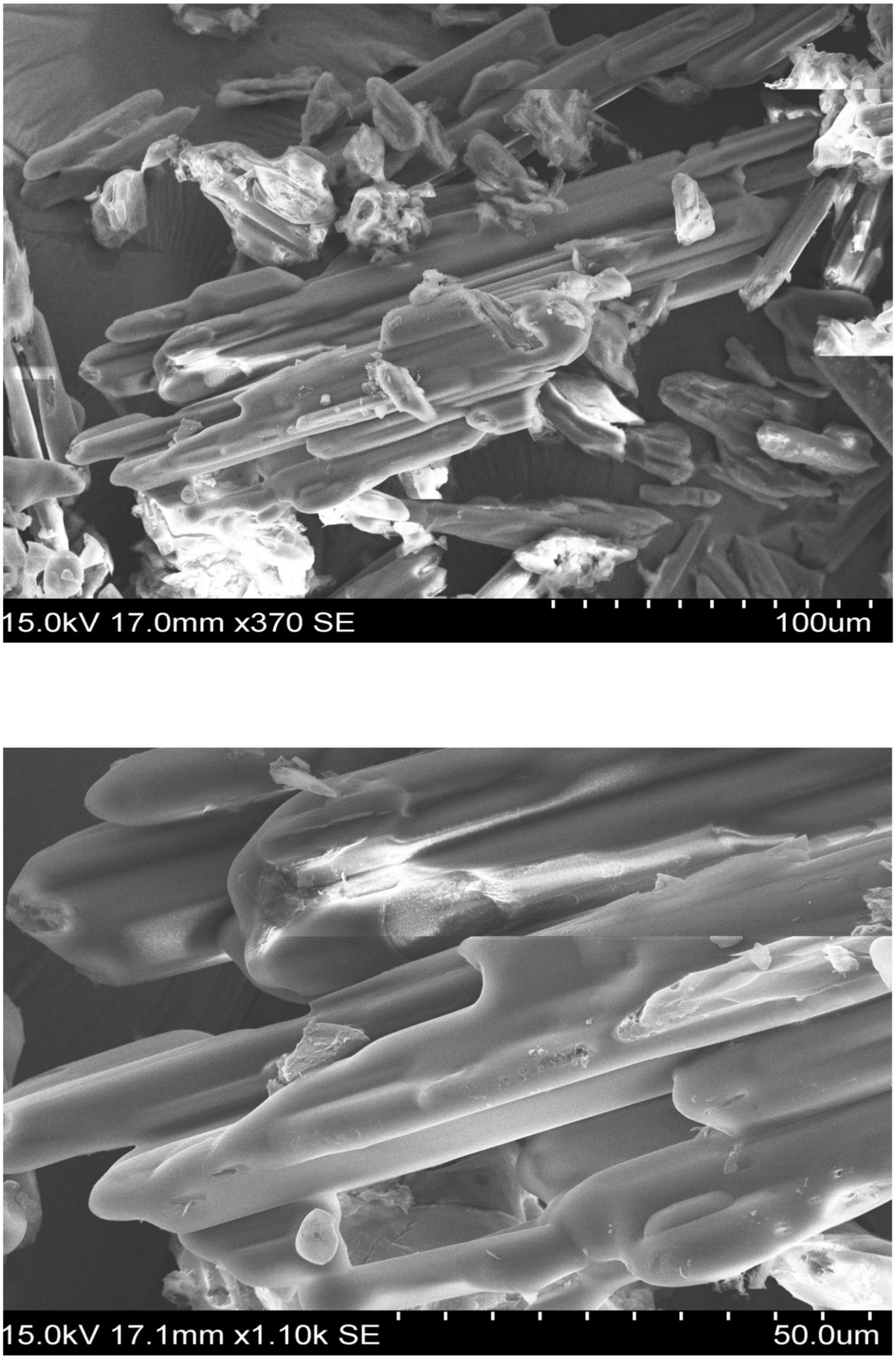


Figure 3.5: SEM images of urea adduct derive from coker kero sample 1

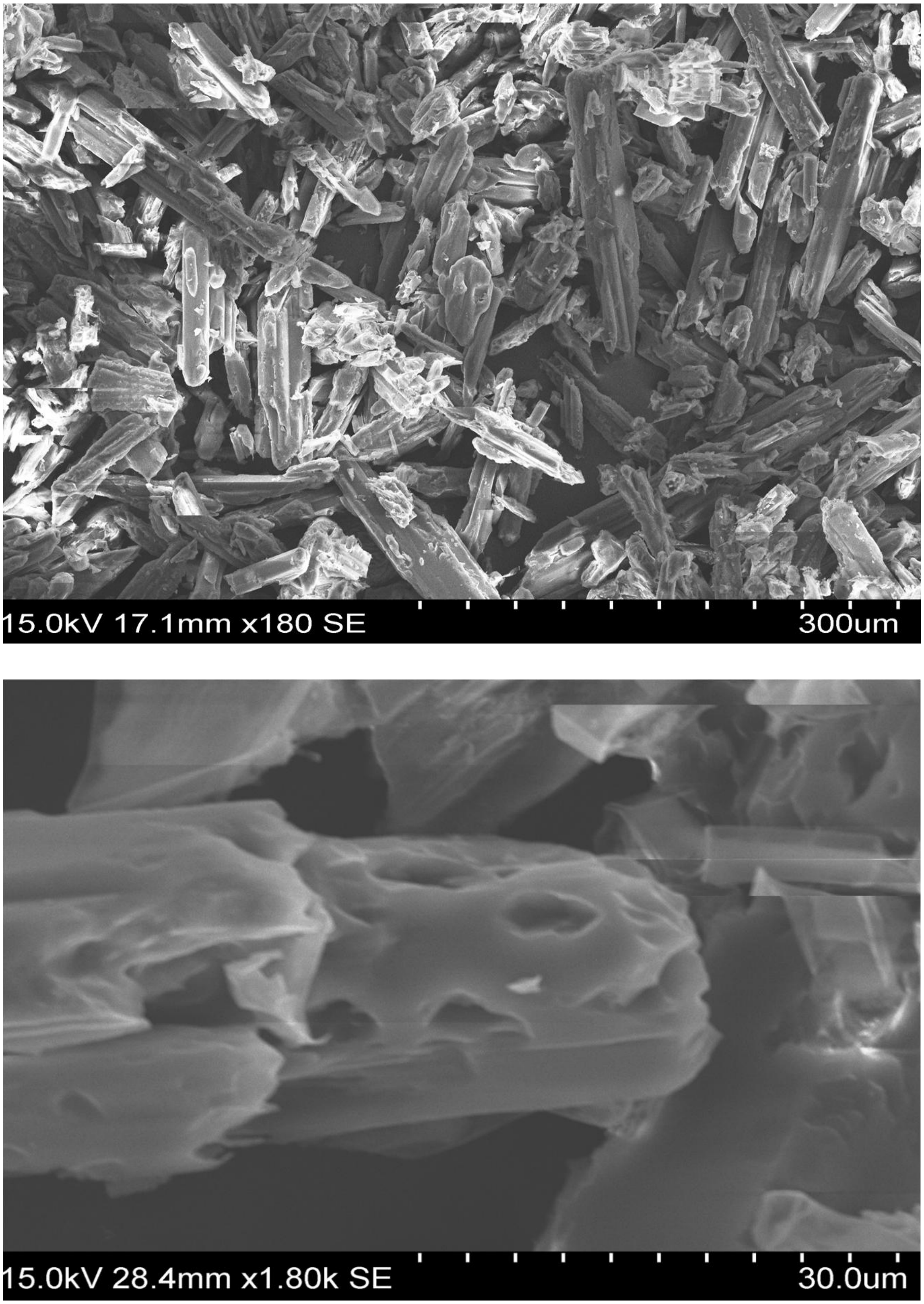


Figure 3.6: SEM images of urea adduct derive from coker kero sample 3

Form the above SEM images it can be easily interpreted that the urea crystal changes morphology in its adducted form. It appears to be needle like hexagonal tunnels to which only linear long chain hydrocarbon can be entrapped. So these images are correlated with the theoretical points.

3.2 NMR OF RECOVERED PRODUCT

The urea adduct recovered products from coker kero of two different refineries were analysed with the help of proton NMR and quantified by in- house method of IOCL R&D Centre. The spectra below clearly show that all of the aromatics had been washed off. From the olefinic region most of the substituted olefins were washed off and the region was only left with linear alpha and internal olefins. Further the distribution of these different types of olefin was reported in the NMR report (Annexure II). From the report it was found that the weight % of linear α-olefins and internal olefins out of total olefins increase to 99% (Table 3.3). This shows that the olefins recovered from this method are mostly linear olefins. From these results the weight of linear α and internal olefins was calculated in both the crude sample and recovered product and finally the yield was calculated. The yield of this urea adduction process was found to be around 64- 69% (Table 3.4).

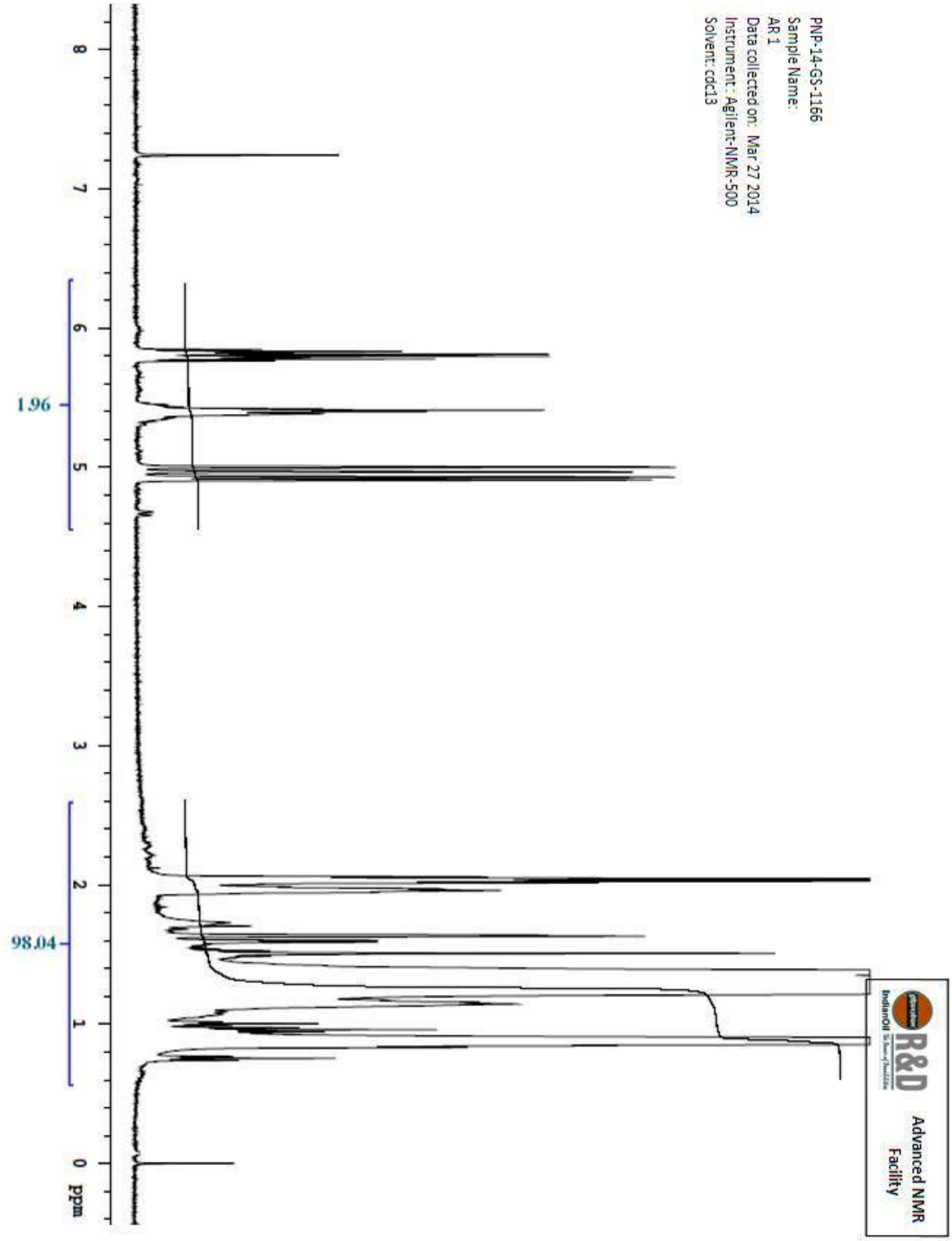


Figure 3.7: Proton NMR of adduct recovered product 1 from coker kero sample 1

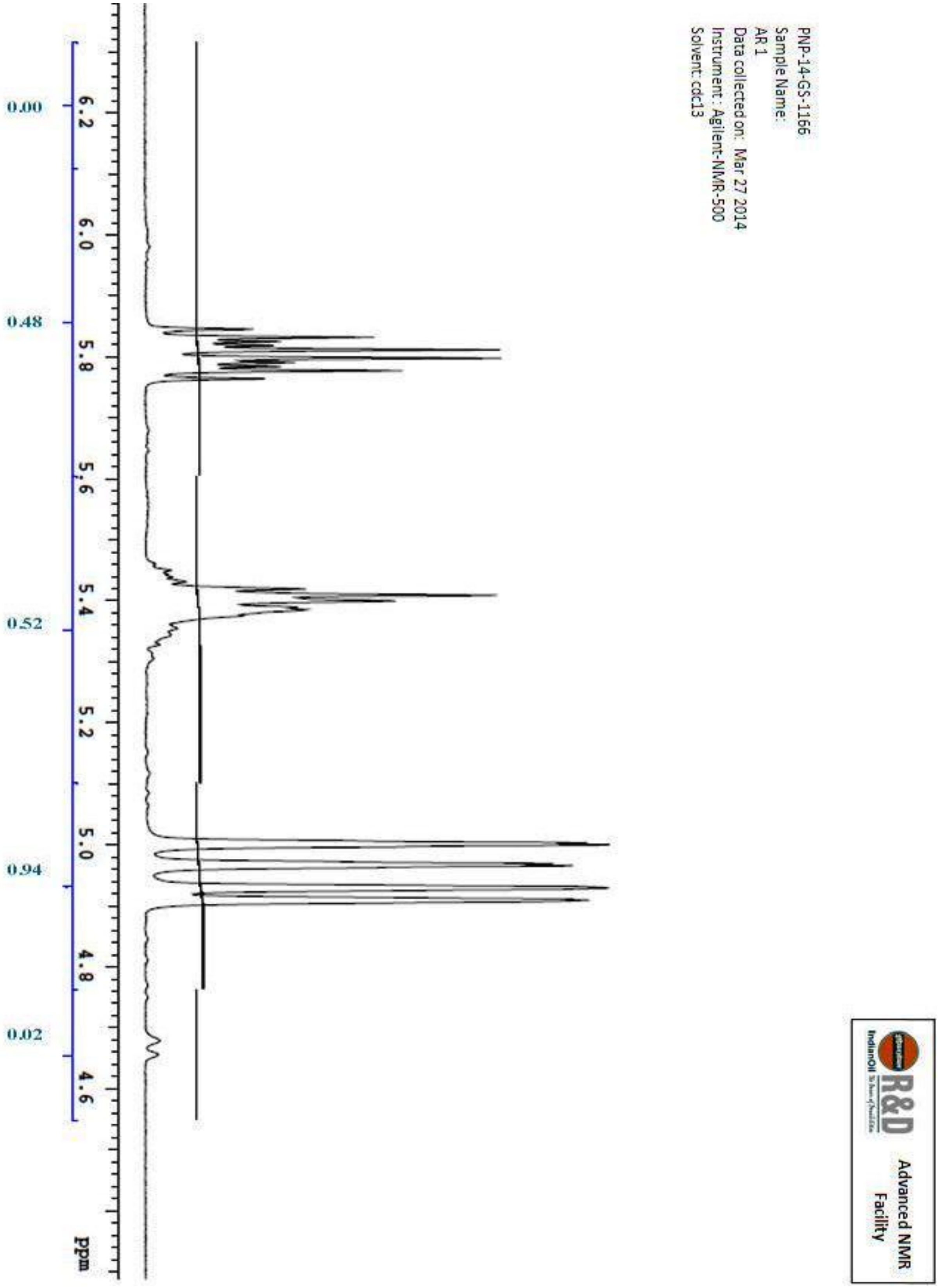


Figure 3.8: Proton NMR spectrum of olefinic region from adduct recovered product 1

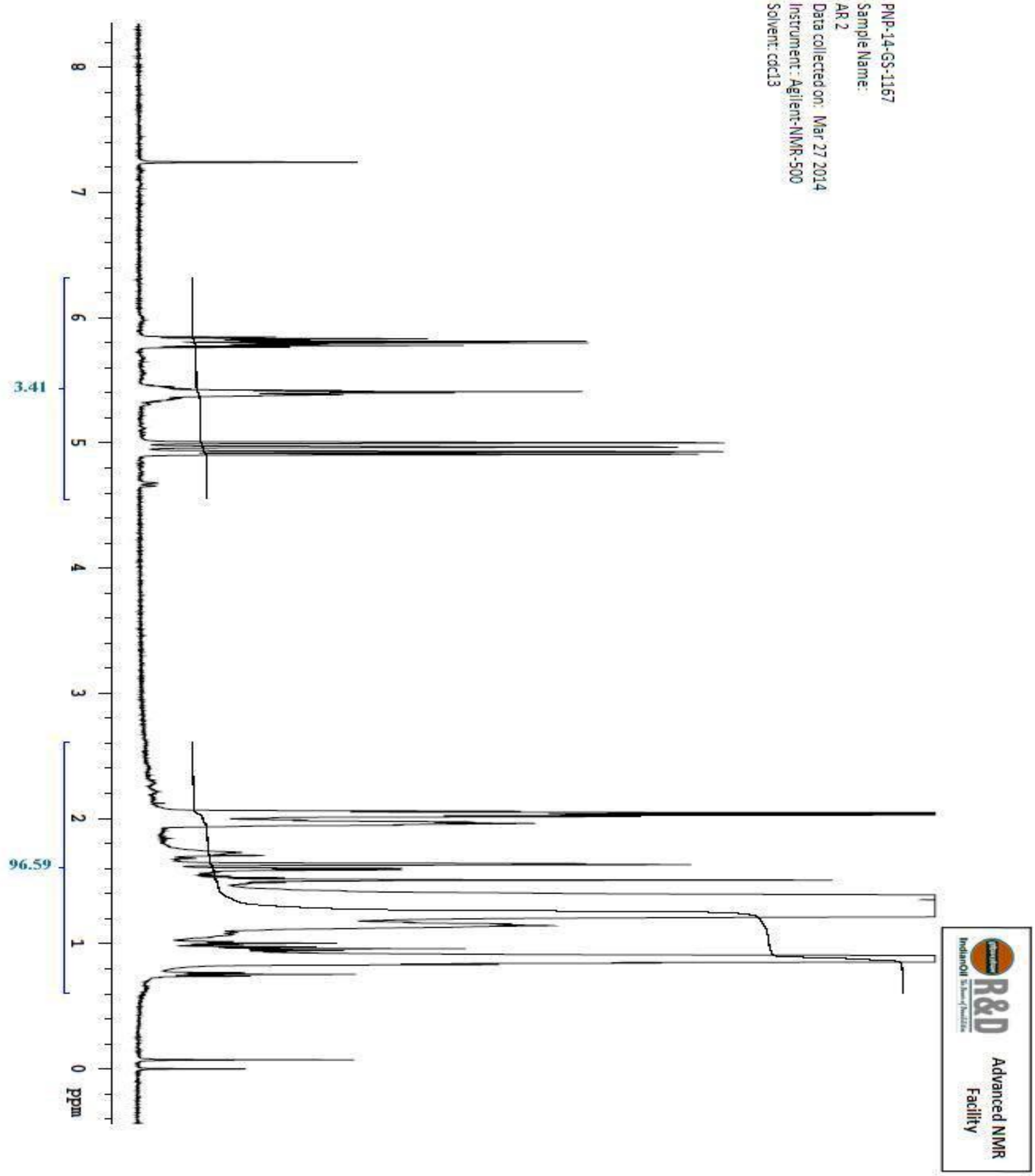


Figure 3.9: Proton NMR of adduct recovered product 2 from coker kero sample 3

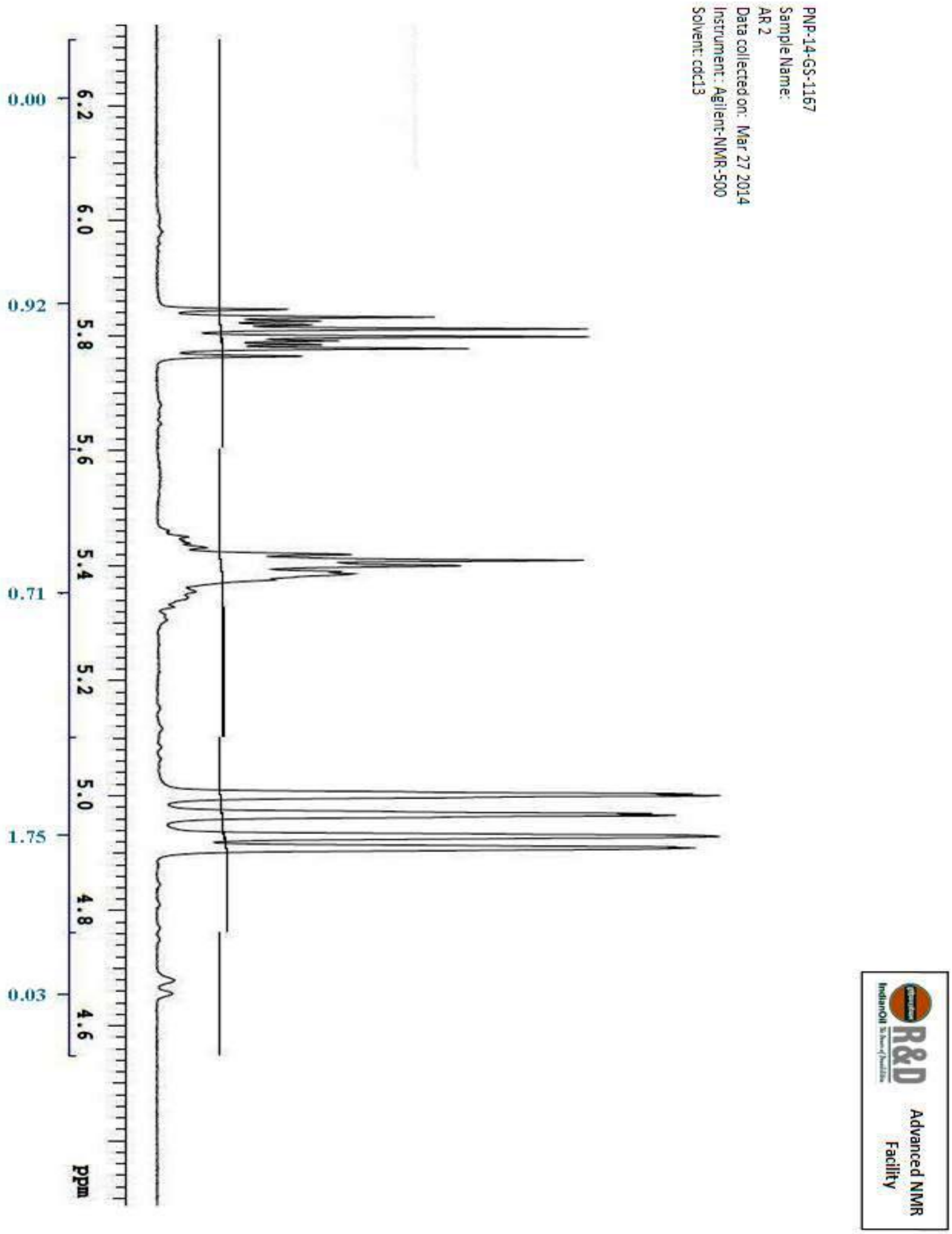


Figure 3.10: Proton NMR spectrum of olefinic region from adduct recovered product 2

Table 3.3: Distribution of olefins in adduct recovered products

Sample	Total Olefin Content (wt%)	Distribution of Olefin (wt%)			Aromatics
		α-Unsubstituted	α-Substituted	Internal Unsubstituted	
Adduct Recovered Product -1	20.53	11.36	0.21	8.96	0
Adduct Recovered Product -2	33.91	21.36	0.31	12.24	0

Table 3.4- Yield of the urea adduction method

Comments	Coker kero 1	Coker kero 3
Total no. of reactions	10	10
Weight of coker kero used per reaction	64g	64g
Total kero used	64 × 10 = 640g	64 × 10 = 640g
Weight of final product	294.506g	304.513g
Linear olefin in coker kero	85.76g	159.36g
Linear olefin in adducted product	59.86g	102.31g
Yield of reaction	69.79%	64.20%

3.3 OBSERVATIONS

The two primary requirements for our experiments were urea and coker kero. The physical characteristics of both these chemicals were observed and it was found that the colour of coker kero varies sample to sample from wine red colour to dark purple. This variation in colour was due to the extent of presence of asphaltene in the crude. On the other hand urea at the beginning was white crystalline powder.

The reaction proceeds by adding coker kero then urea and later petroleum ether and methanol. The methanol here acts as the promoter for hydrogen bonding in urea and also opens up the crystal structure of urea to form hexagonal cages. The petroleum ether was primarily used for dissolving the petroleum impurities in the crude. With the help of air condenser and setting up the temperature of reaction to 60°C would start the reflux of petroleum ether. Along with stirring at 700rpm the above step promotes homogenous mixing of the reaction cocktail.

After three hours of reaction, the urea started turning into whitish brown accumulates. With the passage of time these accumulates changed their shape as crystal needle and started sticking to the wall of the reactor due to accumulation of olefins and paraffin molecules in their crystal structure. The reaction is followed with formation of needle like crystals which accumulate in the reactor.

The urea adducts at this stage show a tint of brownish colour due to other crude impurities which was stuck superficially over it. So these impurities were removed by washing the adduct 7-8 times with petroleum ether (as many crude impurities are soluble in it). With these washing the adduct turn out to be as whitish fine crystals. This adduct is decomposed to get linear alpha olefin and paraffin from it. The decomposition was done with hot water as the solubility of urea increases in hot water and also our final product being oily in nature and lighter than water can be phase separated, using separating funnel in laboratory.

4. CONCLUSION

In the present study, we successfully employed urea adduction process for separation of linear olefins from coker kero stream with a yield ranges from 64-69%. Urea adduction is a physical separation process based on clathration phenomenon in which the host molecule, urea, form a 3-dimensional network which allows cages of channels containing guest molecules, linear olefins and paraffin. The inclusion compounds of urea are one of the most widely studied and have large applicability in the field of petrochemical industry.

Urea forms crystalline helical channels with n-hydrocarbons and other straight chain molecules due to which its crystal structure changes from tetragonal to hexagonal needle like tunnels. These helical channels entrap linear olefins and paraffin from coker kero stream. Further, the structure of adduct urea is independent of these organic moieties indicating that there is no strong molecular interactions between urea and these organic moieties. The only thing need to be required is the long straight chain of the guest molecules.

The coker kero (obtained after distillation) contains aromatics, olefins and paraffin (linear and branched) and excess of asphaltene which make it dark purple in colour. The urea adduction process is so efficient in recovery of linear olefins that all the colour causing anthracene along with aromatics and branched hydrocarbons washed off from the crude and a transparent oily liquid left in the adduct.

The product recovered from this process can be used for making plasticizers, detergents, co-monomers, synthetic lubricants, shampoo, paper treating chemicals, and many more.

5. REFERENCES

1. Angla B., Analytical Chim, 12 (**1945**) 639.
2. Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, E. "*Comprehensive Supramolecular Chemistry"*, Pergamon Press: London, **1996**.
3. Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D. "*Inclusion Compounds"*, Vol. 1-3; Academic Press: New York, **1984**.
4. Bhatnagar V. M, "C*lathrate of urea and thiourea*" Fisk university USA **1967.**
5. Chem.tutorial, "http://www.theochem.unito.it/crystal_tuto/mssc2013_cd/tutorials/bare bone/basic_tutorials.html".
6. Delayed coking by Colorado School of Mines: "http://processengr.com/pdf_documents/co_school_mines_coker_chp5.pdf".
7. EIA reserve estimate, "www.eia.doe.gov".
8. Fetterly I.C., "*Petroleum Refiner"*, 34 (**1955**) 134.
9. Gampert B., Wagner P., "*The Influence of Polymer Additives on Velocity and Temperature Fields"*, Springer-Verlag, New York, **1985**.
10. Hollingsworth, M. D.; Brown, M. E.; Santarsiero, B. D.; Huffman, J. C.; Goss, C. R. "*Chem. Mater"*. **1994**, *6*, 1227.
11. Kenis P. R., Nature 217 (**1968**) 940.
12. Kulicke W. M., Kotter M., Grager, H. "*Advances in Polymer Science*", 1 (**1989**) 68.
13. Matar and Lewis *"Chemistry of Petrochemical Processes*", 2nd edition **2000.**
14. Mina Abdullah refinery: "www.knpc.com.kw/en/Refineries/Pages/AbdullahRefinery.aspx".
15. Phillips Company "liquidpower.com/productsolution/whataredragreducers/Pages/index.aspx".
16. Silva A. C. O, San Gil R. A. S, Kaiser C. R, Azevedo D. A, "*Combining NMR and GC-MS to Characterize Olefin Rich Fractions of Automotive Gasolines*" Ann. Magn. Reson. Vol. 5, Issues 1/3, 11-21, **2006** .
17. Somewhereville: "http://www.somewhereville.com/wpcontent/uploads/ 2013dec20_DIBD_UIC.jpg".

18. Speight, James G. (**1999**), "*The Chemistry and Technology of Petroleum"*. Marcel Dekker p. 215–216.
19. Speight, James G. (**1999**), "*The Chemistry and Technology of Petroleum"*. Marcel Dekker p. 543.
20. Stefansson A, Gunnarsson I, Giroud N (**2007**). "*New methods for the direct determination of dissolved inorganic, organic and total carbon in natural waters by Reagent-Free Ion Chromatography and inductively coupled plasma atomic emission spectrometry*". *Anal*. Chim. Acta 582 (1): 69-74.
21. Takemoto K and Sonoda N, "*Inclusion Compounds"*, (Editors: Atwood J.L, Davies J.E.D and MacNicol D.D), Academic Press, London, **1984**, Volume 2, pp. 47-67.
22. Thomas L. James "*Fundamental of NMR*" university of California **1998.**
23. Toms B. A., (**1948**). "*Some observations on the flow of linear polymer solution through straight tubes at large Reynolds numbers"*. In Proceeding of 1st Int. Congr. Rheol. (pp. 135– 141), Vol. 2, Amsterdam.
24. Tutorial: Delayed Coking Fundamentals, "http://www.coking.com/DECOKTUT.pdf", by Ellis J and Christopher A. Paul of the Great Lakes Carbon Corporation. Presented at the **1998** AIChE Spring National Meeting in New Orleans, LA.
25. United State Patent "*Process for recovery of solid and reusable urea from the urea adduction process*"US5847209A.
26. Virk P. S., Merrill E. W., Mickley H. S., Smithal K. A., Mollo-Christensen E. L., Journal of Fluid Mechanics, 30 (**1967**) 305.
27. Vlachogiannis M., Liberatore M.W., McHugh A.J., Hanratty T.J., Physics of Fluids 15 (**2003**) 3786.
28. Wade J.H.T., Kumar P., Journal of Hydronautics 6 (**1972**) 40.
29. Wells C. S., Spangler J. G., Physics of Fluids, 10 (**1967**) 1890.
30. Xiandeng Hou and Bradley T. Jones *"Inductively Coupled Plasma/Optical Emission Spectrometry"* John Wiley & Sons Ltd, Chichester, **2000.**
31. Xiaorong Yang, "*Solid-State NMR Studies of the Guest Molecules in Urea Inclusion Compounds*", IPCUS **2007.**

Annexure I

Report of proton NMR analysis of coker kero samples

MOLECULAR SPECTROSCOPY GROUP
NMR ANALYSIS REPORT

REPORT NO. : AD //IR/NMR/2014/03
DATE: 23-01-2014

INDENT /GROUP: P&P
PROJECT/ACTION PLAN: Distribution of Olefins in Coker Kero samples-
PNP/13/GS/1084 Coker Kero-1
PNP/13/GS/1085 Coker Kero-2
PNP/13/GS/1086 Coker Kero-3

NATURE OF BASE FLUID/ADDITIVES IN THE SAMPLES: - **No. of Samples: 03**

RESULTS **TECHNIQUE(S): ^{1}H-NMR**

The analysis and distribution of olefins in the above coker kero samples are as follows-

Sample No	Total Olefin Content (wt%)	Distribution of Olefin (wt%)					Aromatics
		α-Unsubstituted	α-Substituted	Internal Unsubstituted	Internal Substituted	Others	
PNP/13/GS/1084 Coker Kero-1	19.4	6.8	1.8	6.6	4.2	-	25.4
PNP/13/GS/1085 Coker Kero-2	33.2	12.8	3.6	10.0	6.8	-	20.6
PNP/13/GS/1086 Coker Kero-3	39.0	14.5	4.8	10.4	7.5	~1.8	20.5

REPORTING SCIENTIST
(Dr. Sujit Mondal)
RO/ NMR

SRO / NMR

CRM (AD)

DGM (AD)
DGM (P&P)

Dr. Gurmeet Singh (DM/P&P)

Annexure II

Report of proton NMR analysis of adduct recovered product

MOLECULAR SPECTROSCOPY GROUP
NMR ANALYSIS REPORT

REPORT NO. : AD //IR/NMR/2014/56
DATE: 16-04-2014

INDENT /GROUP: P&P
PROJECT/ACTION PLAN: Distribution of Olefins in adduct recovered samples-
PNP/13/GS/1166 AR-1
PNP/13/GS/1167 AR-2

NATURE OF BASE FLUID/ADDITIVES IN THE SAMPLES: - **No. of Samples: 02**

RESULTS **TECHNIQUE(S): ^{1}H-NMR**

The analysis and distribution of olefins in the above adduct recovered samples are as follows-

Sample No	Total Olefin Content (wt%)	Distribution of Olefin (wt%)			Aromatics
		α-Unsubstituted	α-Substituted	Internal Unsubstituted	
PNP/13/GS/1166 AR-1	20.53	11.36	0.21	8.96	0
PNP/13/GS/1167 AR-2	33.91	21.36	0.31	12.24	0

REPORTING SCIENTIST
(Dr. Sujit Mondal)
RO/ NMR

SRO / NMR

CRM (AD)

DGM (AD)
DGM (P&P)

Dr. Gurmeet Singh (DM/P&P)