DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

CONVERSION OF NONSTANDARD FUEL-OIL INTO USABLE FUEL VIA HYDROCRACKING PROCESS AND CHARACTERIZATION OF PRODUCT PROFILE

by
Lala MUSAYEVA

January, 2018
İZMİR

CONVERSION OF NONSTANDARD FUEL-OIL INTO USABLE FUEL VIA HYDROCRACKING PROCESS AND CHARACTERIZATION OF PRODUCT PROFILE

A Thesis Submitted to the
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M.Sc THESIS EXAMINATION RESULTS FORM

We have read the thesis entitled **“CONVERSION OF NONSTANDARD FUEL-OIL INTO USABLE FUEL VIA HYDROCRAKING PROCESS AND CHARACTERIZATION OF PRODUCT PROFILE”** completed by **LALA MUSAYEVA** under supervision of **PROF.DR. GÜLSİYE ÖZTÜRK ÜRÜT** and **PROF.DR. JALE YANIK** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Lala MUSAYEVA

CONVERSION OF NONSTANDARD FUEL-OIL INTO USABLE FUEL VIA HYDROCRACKING PROCESS AND CHARACTERIZATION OF PRODUCT PROFILE

ABSTRACT

The aim of this study is converting a petrochemical product/waste to a fuel by hydrocracking process. In petrochemical industries, some by-products or “off-spec” products are produced. Utilization of these products as fuel or chemical feedstock is important either in terms of environmental or economic sides. The “non-standard fuel oil” is a by-product of naphtha steam cracking (NSC) unit in a petrochemical complex. This by-product’s amount is about 4 percent of naphtha charged to system obtained from ethylene plant of Aliağa PETKİM facility and the annual yield of “non-standard fuel oil” is about 95000 tons.

In this study, the conversion of Aromatic Rich Cracked Fuel Oil (ARCFO or non-standard Fuel-Oil) to light petroleum products by co-processing in a refinery unit such as hydrocracking with heavy vacuum gas oil (HVGO) which is the feedstock of this unit was aimed. ARCFO was subjected to thermal and catalytic co-hydrocracking processes. ARCFO and the blends of ARCFO with HVGO were cracked in the presence of H_2. Hydrocracking reactions with or without catalysts were carried out at a 6.0 MPa initial hydrogen pressure at different temperatures of 400, 425 and 450°C for a reaction time of 60 min for ARCFO. The catalyst employed was commercial DHC-8 catalyst. The effects of catalyst and the temperature on the yield and properties of liquid product of ARCFO were investigated. Then these processes were carried out for the blends of ARCFO and HVGO in different ratios at 450°C under thermal and catalytic conditions. The liquid products were analysed by ^{1}H NMR and GC, and Br numbers of liquid products were determined. The asphaltene amounts of liquid products were determined and their properties were investigated by FT-IR and elemental analysis. Also the liquids were sorted out to aliphatic, aromatic and polar fractions and percentages of each other were determined. The aliphatic fractions of each sample were analysed by GC.

Keywords: By-product, Aromatic Rich Cracked Fuel Oil, hydrocracking

STANDART DIŞI FUEL OİL'İN HİDROKRAKİNG PROSESİYLE KULLANILABİLİR YAKITLARA DÖNÜŞTÜRÜLMESİ VE ÜRÜN PROFİLİNİN KARAKTERİZASİYONU

ÖZ

Bu çalışmanın amacı hidrojenle parçalama işlemi ile bir petrokimyasal atığı kullanılabilir bir yakıt haline dönüştürmektir. Petrokimya endüstrisinde standart dışı veya yan ürünler oluşmaktadır. Çevresel ve ekonomik açıdan bu ürünlerin kimyasal hammadde veya yakıt olarak kullanılması oldukça önemlidir. "Standart dışı Fuel Oil" bir petrokimya kompleksinin Nafta Buhar Parçalama (NSC) ünitesinin yan ürünüdür. Bu ürünün miktarı, Aliağa Petkim A.S.'de etilen fabrikasından elde edilen ve NSC ünitesine verilen naftanın yaklaşık olarak yüzde 4'ü kadardır ve yıllık "Standart dışı Fuel Oil" miktarı ise yaklaşık olarak 95000 tondur.

Bu çalışmada Aromatik yağın (ARCFO veya Standart dışı Fuel Oil) hidrokraking rafineri ünitesinde, bu ünitenin ham maddesi olan ağır vakum gaz yağı birlikte işlenerek hafif petrol ürünlerine dönüştürülmesi amaçlanmıştır. Katalizörle veya katalizörsüz hidrokraking tepkimeleri farklı sıcaklıklarda (400, 425 ve 450 °C) 60 dakika süreyle, 6.0 MPa başlangıç hidrojen basıncında ARCFO için gerçekleştirildi. Katalizör olarak ticari DHC-8 katalizörü kullanıldı. Katalizörün ve sıcaklığın sıvı ürünün verimine ve özelliklerine etkisi üzerine araştırmalar yapıldı. Ardından bu işlemler, farklı oranlarda ARCFO ve ağır vakum gaz yağı karışımı ile 450°C'de termal ve katalitik koşullarda gerçekleştirildi. Sıvı fazdaki ürünlerin ^{1}H NMR ve GC ile analizleri yapıldı ve Br sayısı belirlendi, sıvı ürünlerin asfalten miktarları belirlendi ve asfaltenlerin özellikleri FT-IR ve elementel analiz sonuçları ile aydınlatıldı. Ayrıca, asfaltenden ayrılan (deasfaltlanmış) sıvı kısımları, kolon kromatografisi yardımıyla alifatik, aromatik ve polar fraksiyonlara ayrıldı ve her kombinasyonun yüzdeleri hesaplandı. Tüm örnekler için alifatik fraksiyonların GC ile analizi gerçekleştirildi.

Anahtar kelimeler: Yan ürün, aromatik yağ, hidrokraking

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CHAPTER ONE
INTRODUCTION

1.1 Aromatic Rich Cracked Fuel Oil (ARCFO)

Some of the materials in petroleum and petrochemical industries are named as by-products or “off-spec” products (Ozkan, Yanik, Sağlam&Yüksel, 1999), (Cakici, Yanik, Ucar, Karayıldırım&Anil, 2004). One of them is Aromatic Rich Cracked Fuel Oil (ARCFO) which is the off-spec product of Naphtha Steam Cracking (NSC) process. This product is obtained from NFC plant of Petkim Holding Co. in Aliağa in Izmir (Ozel, A., 2017). Approximately 4 % of the feedstock charged to the Naphtha Steam cracking unit is converted to ARCFO. Nearly 3000 MT naphtha is charged to system per day which means 120 MT ARCFO is produced daily. A few quantities of Aromatic Rich Cracked Fuel Oil is used as a feedstock of carbon black generation in Turkey currently (Ozkan etal., 1999).

1.2 Heavy Vacuum Gas Oil (HVGO)

HVGO (Heavy Vacuum Gas Oil) is produced by the Vacuum Distillation Unit, through the separation of the bottom fraction of the atmospheric distillation column (Dik, Klimov, Koryakina, Leonova, Pereyma, Budukva, Gerasimov&Noskov, 2014), (Bezergianni, Kalogianni&Vasalos, 2009), (Karayıldırım, Yanik, Uchar, Saglam&Yuksel, 2001). It is a heavy and viscous product and is only used as an intermediat (Ozkan et al, 1999).

1.3 Cracking

Crude oil consists of long and short chain hydrocarbon molecules (Gray, 1994), (Castañeda, Muñoz&Ancheyta, 2012). If long chain hydrocarbons are present in fuels they can cause carbonisation during combustion. Cracking, hence the name is a unit of petroleum refinery in which very large hydrocarbon molecules are cracked into smaller hydrocarbon productions. The cracking processes are carried out at high temperatures in the absence of catalyst or at lower temperatures in the presence of catalyst. The heavy fractions of crude oil are feedstock for cracking units. By cracking process, the heavy fractions can be converted into useful liquid and gas fuels.

1.3.1 Thermal Cracking

The thermal cracking is the oldest and the simplest unit in the refinery (Raseev, 2003). The petroleum fractions having high boiling point over 450°C and up to 750°C are used as a feedstock in this process. The characteristics of final products vary depending on the process conditions (temperature, initial pressure). The large hydrocarbon molecules are thermally cracked into smaller molecules via radicalic mechanism (Gray, 1994). Besides cracking, larger molecules are also formed via re-polymerization reactions depending on residence time. Generally, the residue of atmospheric and vacuums distillation is feedstock in thermal cracking unit. In modern refineries, thermal cracking has two major applications. These are visbreaking and delayed coking. Visbreaking can be called the slight form of thermal cracking. The viscosity of heavy gas oil is decreased via this process. Delayed coking is very strong form of thermal cracking than visbreaking. The main product of delayed coking is the petroleum coke (petro coke).

1.3.2 Catalytic Cracking

One of the main units of refinery is catalytic cracking unit where heavy hydrocarbon fractions are converted to high-quality liquid fuels (Jens, 2012), (Šimácek&Kubicka, 2009). High molecular weight feedstocks were cracked to lower molecular weight products via catalyst (Bacon&Henke, 1961), (Lavrenov, Bogdanets, Chumachenko&Likholobov, 2011). Use of a catalyst allows lower reaction temperatures to be used. There is a large variety of process designed for catalytic cracking (Castañeda et al., 2012). The final products are gases, gasoline blending components, light and heavy cycle oil and coke. A widely range of residues are catalytically cracked in this unit to produce liquid fuels.

Catalytic cracking process was developed in 1920’s for upgrading of residues (Mohanty, Kunzru&Saraf, 1990). Generally light gas oil (from the vacuum distillation section) is used as a feedstock of catalytic cracking (Raseev, 2003).

During the catalytic cracking the following processes take place:

- Cracking
- Isomerisation
- Dehydrogenization
- Hydrogen transfer
- Cyclization
- Condensation
- Alkylation and dealkylation

And the chemical steps of catalytic cracking are as following (Discovery Store channel, nd):

Paraffin → shorter paraffin + olefins
Alkyl naphthene → naphthene + olefin
Alkyl aromatic → aromatic + olefin
Multiringnaphthene → naphthene with fewer rings

1.3.3 Hydrocracking Process

In petroleum refineries, hydrocracking is used for converting the high-boiling hydrocarbons into more valuable lower-boiling products (Citizendium, 2013), such as high grade gasoline, diesel and jet fuel. In hydrocracking unit petroleum feedstock was upgraded by adding hydrogen, removing impurities, and cracking to a desired boiling range. The best benefit of this unit is to require less investment to post-treatment of products (Bezergianni, Kalogianni&Vasalos, 2009). The other benefit of hydrocracking process is having a large feedstock possibility. The feedstock is ranging from heavy vacuum gas oils to atmospheric gas oils. Products usually range from heavy diesel to light naphtha. Any sulfur and nitrogen compounds present in the feedstock are also hydrogenated, forming hydrogen sulfide and ammonia (David&Peter, 2006). There are a number of different hydrocracker process equipment configurations. Single stage hydrocracker, single stage hydrocracker with recycle and two- stage hydrocracker are the most used configuration.

1.3.3.1 Hydrocracking Catalyst

Hydrocracking catalyst is a bi-functional catalyst with cracking and hydrogenation-dehydrogenation functions (Özkan et al, 1999). Cracking activity is supplied by acid sites provided. The hydrogenation-dehydrogenation functions are provided via metal side of the catalyst. The metal side of the catalyst affects the cracking reactivity of the feedstock and reduces the coke formation. Hydrocracking catalysts with zeolite base have naphtha selectivity, better cracking activity and easy regeneration characters (Gosh, 2006).

1.3.3.2 Effects of Operating Parameters

The operating parameters affecting the results of hydrocracking are the temperature, reaction time and initial H_2 pressure (Kim et al. 2013). Increase of the temperature causes an increase in cracking reaction speed on acid sites, also displacement of the hydrogenation reactions equilibrium toward dehydrogenation. The aromatic molecules hydrocracking is limited at very high temperatures. Changing the pressure yields evidence in dehydrogenation-hydrogenation reactions equilibrium which takes place on the metallic sites (Raseev, 2003). The increase of the pressure causes the increase of the amount of saturated products. The reason of this is the increasing of the partial pressure of hydrogen. It means these changes are good for the quality of jet fuels.

1.4 Asphaltenes

In recent years, the appearance of the heavier crude oils in refinery feedstocks has become an approved norm (Francisco&Speight, nd). These feedstocks are rich with asphaltene, which are inappropriate in refinery process. They may cause coke lay-down and catalyst deterioration. Because of having high heavy metal and sulfur contents and high potential to produce coke, the asphaltene is named as the “bad guys” in upgrading processes (Martha, Chacon, Cristian, Jorge&Andrea, 2015). Asphaltenes are the carbonaceous origin of petroleum or oil shale. The asphaltenes are insoluble in aliphatic solvents such as n-heptane, n-pentane (Sun, Zhi-Hui, Dong, Hai-Xai Pan-Pan Xue-Kun, Wen-Hong, Yong-Hong, 2015). During usage of petroleum products, asphaltene causes different problems such as blocking pipes. Also the occurrence of asphaltene causes deactivation of the catalyst during the hydrotreating processes. Because of these reasons, isolation and structural characterizations of asphaltene gets more noticeable. Various molecular weight of asphaltene are related to various asphaltene sources and properties.

Asphaltenes are complex mixtures and they have molecular structure generally consisting of pericondensed aromatic rings with heteroatoms existing in the form of functional groups such as sulfide, sulfoxide, thiophene, hydroxyl, carboxyl, carbonyl, pyrrol, pyridine and so on (Martha etal, 2015.). Heavy metals like V and Ni were generally found in the metal complex form such as petro-porphyrins in asphaltenes.

1.4.1 Deasphalting

Petroleum based materials such as atmospheric and vacuum residues, heavy vacuum gas oil is subjected to the deasphalting process to separate the asphaltene and produce deasphalted liquid (deasphalted oil) (Sheu et al, 2002). Also resins are produced by this way. The obtained deashpalted liquid could be used as a feedstock in hydrocracking process or other units of refinery (ShanShan, Chuang, ChunMing, SuoQi&Quan, 2013). Deasphalting is consisting of the reflux of the feedstock with a convenient solvent. The reflux is performed at the boiling point of the solvent. Asphaltene is the insoluble part of liquid in this solvent.

1.4.2 Asphaltene Characterization

Different analytical methods are used to follow the molecular changing of asphaltene, such as Nuclear Magnetic Resonance (NMR), X-ray diffraction (XRD), and Infrared Spectroscopy (IR) (Martha et al, 2015), (Al-Muhareb, Morgan, Herod&Kandiyoti, 2011). Because of its applicability, rapidity, low price, simplicity to sample preparation, the Fourier transform infrared (FTIR) spectroscopy is more pertinent for characterizations of asphaltenes (Coelho, Hovell, Moreno, Souza&Rajagopal, 2011). Sometimes percentages of aromatic and aliphatic hydrogen in asphaltenes are calculated according to peak areas. Elemental composition of carbon, nitrogen, sulfur and hydrogen content of asphaltenes can be detected by elemental analysis (Sun, Li, Ma, Tian, X.Li, W.Li& Zhu, 2014). Also NMR spectroscopy is considered as a useful method for characterizations of asphaltenes due to being powerful and highly useful (Coelho et al, 2011). In addition, NMR has multi-pulse, multi-nuclei, multi-directional capability. It provides structural information.

Asphaltene's qualitative and quantitative analyses are also available by UV-vis spectroscopy (ShanShan, Chuang, ChunMing, SuoQi&Quan, 2013). Moreover, Atomic force microscope (AFM), Quartz crystal microbalance (QCM), Secondary ion mass spectroscopy (SIMS) is used to characterize the asphaltene's surface.

1.5 Literature review

Mar Jaurez et al (2014) experimented catalytic hydrocracking process of residues in presence of a liquid catalyst. They proposed the use liquid catalyst which has a strong acid function for cracking heavy hydrocarbons and a hydrogenation function to promote sulfur and nitrogen removal.250 g of the Vacuum residue which obtained directly from a refinery was hydrocracked with 1 g of liquid catalyst (About 50 ml of demineralized water + 1 g H_2SO_4 + 5 g NH_4 $6Mo_7O_{24}$ $4H_2O$ + 10 g $NiSO_4$ $6H_2O$) in a 500 cm^3 Parr reactor. The reactor hydrogen pressure was 100 $kg/cm^2$and the experiments were performed at 380, 390, 400, 410, 420°C and the process continued for 1 h. On the other side, thermal cracking and hydrocracking of the residue in the presence of Ni-Mo catalyst were conducted at the same conditions and the results were compared.

Vacuum residue was comprised by hydrocarbons which were very large and have complex molecules with more than 40 carbon atoms which boil above 540°C and it was solid at room temperature. After hydrocracking process in the presence of the liquid catalyst, those hydrocarbons were transformed into a small amount of gases (less than 4 wt. % at the highest reaction temperature) and liquid hydrocarbons boiling below 540° C. at 380° C the conversion increased from 40.3 wt. % to 65.5 wt. % at 420° C, from this, less than 10% was transformed to methane–ethane, 6% to hydrogen sulfide and about 86% into liquid distillates. In all the experiments, the main product was liquid fuel, which had lower density and viscosity than the residue. The liquid product had a boiling range from 160°C to 540°C. As the reaction temperature increased correspondingly the liquid yield decreased while the density and viscosity of liquid product decreased.

Bezergianni et al. (2009) studied the co-processing of vegetable oil with vacuum gas oil to produce biofuel by hydrocracking. In that study, three different feedstocks were used; raw sunflower (bio-based), straight run VGO and hydrotreated VGO (fossil based). Also three different commercial hydrocracking catalysts were tested. These were A-mild and B, C-severe hydrocracking catalysts. Hydrocracking of vegetable oil and vacuum gas oil-vegetable oil mixtures (70/30 v/v and 90/10 v/v VGO/vegetable oil) were performed at different temperatures (350, 370, 390°C) for 1.5 h with catalysts. In co-processing of vacuum gas oil-vegetable oil mixtures, the higher conversion was obtained from blend containing higher vegetable oil. Hydrocracking of hydrotreated vacuum gas oil-vegetable oil blends resulted in higher conversion than that of straight run VGO-vegetable oil blends. In addition, the poorest heteroatom removal (S and N) was observed in non-hydrotreated VGO-vegetable oil mixtures. These results showed the necessity of a pre-treatment step for VGO prior to the co-processing with vegetable oil. The highest conversion was obtained by using catalyst A, whereas the best diesel selectivity was obtained from catalyst B and the higher naphtha selectivity from catalyst C.

Huber at al. (2007) investigated the effects of reaction conditions on the hydrocracking/hydrotreating of heavy vacuum oil, sunflower oil and the blend of sunflower oil-heavy vacuum oil. Hydrocracking/hydrotreating experiments were performed in a fixed bed reactor with 50 bar H_2 pressure at 300-450°C in presence of a sulfide $NiMo/Al_2O_3$ catalyst. As the result of their experiment they concluded that bio-liquid alkanes can be produced by hydrotreating of vegetable oils and vegetable oil–heavy vacuum oil (HVO). The reaction road involved hydrogenation of the C=C bonds, decarbonylation, decarboxylation and hydrodeoxygenation reactions. In case of hydrotreating of pure vegetable oil, they obtained a yield of straight chain C_{15}–C_{18} alkanes of 71% on a carbon based (which is 75% of the maximum theoretical yield for these products). Addition of the vegetable oils at low percentage into HVO led to an increase in the yield of straight chain alkanes. The selectivity to decarbonylation plus decarboxylation products increases with increasing temperature and increasing sunflower oil content (for the HVO–sunflower oil mixture). The addition of sunflower oil into HVO did not have effect on the desulfurization of HVO. They concluded that vegetable oil sand blend containing vegetable oil–HVO could be converted into liquid alkanes by hydrotreating.

Ozkan et al. (1999) investigated upgrading one of the petroleum byproduct. They hydrocracked aromatic-cracker fuel oil (ARCFO) with zeolite catalyst loaded one-metal (Co or Mo) and two-metal (Co/Mo) oxide. Experiment were carried out in a shaking-type autoclave, ARCFO and catalyst were loaded into autoclave and hydrocracked at 375-450 °C under 10 MPa initial H_2 pressure for 90 min. They investigated the fuel and chemical characteristics of liquid product obtained from hydrocracking. The loading of the metal oxide on zeolite increased the cracking and hydrogenation performance of the catalysts. Molybdenum loaded zeolite showed more hydrogenation activity, whereas cobalt loaded zeolite had a good cracking effect. They compared the effect of one-metal-loaded catalysts with two-metal-loaded catalysts. And they concluded that the cracking effect of two-metal catalysts was much more than one-metal catalysts. However, the hydrogenation performances of one-metal and two-metal catalysts were approximately equal to each other and the type of the catalyst was not effective on the distribution of aliphatic, aromatic, and polar fractions.

In another study, Sahu et al. (2015) investigated the production of high value transportation fuels from vacuum residue (VR) and heavy oils by hydrocracking process. They used heterogeneous supported metal catalyst, water soluble catalyst, and oil soluble homogeneously dispersed catalysts. They observed that the heterogeneous solid powder catalysts had low catalytic activity (due to their lower dispersion in the reactor), while the homogeneous catalysts showed high catalytic activity (due to their highly dispersion). They concluded that hydrocracking with homogeneous catalysts in slurry-phase type reactor is a promising technology to convert low value feeds, such as heavy oil and VR, into high value transportation fuels and petrochemical products.

Dik et al. (2014) studied hydrocracking of vacuum gasoil with Ni, Mo supported pAl_2O_3, ASA-Al_2O_3 andY-Al_2O_3catalysts. Hydrocracking of vacuum gasoil in staked bed with different catalyst gave following results: the NiMo/Al_2O_3catalyst had the maximum selectivity to diesel fuel. The yield of diesel fuel did not exceed 50 wt.% with NiMo/Y-Al_2O catalyst. At 400°C, hydrocracking with NiMo/ASA-Al_2O_3 had an optimal ratio of activity to selectivity for the production of diesel fuel and provided the diesel fuel yield by over 60 wt.%.

CHAPTER TWO
EXPERIMENTAL SECTION

2.1 Materials

Aromatic Rich Cracked Fuel Oil which is a by-product of Naphtha Steam Cracking unit was purchased from Petkim, Aliaga, Izmir. Heavy vacuum gas oil (HVGO) was provided by TÜPRAŞ Petrochemical Holding Co. located in Izmir. HVGO is a feedstock of hydrocracking unit in Aliaga refinery, Izmir. The DHC-8 is a commercial shapeless bifunctional catalyst having both hydrotreating and hydrocracking functions. Silica Gel (0.063-0.200mm) and Aluminium Oxide (particle size 0.1-0.2 mm) were purchased from MERCK. Solvents (n-hexane, toluene and methanol) were of technical purity and were distilled before use.

2.2 Hydrocracking Operation

Experiments were carried out in a shaking-type autoclave (100 cm^3) according to literature (Ozkan, Yanik, Saglam&Yuksel, 1998), (Olukcu, Yanik, Saglam, Yuksel&Karaduman, 1999). Two sets of experiments were performed (Table 2.1). In the first set of the typical run, homogeneous mixture of ARCFO was loaded into the autoclave. If the process was catalytic, the catalyst was also added to the sample. The catalyst and feedstock ratio was 1/10 in all experiments. Previously the autoclave was sealed and purged with hydrogen gas. Thereafter, it was pressurized to 6 MPa with hydrogen. The hydrocracking reactions were performed at temperatures of 400, 425 and 450 °C and for a reaction time of 60 min. At the end of the reaction time, the reactor was cooled to room temperature. The gas content of the autoclave was collected using Tedlarbag. The reactor content was filtered by membrane filter to separate the liquid product, and then the residues in reactor were withdrawn by washing with methylene chloride. The residue on the filter paper was consisted of the coke (insoluble in CH_2Cl_2) and catalyst (if the process was catalytic). The liquid and coke amount were determined by weighting and the gas amount calculated by difference.

The same procedures were applied for the blends of ARCFO and HVGO in different percentages at constant temperature of 450°C. The hydrocracking processes are given at Table 2.1

Table 2.1 The hydrocracking runs

Sample	**Temperature**	**Catalyst**
ARCFO	400	None
ARCFO	425	None
ARCFO	450	None
ARCFO	400	DHC-8
ARCFO	425	DHC-8
ARCFO	450	DHC-8
HVGO	450	None
HVGO	450	DHC-8
ARCFO/HVGO(25/75)	450	None
ARCFO/HVGO(25/75)	450	DHC-8
ARCFO/HVGO(50/50)	450	None
ARCFO/HVGO(50/50)	450	DHC-8

2.3 Analysis of the Gas Products

Gas products were analysed by a refinery gas analyser (Gas Chromatograph Agilent 7890A). The system has five valves and three detectors. The FID channel is configured to analyse the hydrocarbons from C_1 to C_5. The first TCD channel is configured to analyse fixed gases which include CO_2, CO, O_2 and N_2. The second TCD channel is dedicated to analyse hydrogen only.

2.4 ^{1}H NMR Analysis

The liquids were investigated by ^{1}H-NMR on Varian VNMRJ 400 NMR spectrometer at 400 MHz using $CDCl_3$ as solvent.

2.5 SIMDIS Analysis

Boiling point distribution of liquid products obtained from hydrocracking were analysed according to ASTM D2887-16 by gas chromatograph with a flame ionization detector (GC-FID) using a Hewlett–Packard 6890 GC. An HP-5 capillary column (30mm length × 0.32 mm diameter coated with cross-linked 5% phenylmethyliloxane at a thickness of 0.25 mm) was used in the GC system. The cumulative volumes of heavy gas oil, light gas oil, heavy naphtha and light naphtha in the liquid products were determined according to literature (Karagoz, Yanik, Ucar & Song, 2002).

2.6 Bromine Number

The Bromine Number is an indication of the aliphatic unsaturation present in petroleum samples (Borrull, Cerda, Podriguez&Torres, 1989). The Bromine number value is the symbol of the bromine reactive constituents. Br number was determined according to ASTM D1159 by Mettler Toledo T70 Electromagnetic Titrator.

2.7 Deasphalting

Asphaltene amounts were determined according to ASTM D6560. Separation of hydrocracking liquids into asphaltene and deasphalted oil fractions were carried out by heating the blend of the liquid product and n-hexane (1 g liquid: 30 ml n-hexane) under reflux for 1 hour. At the end of reflux, the hot mixture was filtered through membrane filter. Residue on the filter paper (asphaltene) was washed with hot n-hexane until the solvent became colourless. After drying the residue at 110 °C for 3 hours, the asphaltene amount was determined by weighing. Filtrate was evaporated under vacuum to remove n-hexane. The n-hexane soluble (de-asphalted liquid) were sealed to further processing (column chromatography).

2.8 Elemental Analysis

Elemental analysis (CHNS) of the asphaltenes was carried out in LECO CHNS 932 Elemental Analyst testing according to ASTM D5291-96 standard.

2.9 FTIR Analysis

The infrared spectrum of asphaltene was obtained by using a Perkin Elmer Spectrophotometer. Pellets of the asphaltene samples were prepared by mixing and grinding few mg (not more than 300 mg) of dry IR-grade KBr and asphaltene samples about 1-2% of KBr.

2.10 Liquid Absorption Chromatography

The deasphalted liquid products were separated by liquid adsorption chromatography on a glass column (50 cm × 2.1 cm). The lower part was packed with 14 cm silica gel (particle size 0.063-0.200 mm) and the upper part was packed with 6.5 cm neutral aluminium oxide. 2 g of the deasphalted liquid product was dissolved in n-hexane (3 mL per 1 g of sample) and applied to the adsorbent column wetted with n-hexane. The samples were eluted with the following series of mobile phases: First in order to separate the aliphatic content 250 mL of n-hexane was used and collected. Then 250 mL of toluene was applied for separation of aromatic fractions and finally by 250 mL of methanol the polar fractions were collected. After stripping off the solvent by a rotary evaporator the products obtained were weighed and percentages of aliphatic, aromatic and polar fractions were calculated.

2.11 Analysis of aliphatic fractions by GC

The aliphatic fractions were analysed by gas chromatography with flame ionization detector (Hewlett-Packard 6890 GC).

CHAPTER THREE
RESULTS AND DISCUSSION

3.1 Hydrocracking Yields

In first group experiments, the hydrocracking of ARCFO was carried out in presence and absence of catalyst at different temperatures (Figure 3.1). The liquid yields were given in Figure 3.2. The liquid yield was considerable decreased by increasing the temperature from 400 to 425°C, and then almost unchanged. The catalyst affected the liquid yield (leading to decrease in liquid yield) only at 400°C of the hydrocracking.

In second group experiments, co-processing of ARCFO with HVGO decreased the liquid product yield in comparison to hydrocracked HVGO alone (Figure 3.3 and Figure 3.4). The experimental yield was less than the theoretical (predicted) yield, especially more evident for the blend 50% ARCFO + 50%HVGO due to the formation of gas products. Also, the catalyst decreased the liquid yield only for this blend. In case of 25 % ARCFO and 75 % HVGO experimental yield is similar to the theoretical one. In general, the liquid yield of blends is lower than expected which can be attributed to the fact that the presence of ARCFO improved the gas product formation during the hydrocracking.

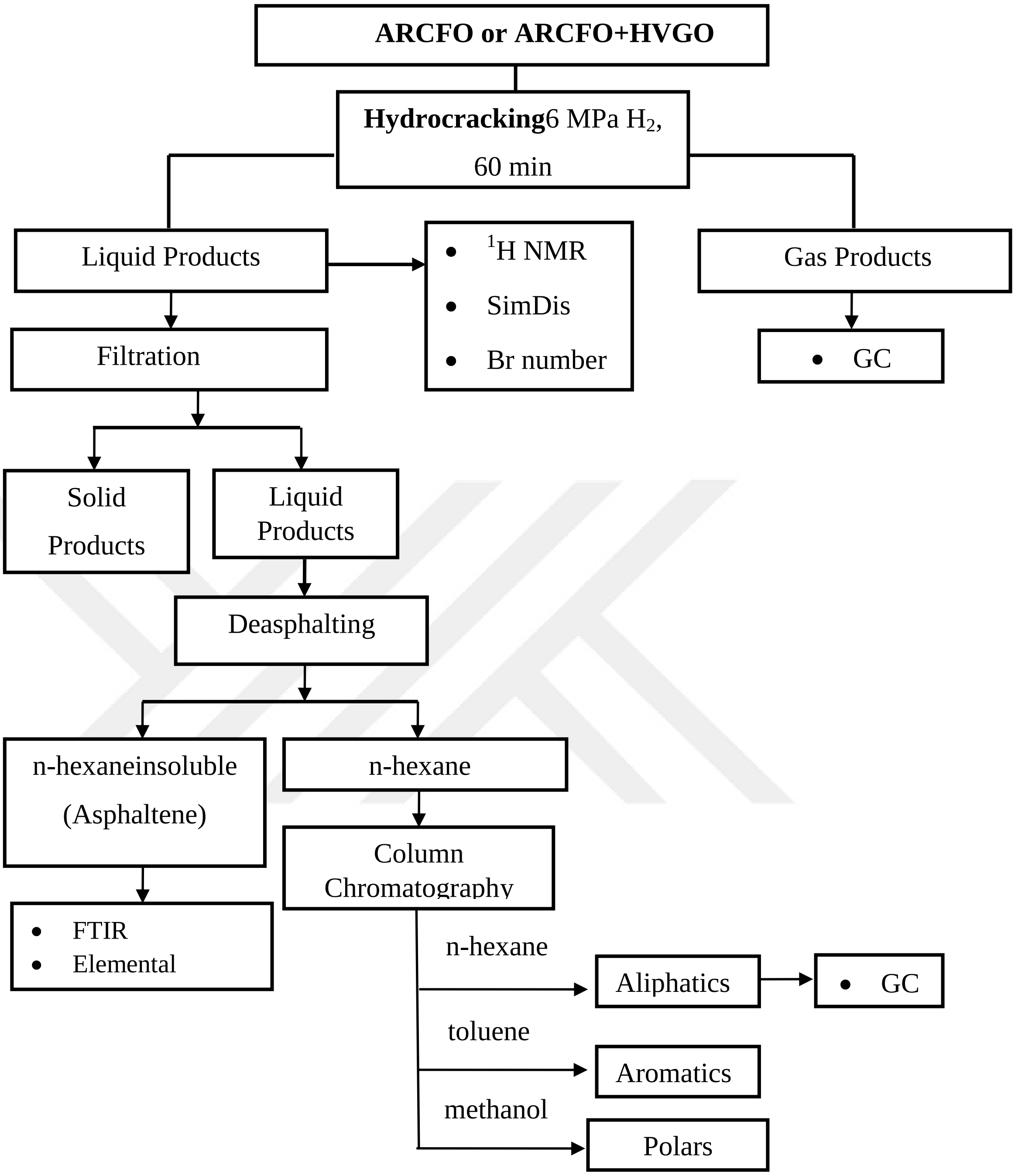

Figure 3.1 Sequence of experimental procedures and product analysis

In two group hydrocracking experiments, hydrocracking yielded less amount of coke.

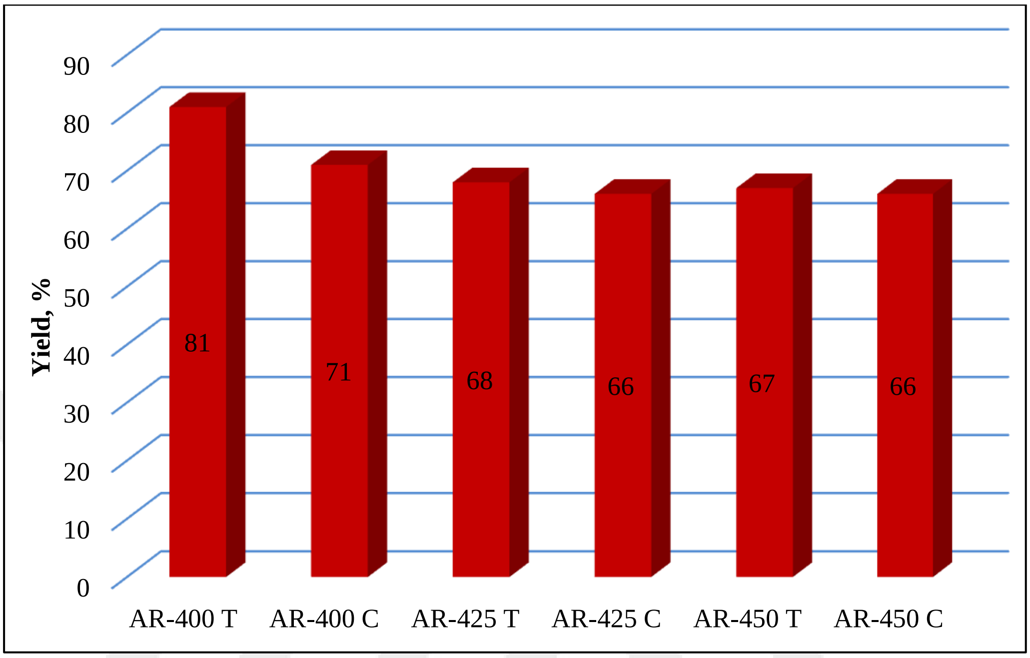

Figure 3.2 The yield of liquid products obtained from hydrocracking of ARCFO at different temperatures (at 6 MPa H_2 pressure, 60 min): AR-400-T -Hydrocracked ARCFO at 400°C thermal; AR-400-C -Hydrocracked ARCFO at 400°Ccatalytic; AR-425-T -Hydrocracked ARCFO at 425°C thermal; AR-425-C -Hydrocracked ARCFO at 425°C catalytic; AR-450-T -Hydrocracked ARCFO at 450°C thermal; AR-450-C -Hydrocracked ARCFO at 450°C catalytic

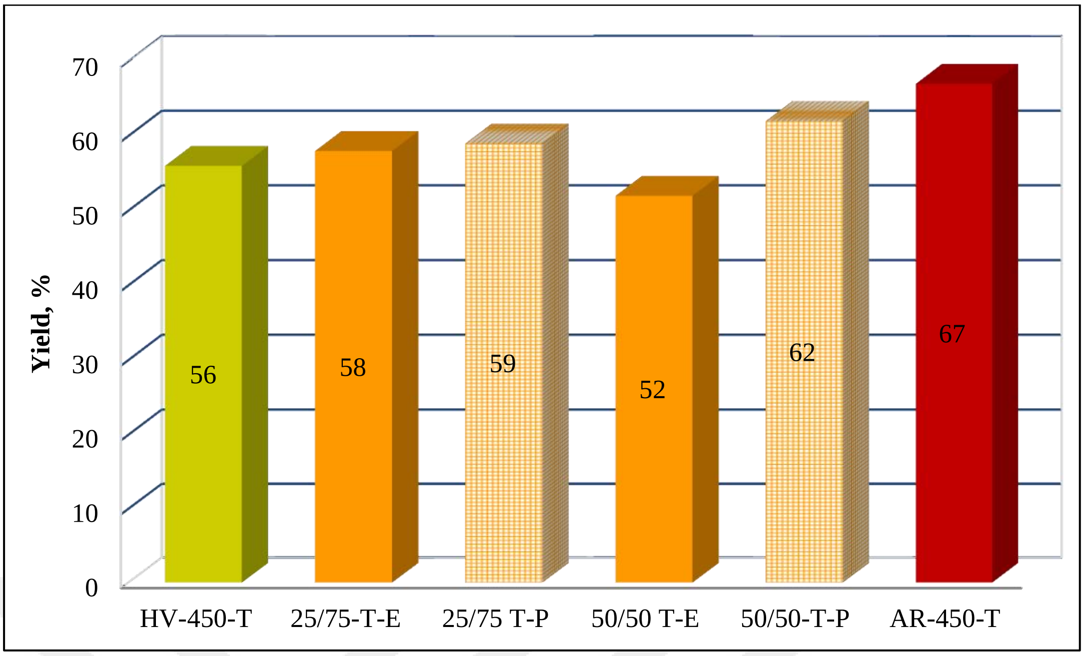

Figure 3.3 The yield of liquid products obtained from hydrocracking of the blends of ARCFO and HVGO in thermal condition (HV: Heavy Vacuum Gas Oil; AR: Aromatic rich Cracked Fuel Oil; AB/CD refers to ARCFO%/HVGO%, T: thermal, E: experimental, P: predicted; hydrocracking conditions: 450°C, 60 bar H_2, 60 min): HV-450: Hydrocracked HVGO at 450°C; AR-450: Hydrocracked ARCFO at 450°C

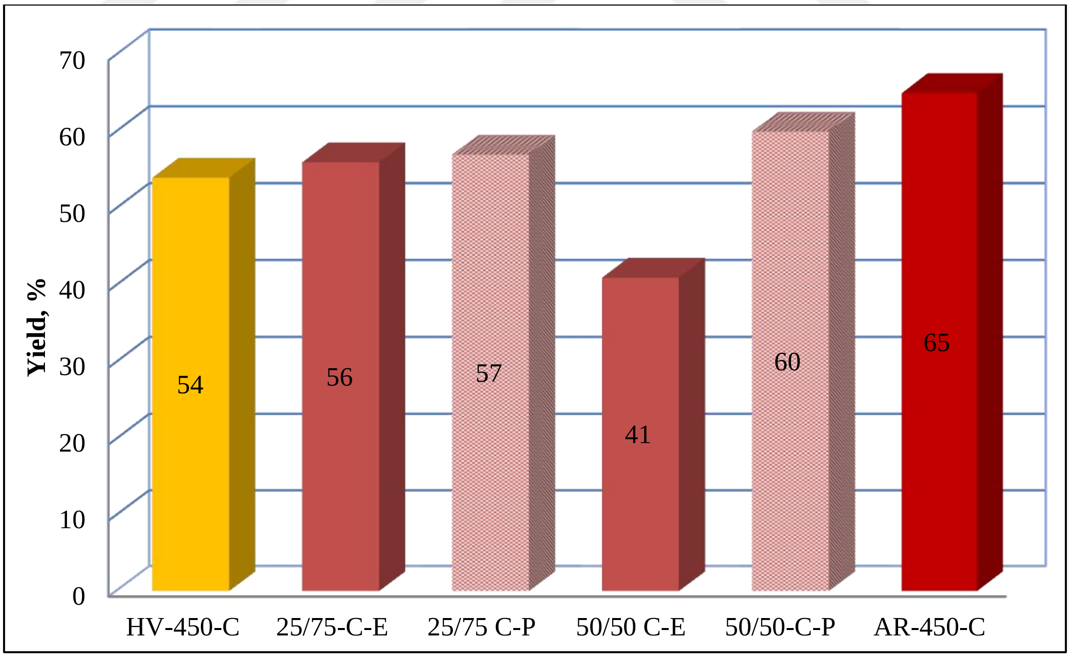

Figure 3.4 The yield of liquid products obtained from hydrocracking of the blends of ARCFO and HVGO in catalytic condition (HV: Heavy Vacuum Gas Oil; AR: Aromatic rich Cracked Fuel Oil; AB/CD refers to ARCFO%/HVGO%, T:thermal, C:catalycal, E: experimental, P: predicted; hydrocracking conditions: 450°C, 60 bar H_2, 60 min): HV-450:Hydrocracked HVGO at 450°C; AR-450:Hydrocracked ARCFO at 450°C

3.2 Liquid Product Properties

3.2.1 GC Analyst of Liquid Product (SIMDIS)

The simulated distillation curves of liquids from catalytic and non-catalytic hydrocracking of ARCFO at 400-425-450°C are given in Figure 3.5. The fractions of liquids were classified as naphtha (<204°C), light gas oil (204-343°C) and heavy gas oil (>343°C) according to petroleum fractions and the percentages naphtha, light gas oil and heavy gas oil fractions of liquids obtained from ARCFO hydrocracking are given in Figure 3.6.

Hydrocracking of ARCFO at high temperatures (450°C) increased the amount of heavy gas oil and naphtha fraction. Catalyst has not significant effect at high temperature. At 400°C and 425°C using catalyst increased amount of heavy gas oil fraction of hydrocracked ARCFO.

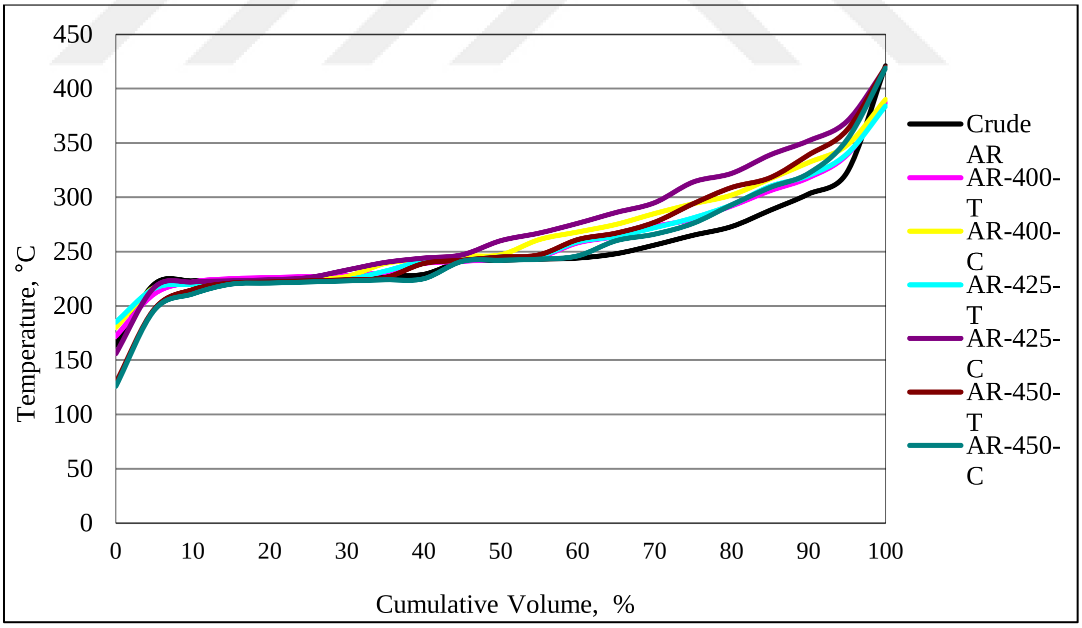

Figure 3.5 Simulated distillation curves of thermal hydrocracked of aromatic rich cracked fuel oil in different conditions: (HV: HVGO, AR:ARCFO, T:thermal, C:catalycal, hydrocracking conditions: 450°C, 60 bar H_2, 60 min): AR-400:Hydrocracked ARCFO at 400°C; AR-425: Hydrocracked ARCFO at 425°C; AR-450: Hydrocracked ARCFO at 450°C

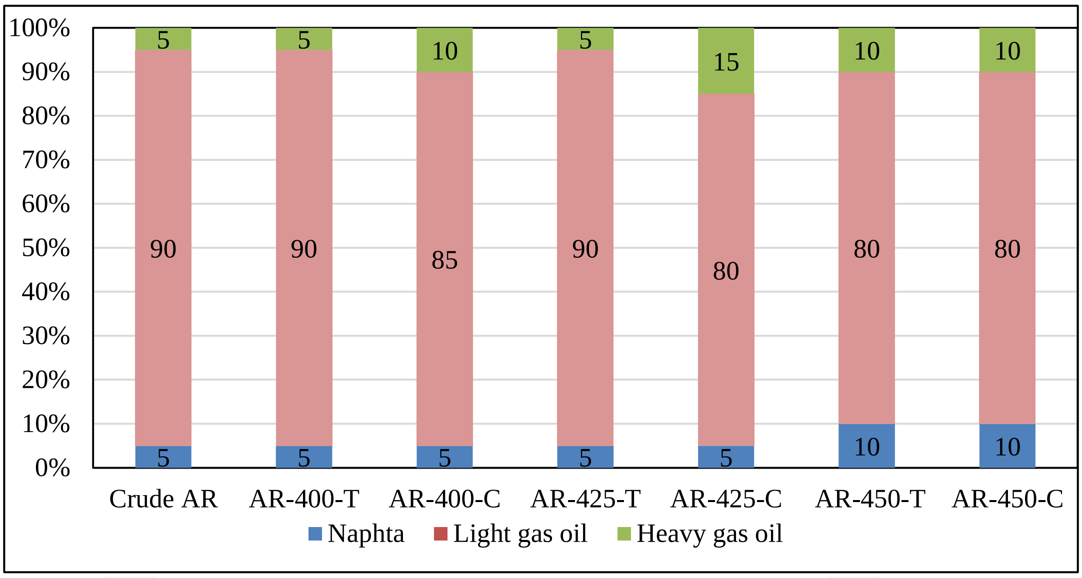

Figure 3.6 Through boiling point, percentages of liquids obtained from thermal hydrocracking as naphtha, light gas oil and heavy gas oil fractions. (HV: HVGO, AR: ARCFO, T: thermal, C: catalytic, hydrocracking conditions: 450°C, 60 bar H_2, 60 min): AR-400: Hydrocracked ARCFO at 400°C; AR-425: Hydrocracked ARCFO at 425°C; AR-450: Hydrocracked ARCFO at 450°C

Simulated distillation curves of liquid products from thermal hydrocracking of ARCFO, HVGO and their blends at 450°C are given in Figure 3.7 and amount of naphtha, light gas oil and heavy gas oil fractions of these samples were given in Figure 3.8.

Adding ARCFO at the ratio of 25% to the HVGO decreased the heavy gas oil fraction in liquid product. In case of the blend of 50 % ARCFO and 50 % HVGO, the amount of naphtha fraction decreased and also heavy gas oil fraction almost absence while light gas oil fraction increased.

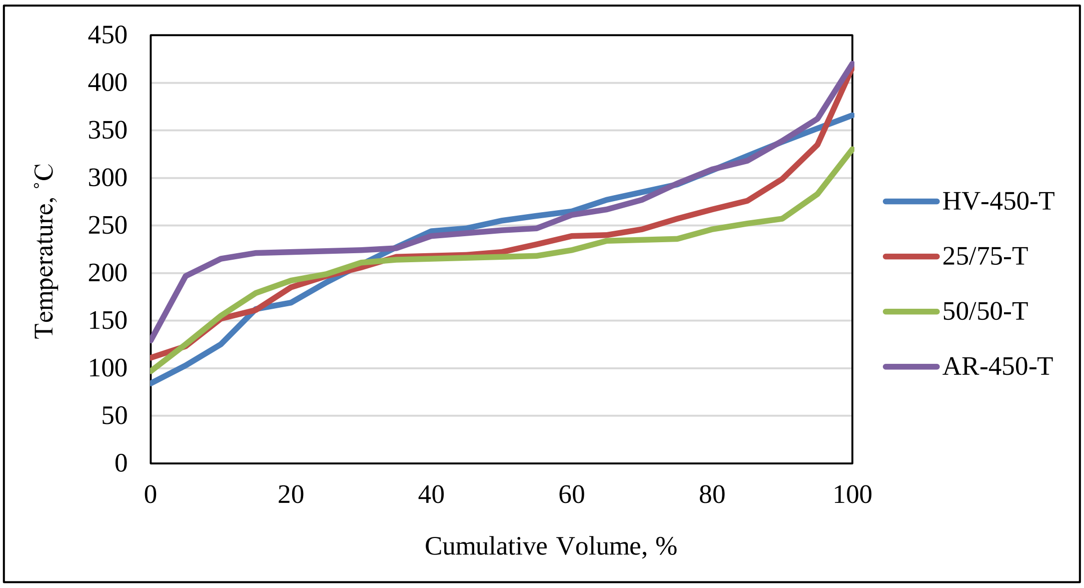

Figure 3.7 Simulated distillation curves of thermal hydrocracked of HVGO, ARCFO and blends of them in different amounts. (AB/CD refers to ARCFO%/HVGO%, T: thermal, C: catalytic, AR: ARCFO, HV: HVGO; hydrocracking conditions: 450°C, 60 bar H_2, 60 min): HV-450: Hydrocracked HVGO at 450°C; HV-450: Hydrocracked HVGO at 450°C; AR-450: Hydrocracked ARCFO at 450°C

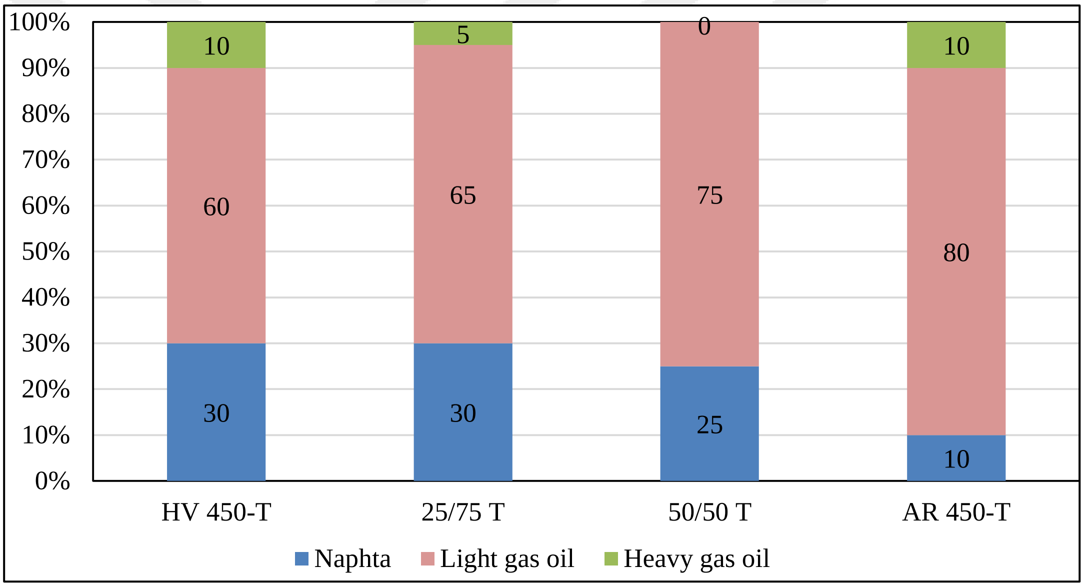

Figure 3.8 Through boiling point, percentages of liquids obtained from thermal hydrocracking as naphtha, light gas oil and heavy gas oil fractions. (AB/CD refers to ARCFO%/HVGO%, T: thermal, C: catalytic, AR: ARCFO, HV: HVGO; hydrocracking conditions: 450°C, 60 bar H_2, 60 min): HV-450: Hydrocracked HVGO at 450°C; AR-450: Hydrocracked ARCFO at 450°C

Simulated distillation curves of liquid products from catalytic hydrocracking of ARCFO, HVGO and their blends at 450°C are given in Figure 3.9 and the amount of naphtha, light gas oil and heavy gas oil fractions of these samples were given in Figure 3.10. The naphtha fraction increased as the percentages of ARCFO increase in blends, while the amount of heavy gas oil increased.

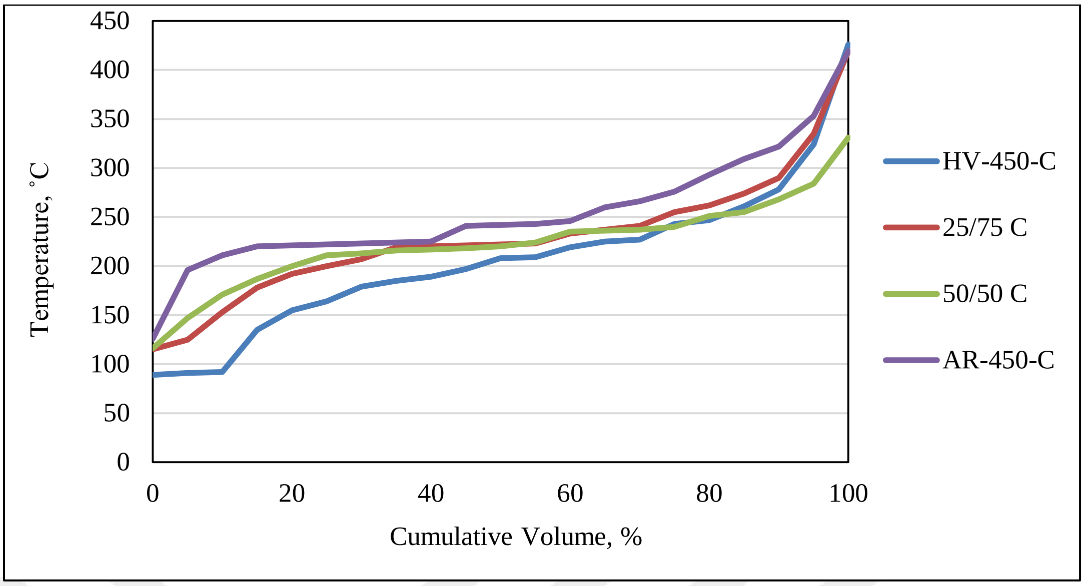

Figure 3.9 Simulated distillation curves of liquids obtained from catalytic hydrocracking of heavy vacuum gas oil, aromatic rich cracked fuel oil and blends. (AB/CD refers to ARCFO%/HVGO%, T: thermal, C: catalytic, AR: ARCFO, HV: HVGO; hydrocracking conditions: 450°C, 60 bar H_2, 60 min): HV-450: Hydrocracked HVGO at 450°C; AR-450: Hydrocracked ARCFO at 450°C

As a conclusion the catalyst decreased the amount of naphtha fraction. The reason of this was the naphtha fraction in liquid cracked in the presence of catalyst.

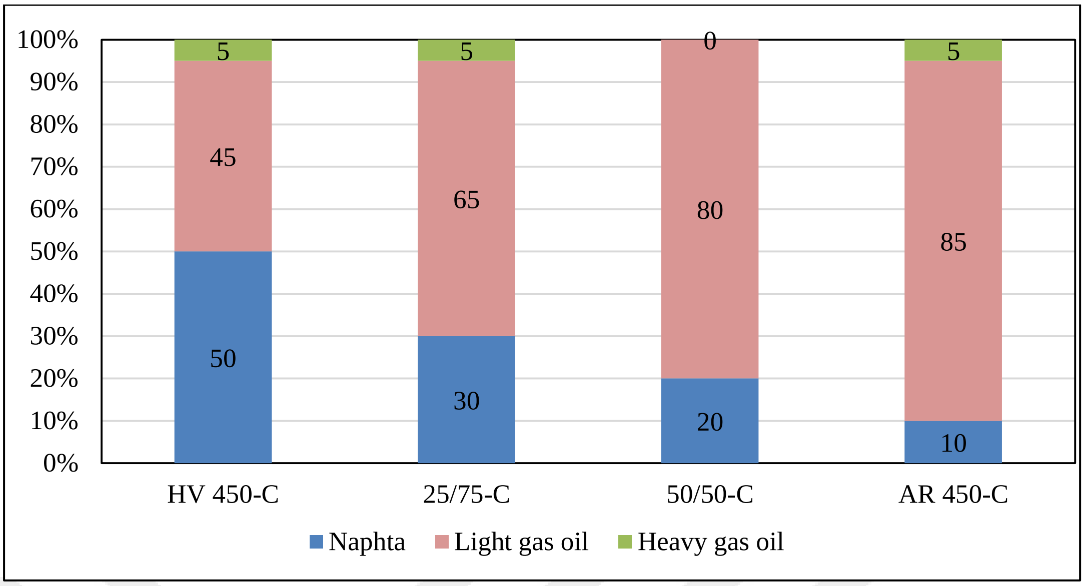

Figure 3.10 Through boiling point, percentages of liquids obtained from catalytic hydrocracking as naphtha, light gas oil and heavy gas oil fractions (AB/CD refers to ARCFO%/HVGO%, T: thermal, C: catalytic, AR: ARCFO, HV: HVGO; hydrocracking conditions: 450°C, 60 bar H_2, 60 min): HV-450: Hydrocracked HVGO at 450°C; AR-450: Hydrocracked ARCFO at 450°C

3.2.2 Hydrocarbon Types in Liquid Products

From ^{1}H NMR data insight for the structural changes accompanied by employing different temperatures in ARCFO liquids case and different ratios of ARCFO/HVGO blend liquids under thermal and catalytic conditions was provided. The effect of the temperature over the hydrocarbon contents of ARCFO liquid under thermal and catalytic treatment were given in Table 3.2. The catalyst caused decrease in aromaticity at low temperatures of 400˚C and 425˚C and an increase at 450˚C. In case of thermal conditions at low temperatures catalyst has insignificant effect over aromaticity, but at high temperature of 450˚C the aromaticity increased. At 400 ˚C under thermal conditions the paraffinic content increased while the catalyst decreased the paraffinic content slightly. At 425 and 450˚C, in the presence of the catalyst, the amount of paraffinic structures was similar to that of thermal conditions. As the temperature increased the paraffinic species decreased. The liquids provided from thermal runs had no olefinic content. There were not any olefinic compounds at 450˚C under catalytic runs, while at 400 and 425˚C very small percentages of olefins were observed. Low percentages of methylene protons indicate no long chain paraffins in the structure in processed ARCFO liquids. It could be concluded from higher percentages of methine protons than methylene proton that branched structures are more than the long chain or cyclic structures in paraffins.

The hydrocarbon contents of HVGO and ARCFO/HVGO blends liquids in different ratios under noncatalytic and catalytic runs at 450˚C are given in Table 3.2. HVGO has less aromatic content than ARCFO whereas HVGO possessed more paraffinic content than ARCFO. The amounts of olefinic structures are negligible in HVGO. In case of blends the aromatic content is lower, but paraffinic content is higher than ARCFO liquids. In comparison to HVGO, the aromatic content of the blends increased while the paraffinic content decreased. In case of 25 % ARCFO+ 75 % HVGO blend the catalyst have very small effect over the aromaticity, while at 50 % ARCFO + 50 % HVGO blend the catalyst increased the aromatic content. Also the paraffinic ratio was similar in both thermal and catalytic runs for 25% ARCFO + 75% HVGO liquids, while in case of 50 % ARCFO + 50 % HVGO blend the catalyst decreased the relative amount of the paraffins. In general, in blends the methylene content is higher than that of methine indicating long chain or cyclic paraffins ratio is more than the branched ones. This effect is more significant for 25% ARCFO + 75% HVGO. The ^{1}HNMR spectrums of all examples are given in appendices (Appendix1-13).

Table 3.1 The integrations and amount of specific areas of crude and hydrocracked ARCFO examples

Name	Proton Type	Ring Aromatics	Olefin	Aliphatic H band to aromatic ring	α–methyl	Paraffins			
						Methine	Methyl	Methylene	Total
	Chemical Shift	6.6 – 9.5 ppm	4.5 – 6.5 ppm	3-4.5 ppm	2.0 – 3.0 ppm	1.5 – 2.0 ppm	1.0 – 1.5 ppm	0.6 -1.0 ppm	
AR-Crude	Integration	25.62	0.57	3.48	11.11	5.03	4.24	1.88	
	Relative amount (%)	49.3	1.09	6.70	21.4	9.7	8.17	3.62	21.49
AR-400-T	Integration	29.59	0	2.99	12.59	2.93	8.56	2.67	
	Relative amount (%)	49.87	0	5.04	21.22	4.94	14.43	4.5	23.28
AR-400-C	Integration	1.00	0.02	0.21	0.48	0.17	0.25	0.02	
	Relative amount (%)	46.5	0.93	9.77	22.33	7.91	11.63	0.93	20.47
AR-425-T	Integration	80.83	0	14.78	35.12	11.56	16.58	2.38	
	Relative amount (%)	50.13	0	9.17	21.78	7.17	10.28	1.48	18.93
AR-425-C	Integration	1.00	0.05	0.19	0.45	0.13	0.24	0.04	
	Relative amount (%)	47.6	2.4	9.05	21.4	6.2	11.4	1.9	19.5
AR-450-T	Integration	1.00	0	0.13	0.43	0.10	0.19	0.05	
	Relative amount (%)	52.6	0	6.84	22.6	5.32	10	2.63	17.9
AR-450-C	Integration	1.03	0	0.11	0.40	0.09	0.18	0.08	
	Relative amount (%)	54.5	0	5.82	21.43	4.76	9.52	4.2	18.48

(HV: HVGO, AR: ARCFO, T: thermal, C: catalytic hydrocracking conditions: 450°C, 60 bar H2, 60 min): AR-400: Hydrocracked ARCFO at 400°C; AR-425: Hydrocracked ARCFO at 425°C; AR-450: Hydrocracked ARCFO at 450°C;

Table 3.2 The integrations and amount of specific areas of hydrocracked ARCFO and HVGO together

Name	Proton type	Ring Aromatic	Olefinic	Aliphatic H band to aromatic ring	α–methyl	Paraffins			
						Methine	Methyl	Methylene	Total
	Chemical Shift	6.6 – 9.5 ppm	4.5 – 6.5 ppm	3-4.5 ppm	2.0 – 3.0 ppm	1.5 – 2.0 ppm	1.0 – 1.5 ppm	0.6 -1.0 ppm	
AR-450-T	Integration	1.00	0	0.13	0.43	0.10	0.19	0.05	
	Relative amount (%)	52.6	0	6.84	22.6	5.32	10	2.63	17.95
AR-450-C	Integration	1.03	0	0.11	0.40	0.09	0.18	0.08	
	Relative amount (%)	54.5	0	5.82	21.43	4.76	9.52	4.2	18.48
25/75-T	Integration	1.00	0.01	0.04	0.59	0.25	1.21	0.58	
	Relative amount (%)	27.2	0.3	0.12	16	6.8	32.9	15.8	55,5
25/75-C	Integration	1.00	0.04	0.04	0.55	0.26	1.35	0.69	
	Relative amount (%)	25.5	1.02	1.02	14.00	6.62	34.3	17.6	58.52
50/50-T	Integration	1.00	0	0.19	0.72	0.33	1.24	0.49	
	Relative amount (%)	25.2	0	4.79	18.14	8.3	31.22	12.34	51.86
50/50-C	Integration	1.00	0	0.30	0.49	0.19	0.74	0.21	
	Relative amount (%)	34.1	0	10.24	16.72	6.5	25.26	7.2	38.95
HV-450-T	Relative amount (%)	8.83	0.33	0	12.95	6.90	46.26	24.75	77.91
HV-450-C	Relative amount (%)	12.48	0.61	0	12.68	6.15	45.02	23.06	74.23

(AB/CD refers to ARCFO%/HVGO%, T: thermal, C: catalytic, AR: ARCFO, HV: HVGO; hydrocracking conditions: 450°C, 60 bar H_2, 60 min): HV-450: Hydrocracked HVGO at 450°C; AR-450: Hydrocracked ARCFO at 450°C

3.2.3 Bromine Number of Liquid Products

The degree of unsaturation of liquids was determined by bromine number analysis. By increasing of temperature in hydrocracking of ARCFO (Figure 3.11), bromine number value decreased significantly. As expected, unsaturated hydrocarbons were saturated in presence of hydrogen.

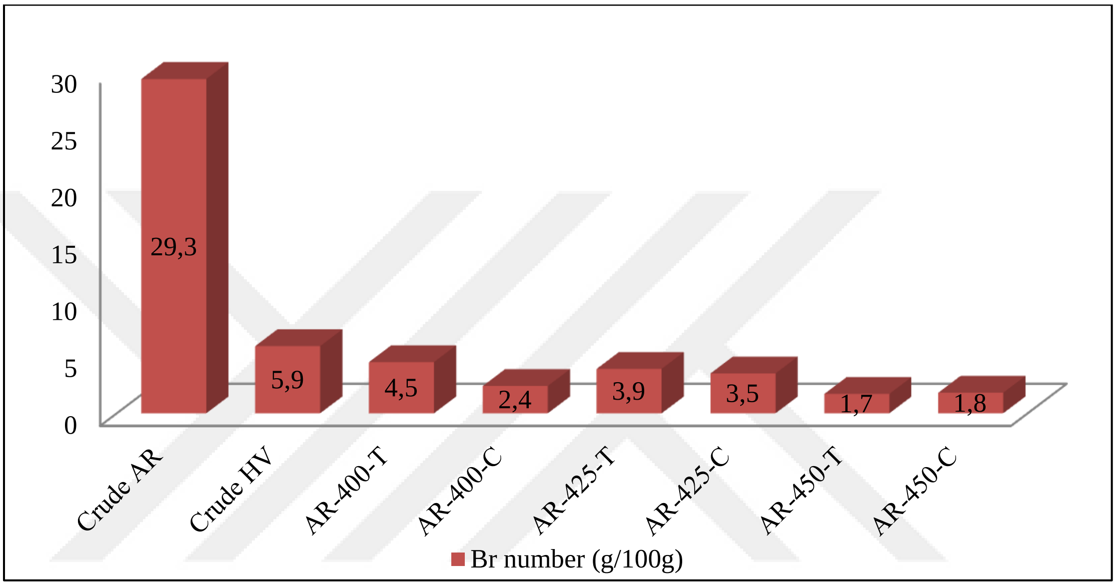

Figure 3.11 Bromine numbers of the liquid products obtained crude ARCFO, HVGO and hydrocracked ARCFO (HV: HVGO, AR: ARCFO, T: thermal, C: catalytic, hydrocracking conditions: 450°C, 60 bar H_2, 60 min): AR-400: Hydrocracked ARCFO at 400°C; AR-425: Hydrocracked ARCFO at 425°C; AR-450: Hydrocracked ARCFO at 450°C

In case of hydrocracking of HVGO, the Br number of liquid obtained from HVGO hydrocracking was slightly higher than that of raw HVGO. This may be due to the formation of olefinic compounds during cracking.

In blends, adding ARCFO to HVGO led to decrease the Br number, as seen in Figure 3.12. This showed interactions between degradation products of ARCFO and HVGO.

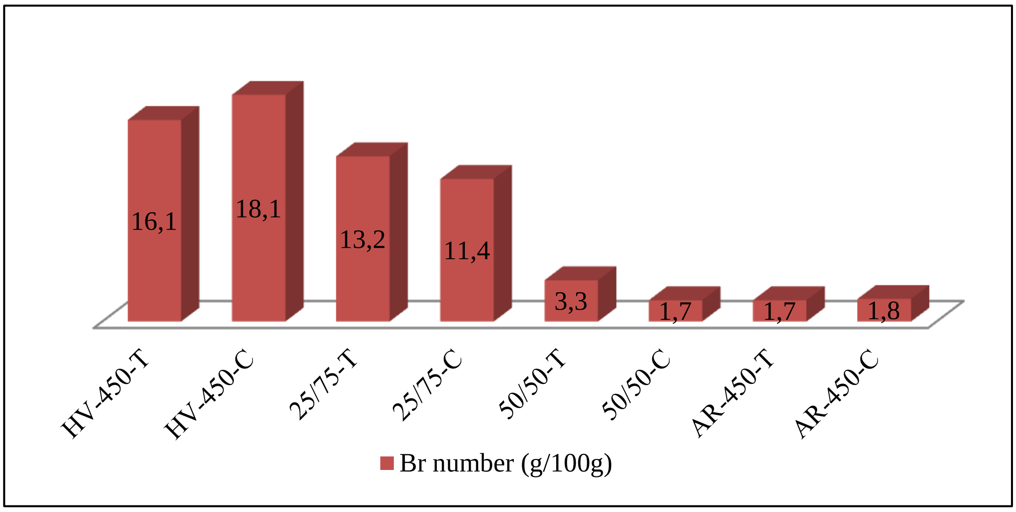

Figure 3.12 Bromine numbers of the liquid products obtained from hydrocracking: ((HV: HVGO, AR: ARCFO, T: thermal, C: catalytic, hydrocracking conditions: 450°C, 60 bar H_2, 60 min in blends AB/CD refers to ARCFO%/HVGO%, hydrocracking conditions: 450°C, 60 bar H_2, 60 min): AR-450: Hydrocracked ARCFO at 450°C; HV-450: Hydrocracked HVGO at 450°C

3.2.4 Fractionation of Liquid Products

Liquid products were subjected column chromatography after deasphalting to determine the chemical groups. Firstly, samples were deasphalted according to ASTM D6560and deasphalted liquids were separated into aliphatic, aromatic and polar fractions by column chromatography. The results were given at Figure 3.13, Figure 3.14 and 3.15.

There was not considerable difference between asphaltene amounts of hydrocracked ARCFO at thermal or catalytic conditions. Only at 400˚C thermal and catalytic conditions, the amount of asphaltene were less than that of crude ARCFO. The percentages of polar fractions were close to each other for all liquids obtained from ARCFO. Although temperature did not affect aliphatic and aromatic contents in liquids, the catalyst increased the aromatic fractions and decreased aliphatic fraction in case of hydrocracking at 400˚C and 425˚C. At high temperatures there was a slight decrease at aromatic fraction amount, while the aliphatic fraction decreased slightly. Consequently hydrocracking did not cause remarkable changes over the content of ARCFO.

HVGO contains negligible amount of asphaltene (Figure 3.14, Figure 3.15). In blends, adding the ARCFO at the ratio of 25 % has not considerably change the fractions in comparison to the fraction of liquid from HVGO alone. The presence of ARCFO slightly increased asphaltene amount while decreased the aromatic content.

In contrast, in case of catalytic coprocessing, the presence of ARCFO increased aliphatic content while decreased the aromatic and polar contents. Also adding ARCFO to HVGO increased the asphalten content in liquid from catalytic hydrocracking in comparison to the fraction of liquid from HVGO alone.

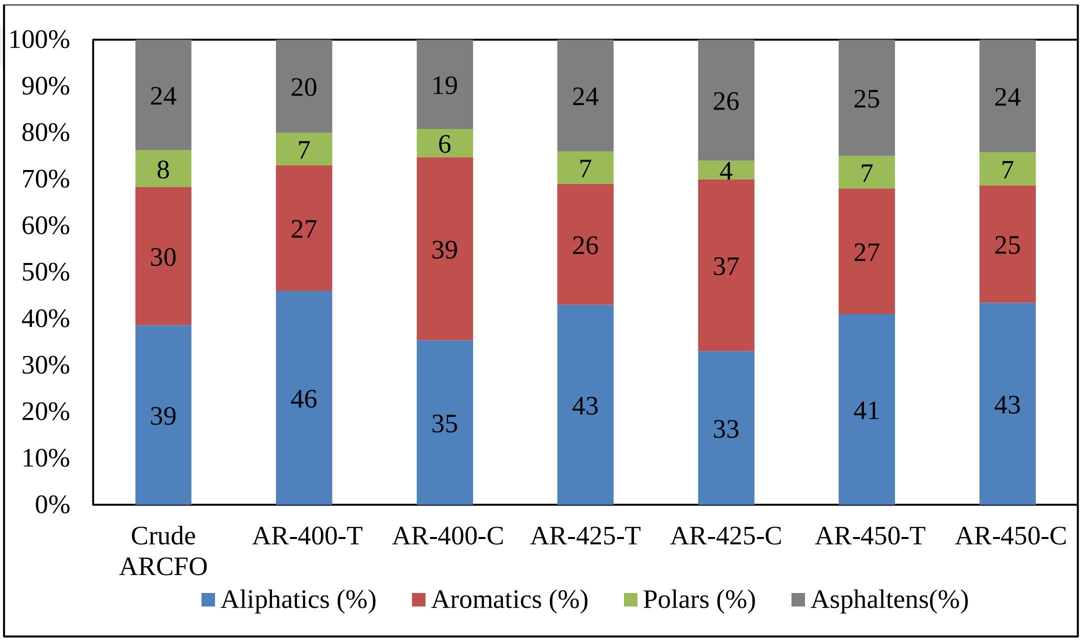

Figure 3.13 Liquid absorption chromatograph results of ACRFO (HV: HVGO, AR: ARCFO, T: thermal, C: catalytic) AR-400: Hydrocracked ARCFO at 400°C; AR-425: Hydrocracked ARCFO at 425°C; AR-450: Hydrocracked ARCFO at 450°C; HV-450: Hydrocracked HVGO at 450°C

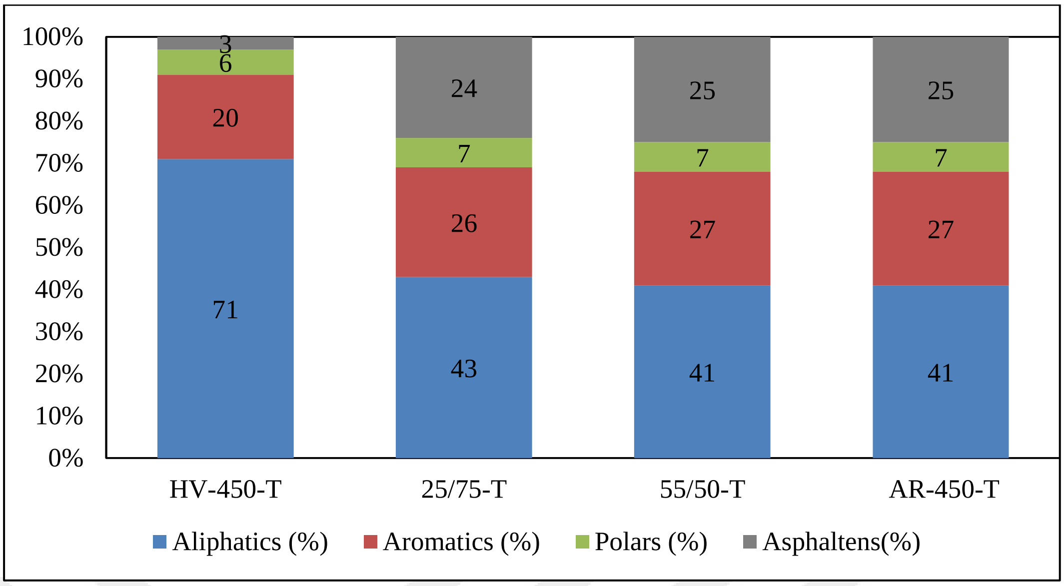

Figure 3.14 Liquid absorption chromatograph results of thermal hydrocracking ACRFO and HVGO and the blends of them. (in blends AB/CD refers to ARCFO%/HVGO%, hydrocracking conditions: 450°C, 60 bar H_2, 60 min HV: HVGO; AR: ARCFO; T: thermal; C: catalytic) HV-450: HVGO hydrocracked at 450°C; AR-450: Hydrocracked ARCFO at 450 °C

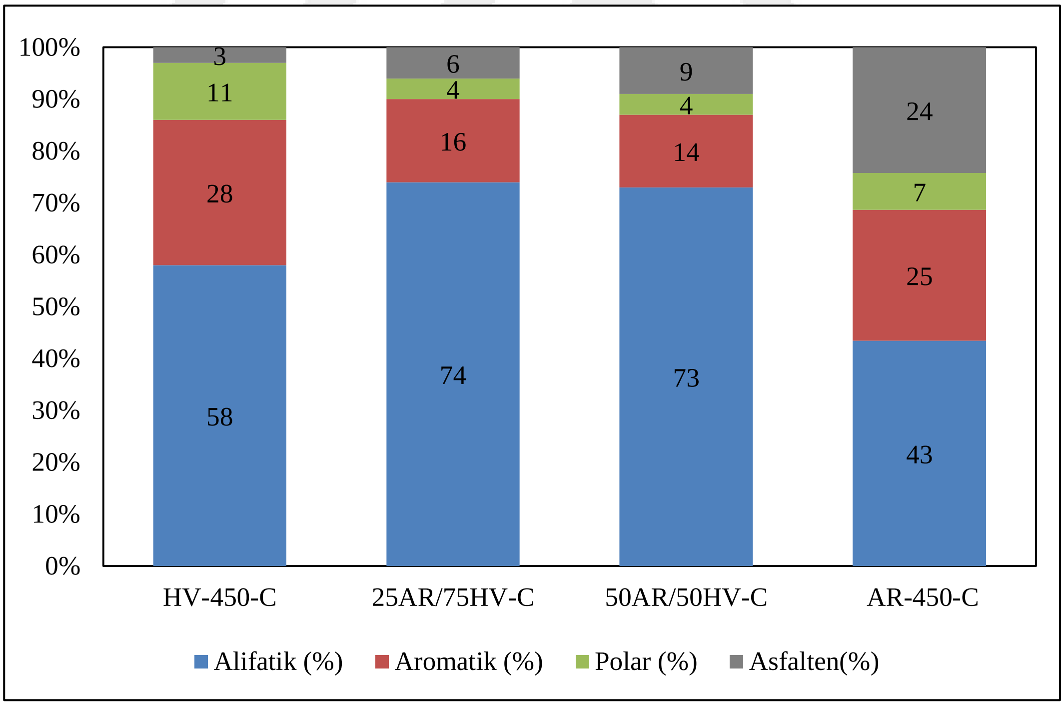

Figure 3.15 Liquid absorption chromatograph results of catalytic hydrocracking ACRFO and HVGO and the blends of them. (in blends AB/CD refers to ARCFO%/HVGO%, hydrocracking conditions: 450°C, 60 bar H_2, 60 min; HV: HVGO; AR: ARCFO; T: thermal; C: catalytic) HV-450: HVGO hydrocracked at 450°C; AR-450: Hydrocracked ARCFO at 450°C

3.3 Asphaltene characterization

The asphatlene yields of the liquids were given in Figure 3.13, Figure 3.14 and Figure 3.15. Asphaltenes were analysed by Elemental analysis and Fourier Transform Infrared Spectrometer.

3.3.1 Elemental Analysis

The H, C, N, S, O contents and H/C and O/C ratios of asphaltenes were determined by elemental analysis. The results obtained are represented in Table 3.3 and Table 3.4. For comparison purpose, the elemental analysis results of crude and hydrocracked ARCFO at different temperatures in the presence of the catalyst and under thermal conditions are given in Table 3.3. Elemental analysis results of crude HVGO and hydrocracked HVGO, coprocessed ARCFO and HVGO together in different amounts are given in Table 3.4.

Table 3.3 Elemental analyst results of crude and hydrocracked Aromatic Rich Cracked Fuel Oil

	AR	AR-400-T	AR-400-C	AR-425-T	AR-425-C	AR-450-T	AR-450-C
C	91.46	91.43	92.13	90.49	92.84	93.12	91.20
H	6.33	5.27	4.70	4.90	5.10	4.84	4.62
N	0.08	0.10	0.12	0.13	0.09	0.15	0.16
S	0.14	0.27	0.28	0.30	0.31	0.36	0.54
O*	1.99	2.93	2.77	4.18	1.66	1.53	3.48
H/C	0.83	0.69	0.61	0.65	0.66	0.62	0.61
O/C	0.02	0.02	0.02	0.03	0.01	0.01	0.03

AR-Crude ARCFO; AR-400-T: Hydrocracked ARCFO at 400°C, thermal; AR-400-C: Hydrocracked ARCFO at 400°C, catalytic; AR-425-T: Hydrocracked ARCFO at 425°C, thermal; AR-425-C: Hydrocracked ARCFO at 425 °C catalytic; AR-450-T: Hydrocracked ARCFO at 450°C, thermal; AR-450-C: Hydrocracked ARCFO at 450°C, catalytic.

According to the H/C ratios given in Table 3.3 it can be concluded that at 400°C hydrocracking conditions the aromaticity increased. Also the catalyst increased the aromatic content further. In general aromaticity increased as the temperature increased. The effect of the catalyst can be observed at 400 and 450°C; at these temperatures the catalyst increased the aromatic content. At 450°C repolymerization processes occurred. Moreover, as the temperature increased the amount of compounds containing N and S also increased. At 425°C the catalyst decreased the N amount. Furthermore, the catalyst utilization increased the percentage of S at 450°C.

Table 3.4 Elemental analyst results of crude Heavy Vacuum Gas Oil and mixture of Aromatic Rich Cracked Fuel Oil and Heavy Vacuum Gas oil in different amount

	AR-450-T	AR-450-C	25/75-T	25/75-C	50/50-T	50/50-C	HV-450-T	HV-450-C
C	93.12	91.20	88.28	91.10	91.71	93.83	83.68	77.12
H	4.84	4.62	4.85	4.89	4.86	4.96	5.1	4.23
N	0.15	0.16	0.46	0.46	0.27	0.18	0.98	1.04
S	0.36	0.54	1.38	1.04	0.79	0.32	1.97	1.10
O*	1.53	3.48	5.03	2.51	2.37	0.71	8.27	16.51
H/C	0.62	0.61	0.66	0.65	0.64	0.63	0.73	0.66
O/C	0.01	0.03	0.04	0.02	0.02	0.01	0.07	0.16

25/75-T: Hydrocracked 25%ARCFO+75%HVGO at 450°C, thermal; 25/75-C: Hydrocracked 25%ARCFO+75%HVGO at 450°C, catalytic; 50/50-T: Hydrocracked 50%ARCFO+50%HVGO at 450°C, thermal; 50/50-C: Hydrocracked 50%ARCFO+50%HVGO at 450°C, catalytic; HV-450-T: Hydrocracked HVGO at 450°C, thermal; HV-450-C: Hydrocracked HVGO at 450°C, catalytic.

In case of the coprocessing of ARCFO with HVGO as the ARCFO content increases the aromaticity according to H/C ratios increases with respect to HVGO alone (Table 3.4). In HVGO itself, the catalyst increased the aromatic content. Catalyst had negligible effect on the aromaticity of blends of 50% ARCFO+ 50% HVGO and 25% ARCFO + 75% HVGO. The N percent at hydrocracked HVGO are more than the hydrocracked HVGO and ARCFO mix. So it could be concluded that utilization of ARCFO reduced the heteroatom content which is a desired property. Moreover, in the case of blends, the catalyst increased the heteroatom content.

3.3.2 Evaluation of Fourier Transform Infrared Spectrum

The FTIR spectra of the asphaltenes obtained from ARCFO and ARCFO-HVGO blends are given in appendices.

The interpretation of FTIR spectra of asphaltene examples obtained from crude ARCFO and hydrocracked ARCFO liquids were given Table 3.5. The FTIR spectra results of crude and hydrocracked HVGO and hydrocracked coprocessing of ARCFO with HVGO were given in Table 3.6. The FTIR spectrums of all samples are given in appendices (Appendix14-26).

Table 3.5 Infrared spectroscopy results of ARCFO

	AR	AR-400-T	AR-400-C	AR-425-T	AR-425-C	AR-450-T	AR-450-C
-OH stretch (3700-3100) -NH stretch (3500-3100)	3436	3425	3422	3434 3232	3434 3277	3676 3340	3435 3271
=CH stretch 3150-3000	3044	3042	3030	3047	3036	3019	3036
-CH stretch 3000-2800	2922 2868	2923 2862	2924 2868	2920 2868	2920 2862	2927	2920 2851
-SH stretch 2600-2550		2556	2500	2625	2610	2571	2598
C=O stretch 1900-1680	1914	1907	1899	1907	1901 1723	1871	1910 1735
-C=C stretch 1660-1600 (aromatic) 1600-1480 (alkenes) -NH -NH_2 bend 1640-1520	1600 1490	1616	1619	1602	1605	1654	1602
-CH_2 bend 1480-1430	1451	1438	1450	1440	1437	1457	1454
-CH_3 bend 1390-1375	1376				1376	1381	
-C-N stretch 1360-1030 -C-O stretch 1250-1050 S=O stretch 1070-1030	1267 1158 1032	1261 1177 1074	1225 1020	1261 1174 1069	1152 1072	1300 1298 1121 1034	1267 1172 1067
=CH out-of-plane bend alkene 1000-650 aromatic 900-690	813 780 750	872 816 760	844 763 752	872 819 760 752	811 754 713	956 875 758	869 819 755
-C-S stretch 705-550	604	660	682	654	674	671 568	651

AR-400-T: Hydrocracked ARCFO at 400°C, thermal; AR-400-C: Hydrocracked ARCFO at 400°C, catalytic; AR-425-T: Hydrocracked ARCFO at 425°C, thermal; AR-425-C: Hydrocracked ARCFO at 425°C, catalytic; AR-450-T: Hydrocracked ARCFO at 450°C, thermal; AR-450-C: Hydrocracked ARCFO at 450°C, catalytic

Table 3.6 Infrared spectroscopic results of ARCFO and heavy vacuum gas oil blends

	25/75-T	25/75-C	50/50-T	50/50-C	AR-450-T	AR-450-C	HV-T	HV-C
-OH stretch (3700-3100) -NH stretch (3500-3100)	3676 3575 3407	3680 3596 3382	3737 3669 3575 3389 3221	3549 3358 3204	3676 3340	3435 3271	3719 3602 3487	3719 3585 3467
=CH stretch 3150-3000	3019	3042	3148 3025	3040	3019	3036	3070	3042
-CH stretch 3000-2800	2927	2910	2918 2862	2847	2927	2920 2851	2957	2918 2857
-SH stretch 2600-2550	2573	2569	2526	2620	2571	2598		2521
C=O stretch 1900-1680	1901 1736	1878 1745	1907 1767	1878 1798 1683	1871	1910 1735	1703	1731 1706
-C=C stretch 1660-1600 (aromatic) 1600-1480 (alkenes) -NH -NH_2 bend 1640-1520	1653	1600	1622 1541	1508	1654	1602	1616 1538	1613 1535
-CH_2 bend 1480-1430	1454	1454	1454	1440	1457	1454	1429	
-CH_3 bend 1390-1375	1372	1365			1381			1393
-C-N stretch 1360-1030 -C-O stretch 1250-1050 S=O stretch 1070-1030	1218 1121 1037	1306 1225 1118 1018	1314 1216 1197 1037	1302 1249	1300 1298 1121 1034	1267 1172 1067	1269 1177	1362 1261 1113 1043
=CH out-of-plane bend alkene 1000-650 aromatic 900-690	959 900 792	956 834	931 844 749	919 783 725	956 875 758	869 819 755	923 883 811	819
-C-S stretch 705-550	673 569	676 569	674 566	602	671 568	651	665	668

(AB/CD refers to ARCFO%/HVGO%, T:thermal, C:catalycal, HV:HVGO; hydrocracking conditions: 450°C, 60 bar H_2, 60 min): HV-450-T -Hydrocracked HVGO at 450°C; AR-450-T -Hydrocracked ARCFO at 450°C

The peaks between 3700-3100 cm^{-1} referred to -OH and -NH stretch (Table 3.5 and Table 3.6). The peaks on the left of 3000 cm^{-1} (between 3150-3000 cm^{-1}) were related to =C-H stretching. Absorption peaks between 3000-2800 cm^{-1} corresponded to aliphatic –C-H stretching. Also methyl and methylene groups had characteristic bending frequency at approximately1390-1375 and 1480-1430 cm^{-1}, respectively which supported the aliphatic content. Bands related to S-H vibrations were observed at about 2600-2550 cm^{-1}. The weak absorption peaks between 1900 and 1680 cm^{-1} related to carbonyl stretching frequency indicated low content of the carbonyl group in the samples. The band intensities in the range of 1660-1480 cm^{-1} were assigned to stretching vibrations of C=C bands. The absorption peaks in the region of 1250-1050 cm^{-1} arise from the C-O stretching vibrations of ethers, phenols and C-O-H in phenolics. It was indicated the literature that generally the oxygen in asphaltene was mainly in the form of C-O bond (Sun, Li, Ma, Tian, X.Li, W.Li, Y.Zhu, 2014). Growth the peaks at the range of 1360-1030 cm^{-1} are threatened of increasing functional groups such as N, S in mixtures of ARCFO and HVGO. This results indicated that C-N, C-S, S=O stretching bands were more evident in FTIR spectrums of mixtures in comparison to ARCFO which was also in agreement as with the elemental analysis results given in Table 3.2. The weak absorbance at 1032 cm^{-1}, related to S=O (sulfoxide functional groups), is observed in the spectrums. The presence of some strong and weak peaks to the right of 1000 cm^{-1} and to the left of 650 cm^{-1} corresponded to carbon-hydrogen out-of-plane bending in aromatic rings. The frequencies at absorption band in 705-550 cm^{-1} range were related to -C-S stretching.

3.4 Gas products

The gases obtained from both hydrocracking of ARCFO alone and the blends of ARCFO/HVGO consisted of hydrocarbon gases, mainly methane and ethane. The composition of gases obtained from thermal hydrocracking of ARCFO at 450 °C is given Table 3.7.

Table 3.7 The composition of gases obtained from thermal hydrocracking of ARCFO, mol %

Methane	69.4
Ethane	18.64
Ethylene	0.14
Propane	8.7
Propylene	0.1
i-Butane	0.8
n-Butane	1.5
c-2-Butene	0.1
i-Pentane	0.3
n-Pentane	0.3

CHAPTER FOUR
CONCLUSION

In this study, conversion of “off spect’’ fuel oil (ARCFO), as a by- product, into petroleum fuels using an existing refinery processes was investigated. For this purpose, hydrocracking of ARCFO and co-hydrocracking of ARCFO/HVGO mixture were performed. The effect of catalyst and temperature on the properties of hydrocraking products was examined. Hydrocracking/co-hydrocracking experiments were carried out with an initial H_2 pressure of 6MPa for 1 hour at different temperature in presence and absence of catalyst. A commercial catalyst (DHC-8) was used in catalytic experiments.

We obtained the following results from our experiments.

- In the case of hydrocracking of ACRFO alone, the liquid yield decreased as the reaction temperature increased. The use of catalyst had no considerable effect on liquid yield. At 400°C, the liquid yield was the highest (71 %).
- Simulated distillation curves of liquid products obtained hydrocracking of ACRFO showed that liquids contained about 5-10 % naphtha fraction and 80-90% light gas oil fraction.
- ^{1}HNMR analysis showed that the liquid products obtained hydrocracking of ACRFO consisted of 46.5-54.5% aromatic rings and paraffins in liquids had mainly branched structures.
- Hydrocracking process (both thermal and catalytic) had no effect on the decrease in asphaltenic and polar compounds in ARCFO. But it led to decrease or increase in aromatic and aliphatic compounds depending on process conditions.
- The co-processing of ARCFO with HVGO decreased the liquid product yield in comparison to hydrocracked HVGO alone. The liquid yield of blends is lower than predicted one.
- Simulated distillation curves of liquid products obtained hydrocracking of ACRFO/HVGO blends showed that the naphtha fraction in liquids increased

as the percentages of ARCFO increase in blends, while the amount of heavy gas oil increased.

- ^{1}HNMR analysis showed that the liquid products obtained hydrocracking of blends had lower aromatic content than ARCFO liquids, they had higher paraffinic content.
- The addition of ARCFO to HVGO increased the asphaltenic and aromatic compounds while decreased the aliphatic compounds in comparison to the fractions of liquid from HVGO alone.
- The Br numbers, which show the degree of unsaturation, of liquid products obtained from both hydrocracking and co-hydrocracking process were much lower than that of ARCFO and HVGO alone.
- The chemical composition of asphaletenes was also investigated in this study. The heteroatom contents of asphaletenes in hydrocracking liquids were found to be higher than that in ARCFO. The addition of ARCFO to HVGO decreased heteroatom and aromatic contents of asphaletenes in comparison to the liquids from HVGO alone.

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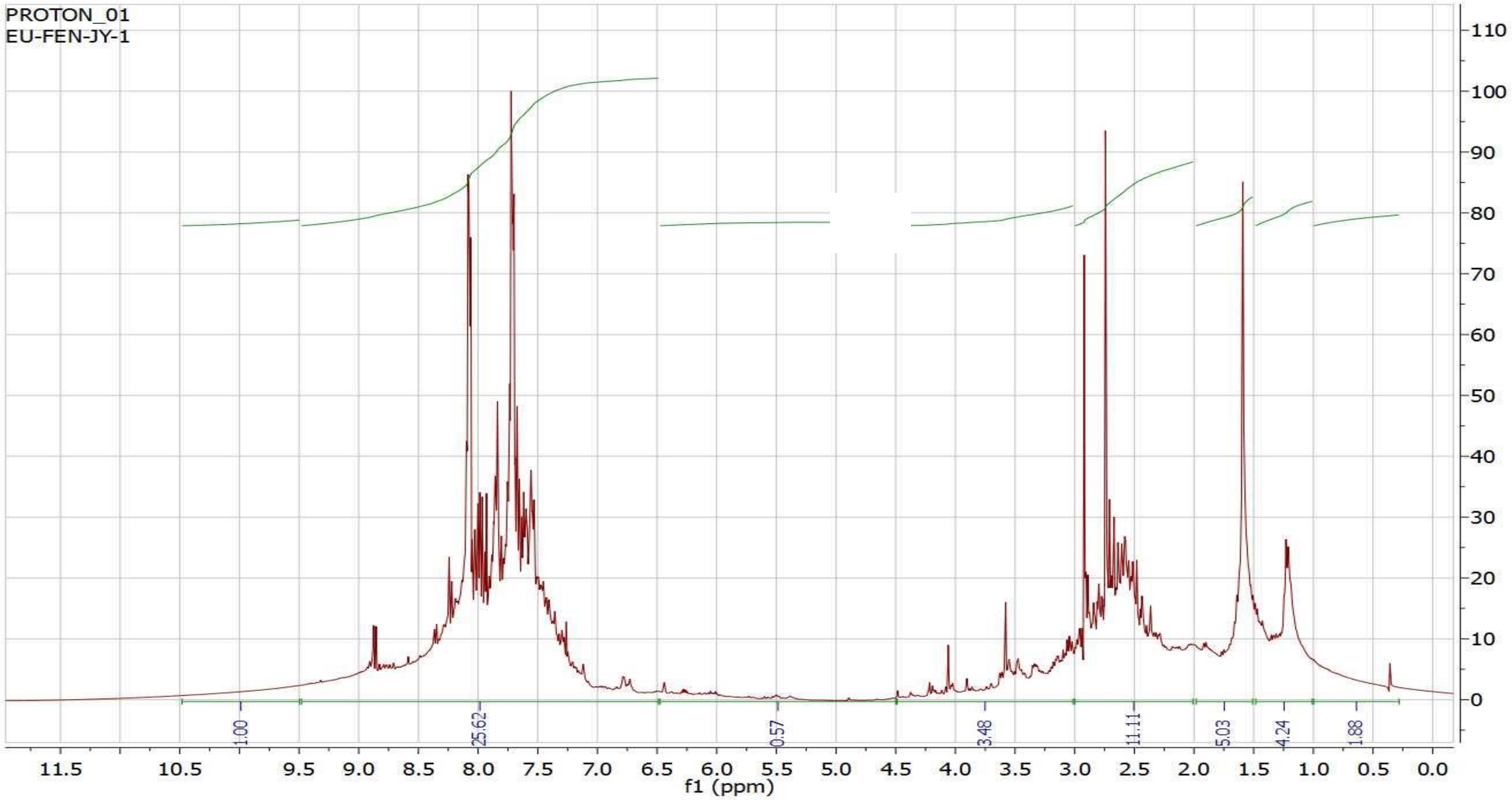
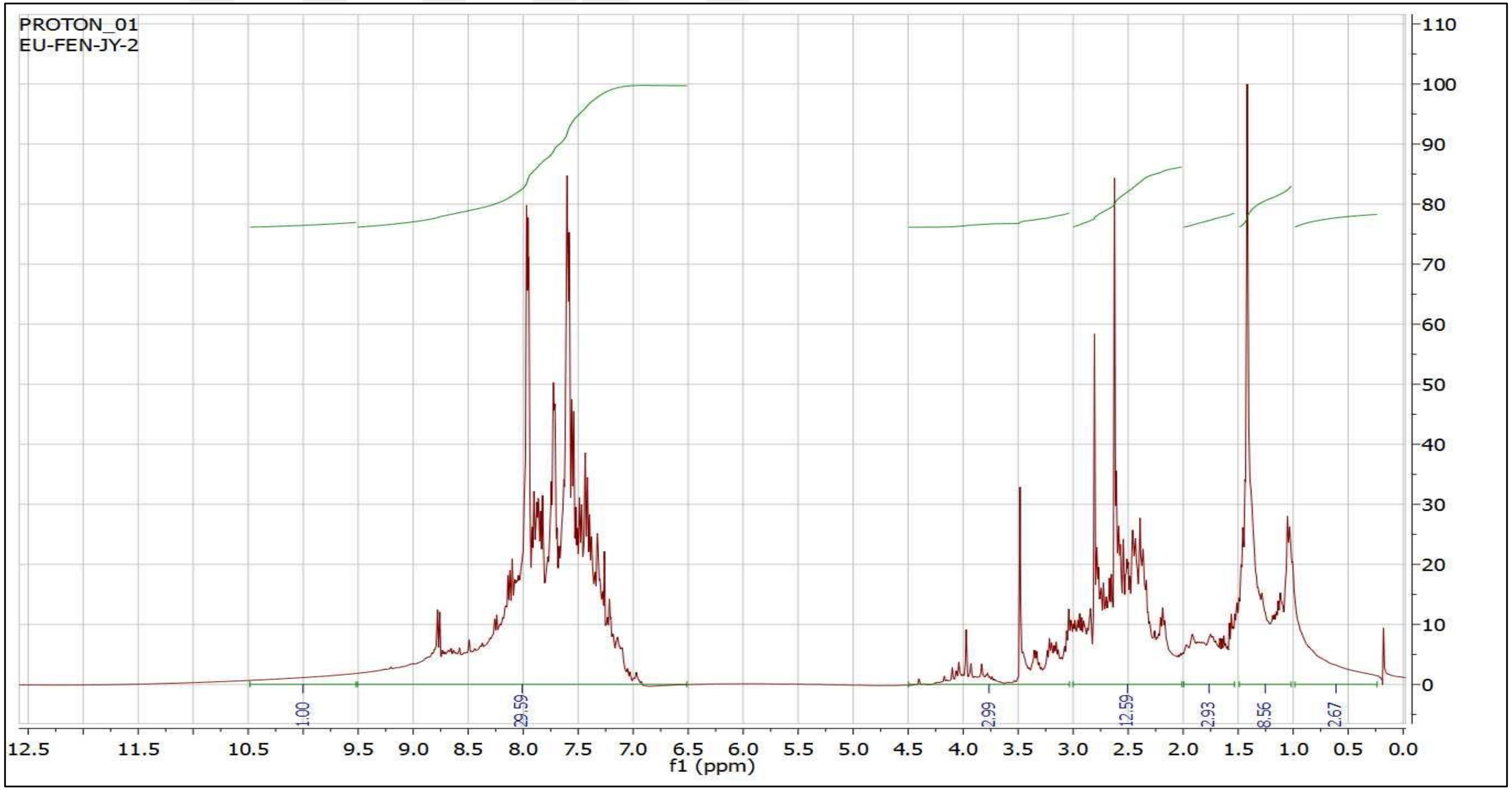
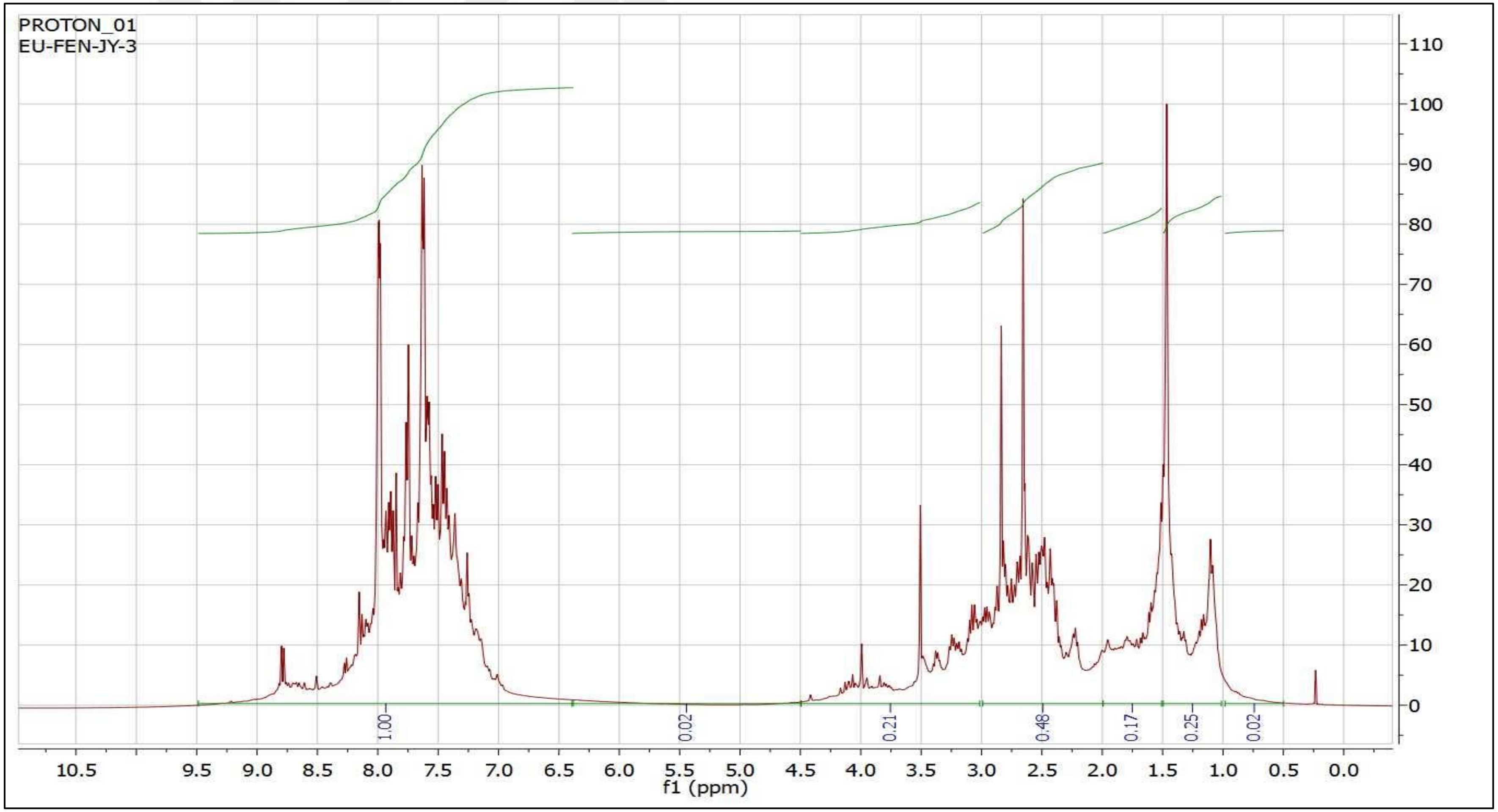
Appendix-1: ^{1}H NMR spectrum of crude ARCFO



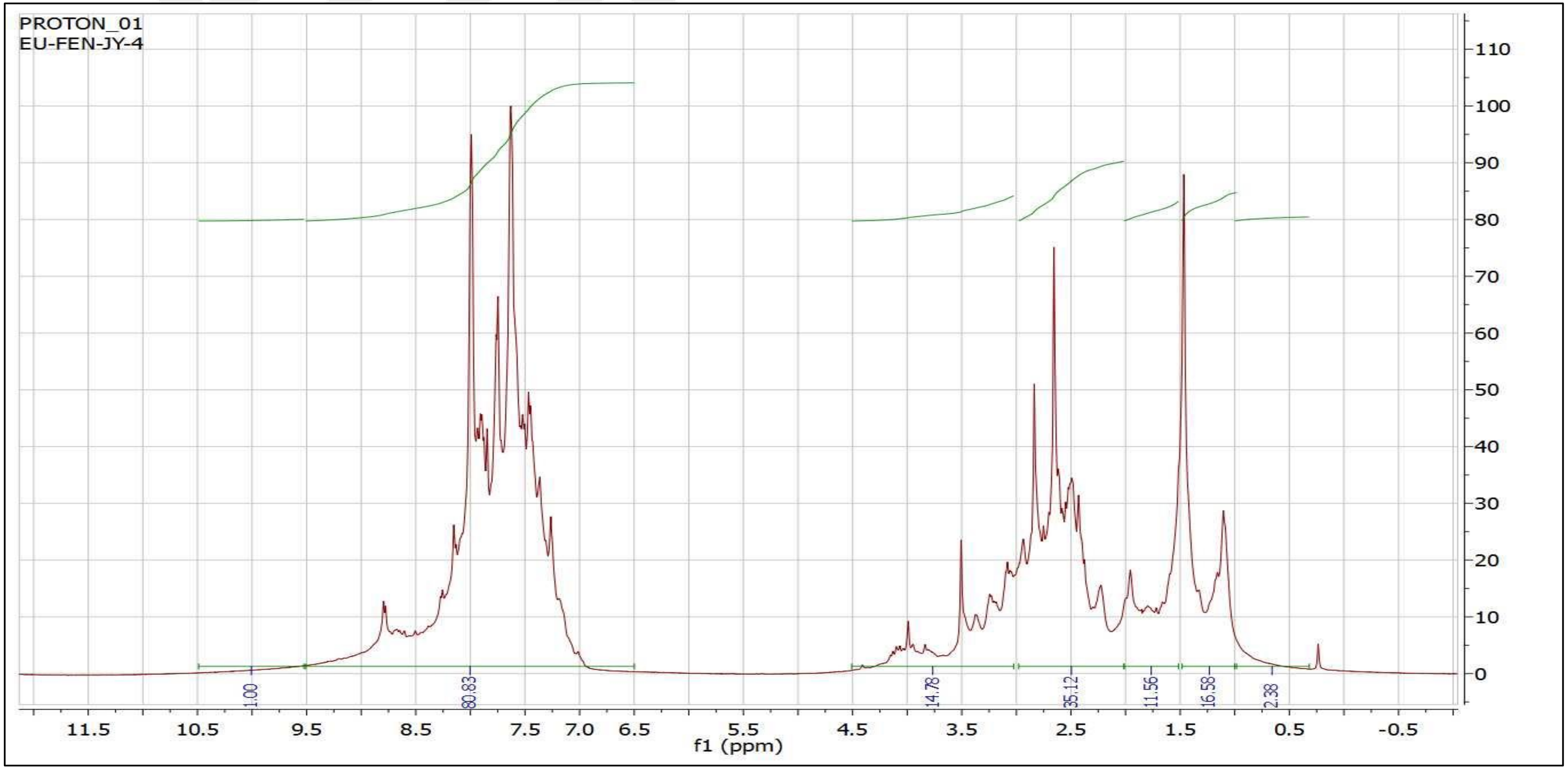
Appendix-2: ^{1}HNMR spectrum of hydrocracked ARCFO at 400° C thermal



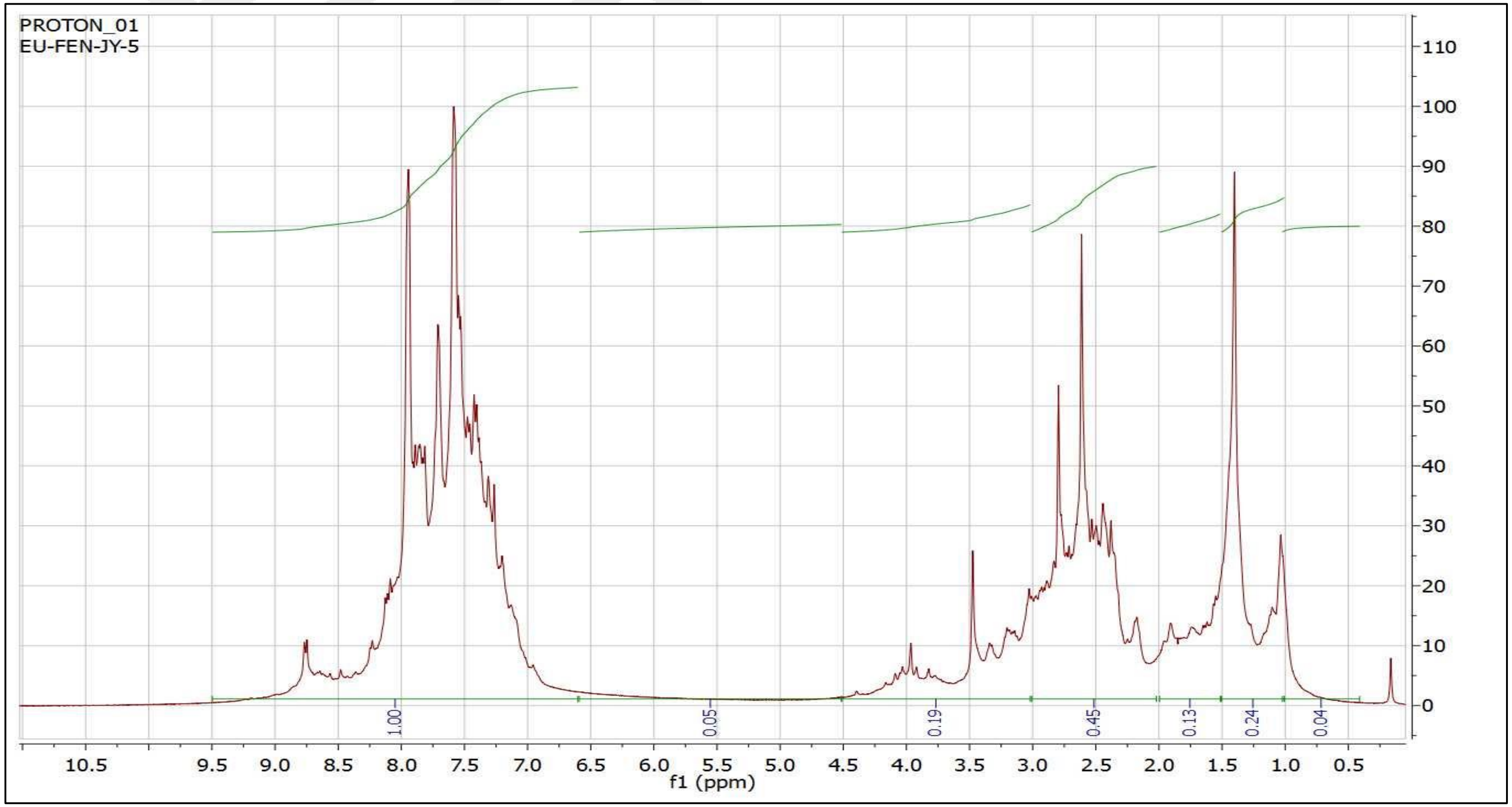
Appendix-3: ^{1}HNMR spectrum of hydrocracked ARCFO at 400° C with catalyst



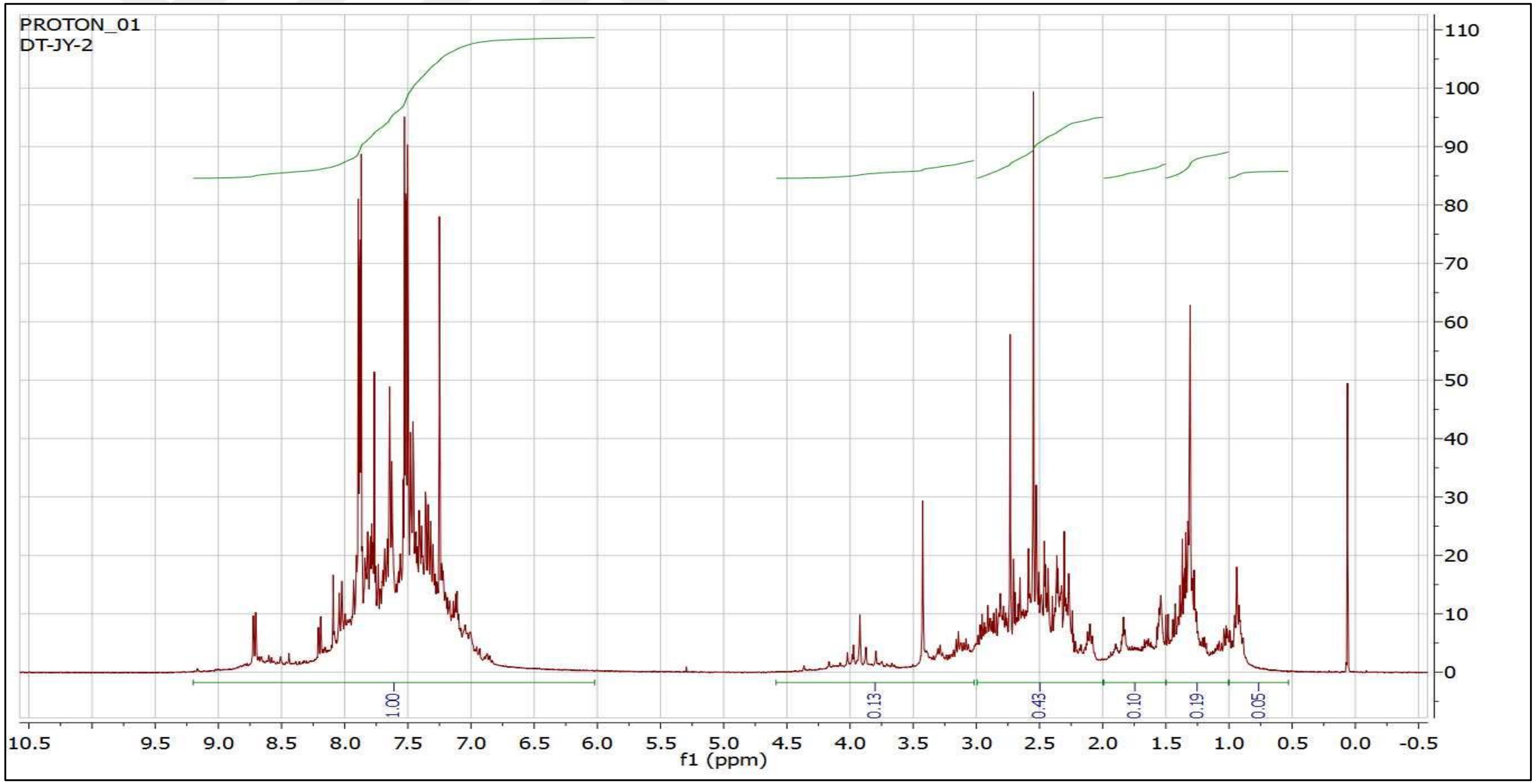
Appendix-4: ^{1}HNMR spectrum of hydrocracked ARCFO at 425° C thermal



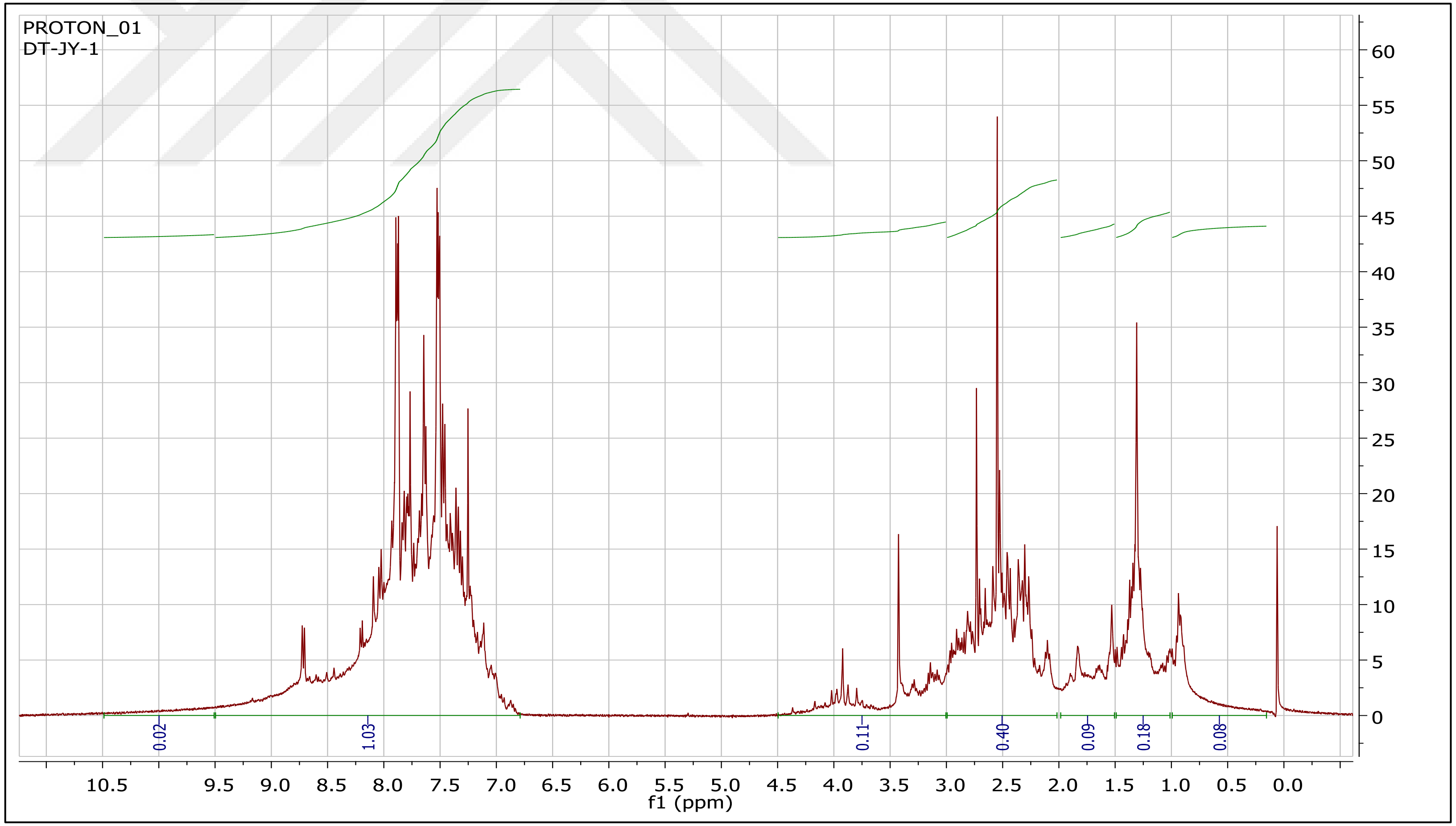
Appendix-5: ^{1}HNMR spectrum of hydrocracked ARCFO at 425° C with catalyst



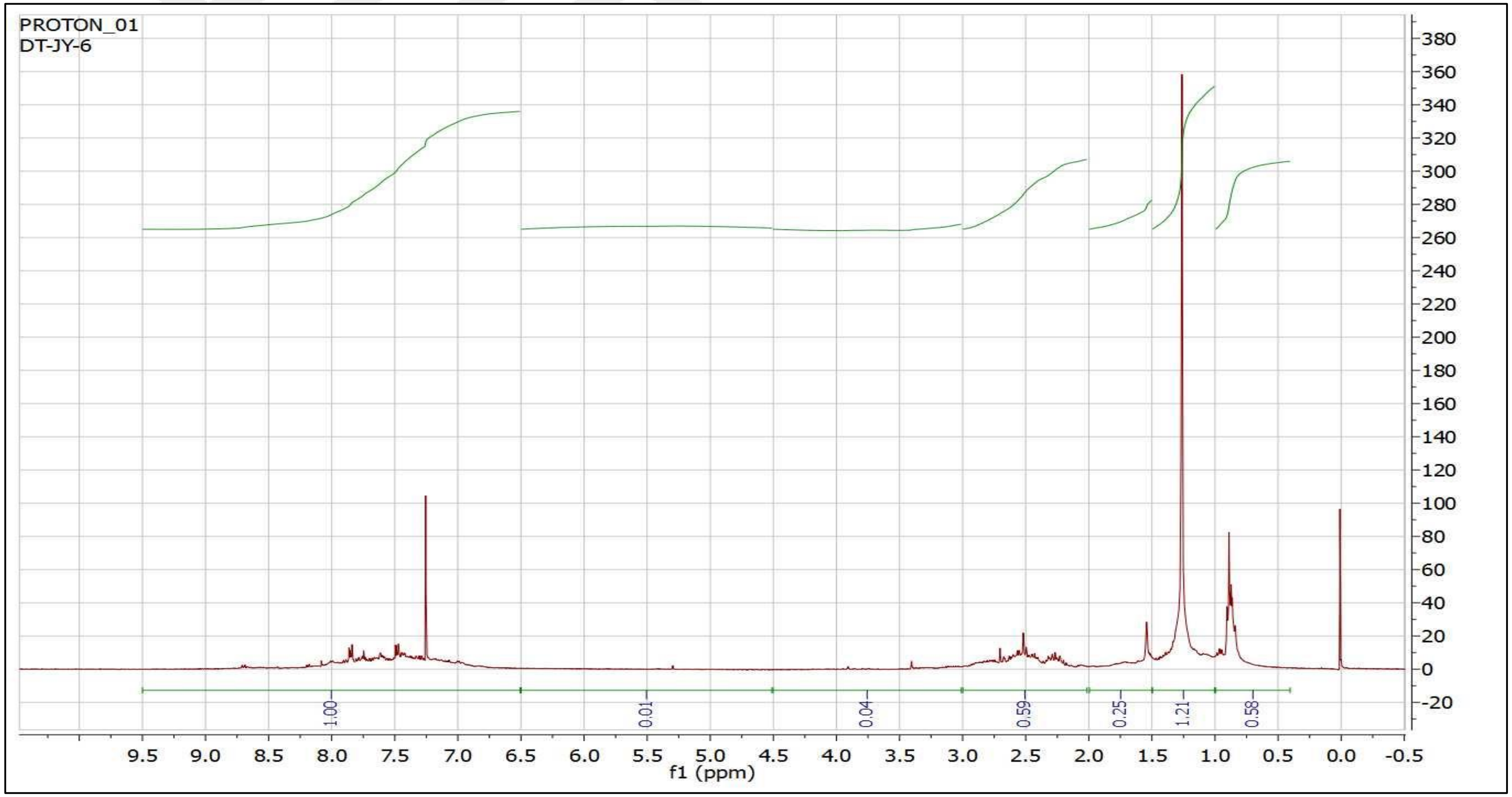
Appendix-6: ^{1}HNMR spectrum of hydrocracked ARCFO at 450° C thermal



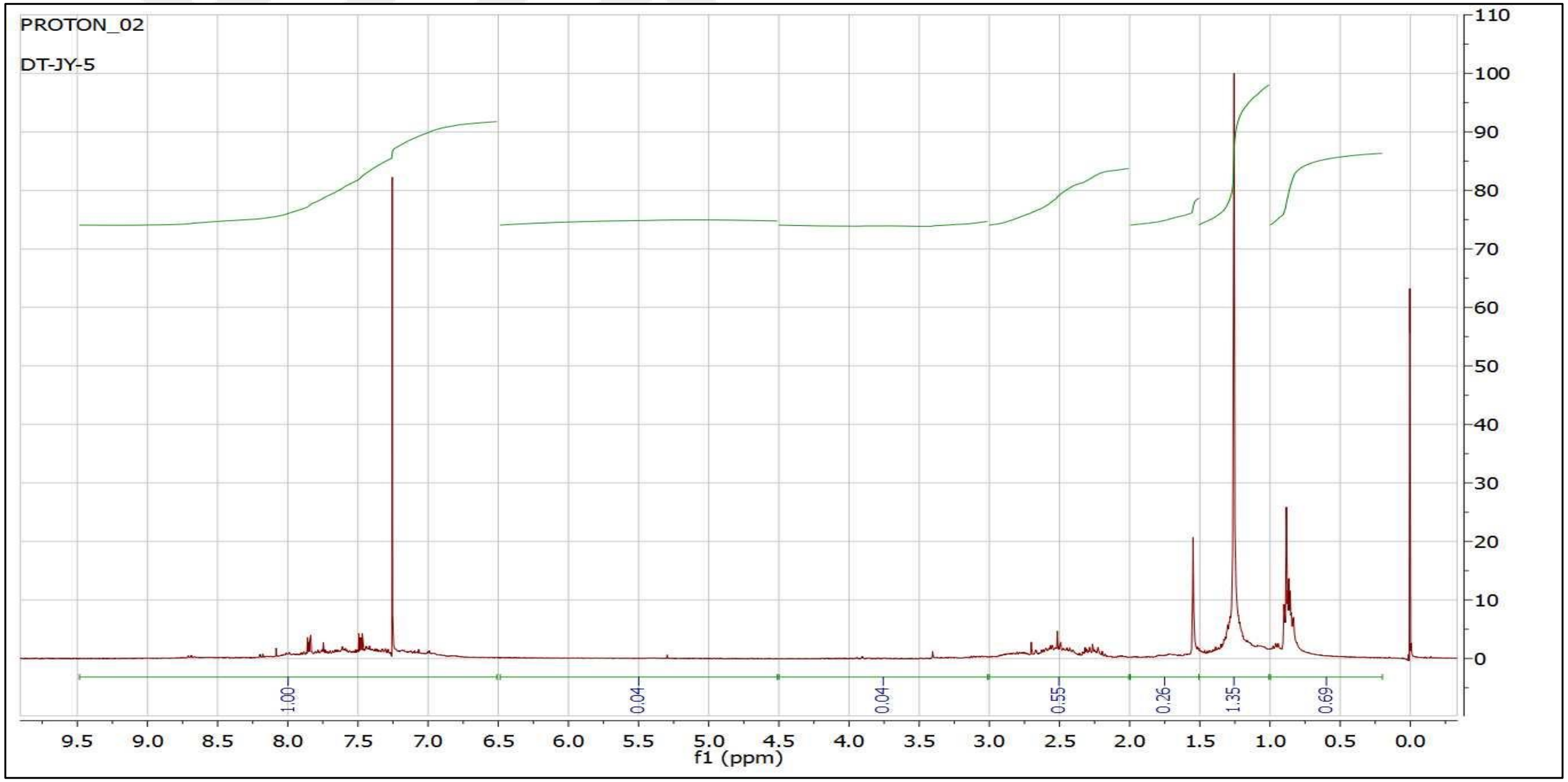
Appendix-7: ^{1}HNMR spectrum of hydrocracked ARCFO at 450° C with catalyst



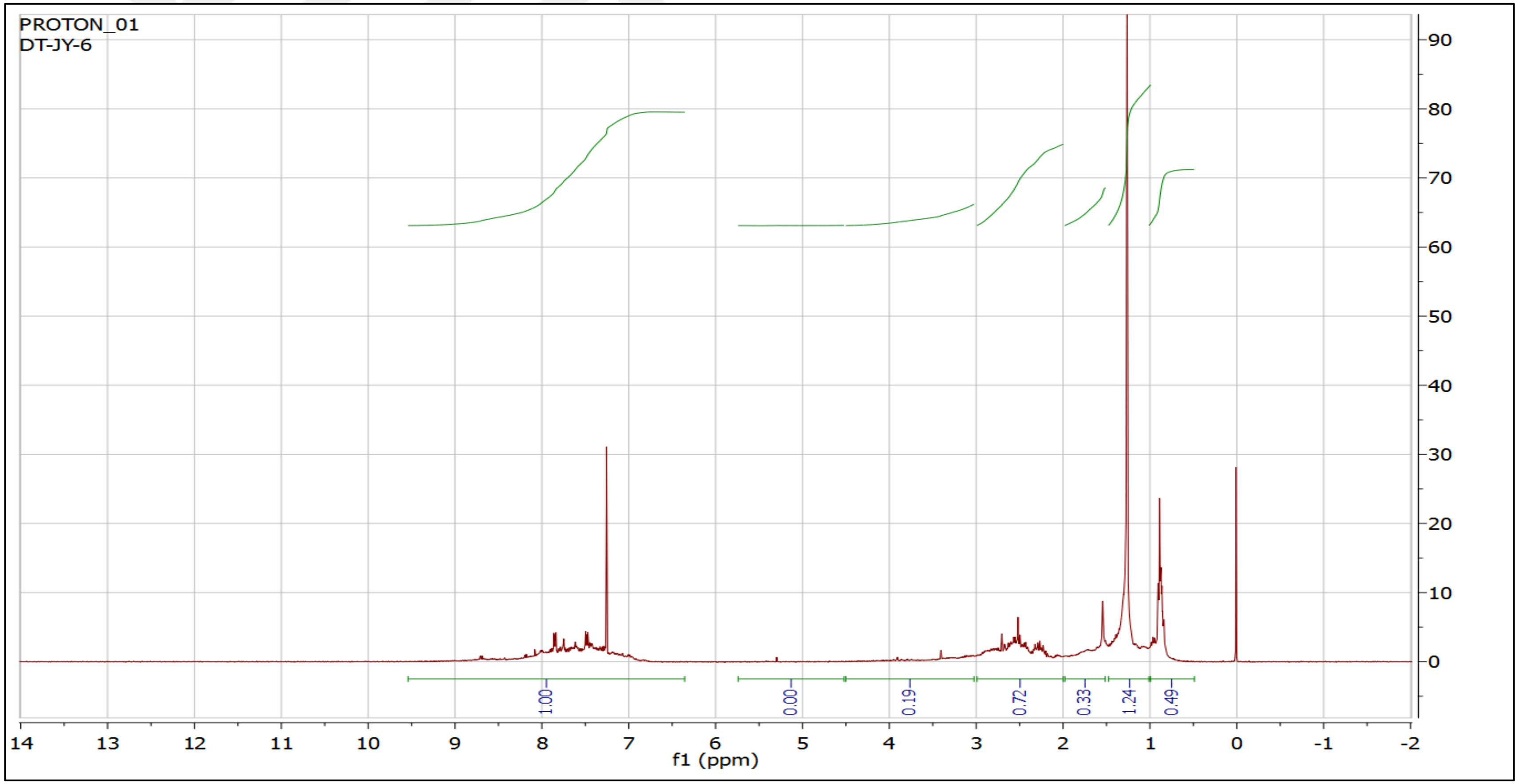
Appendix-8: ^{1}HNMR spectrums of hydrocracked 25 %ARCFO and 75% HVGO mixture at 450°C thermal



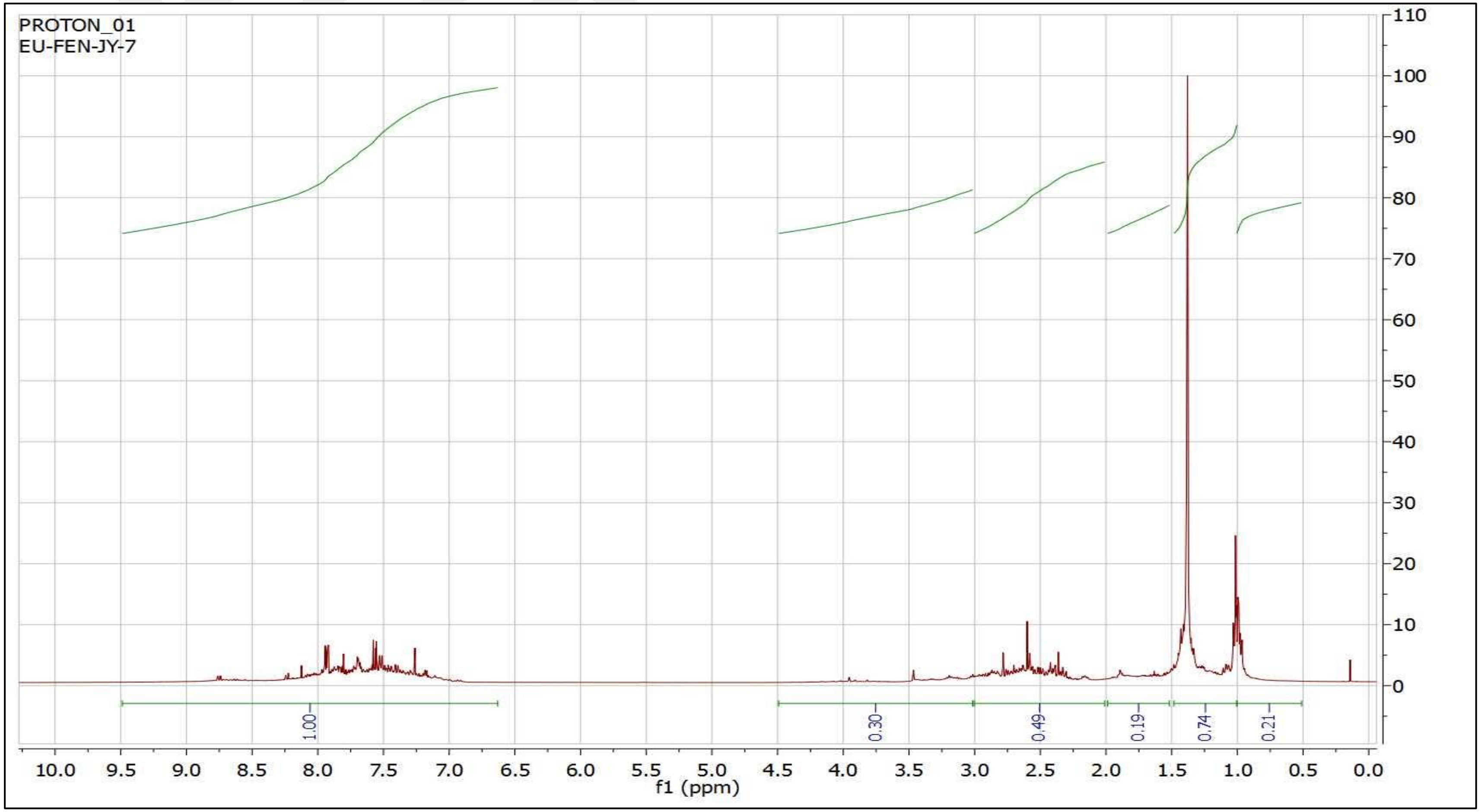
Appendix-9: ^{1}HNMR spectrums of hydrocracked 25 % ARCFO and 75% HVGO mixture at 450°C wıth catalyst



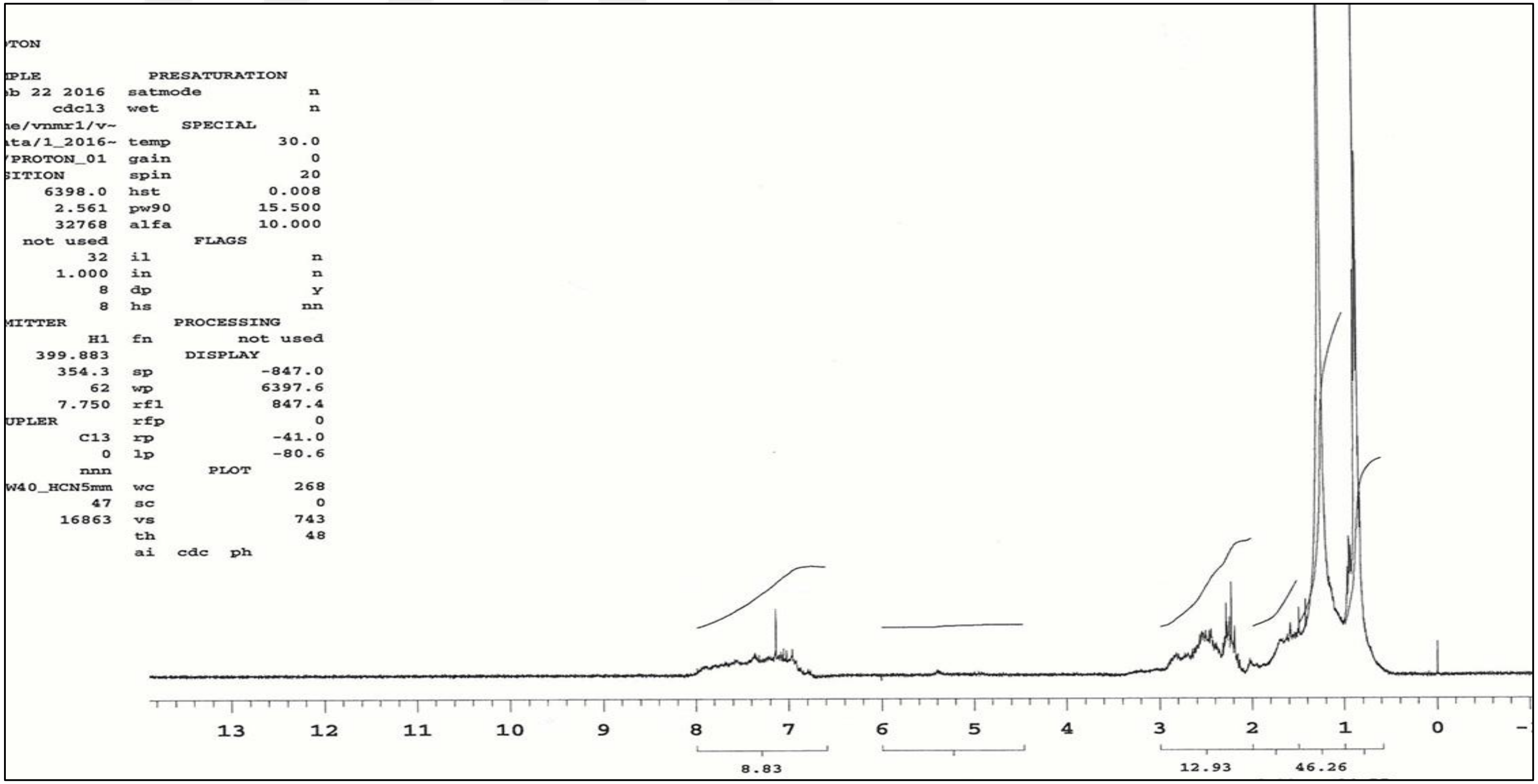
Appendix-10: ^{1}HNMR spectrum of 50% ARCFO and 50% HVGO mixture hydrocracked at 450°C thermal



Appendix-11: ^{1}HNMR spectrum of 50% ARCFO and 50% HVGO mixture hydrocracked at 450°C with catalyst



Appendix-12: ^{1}H NMR spectrum of HVGO hydrocracked at 450°C thermal



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     2.561  pw90          15.500
     32768  alfa          10.000
  not used          FLAGS
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     1.000  in                 n
         8  dp                 y
         8  hs                nn
MITTER             PROCESSING
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     7.750  rfl            847.4
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         0  lp             -80.6
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            th                48
            ai  cdc  ph
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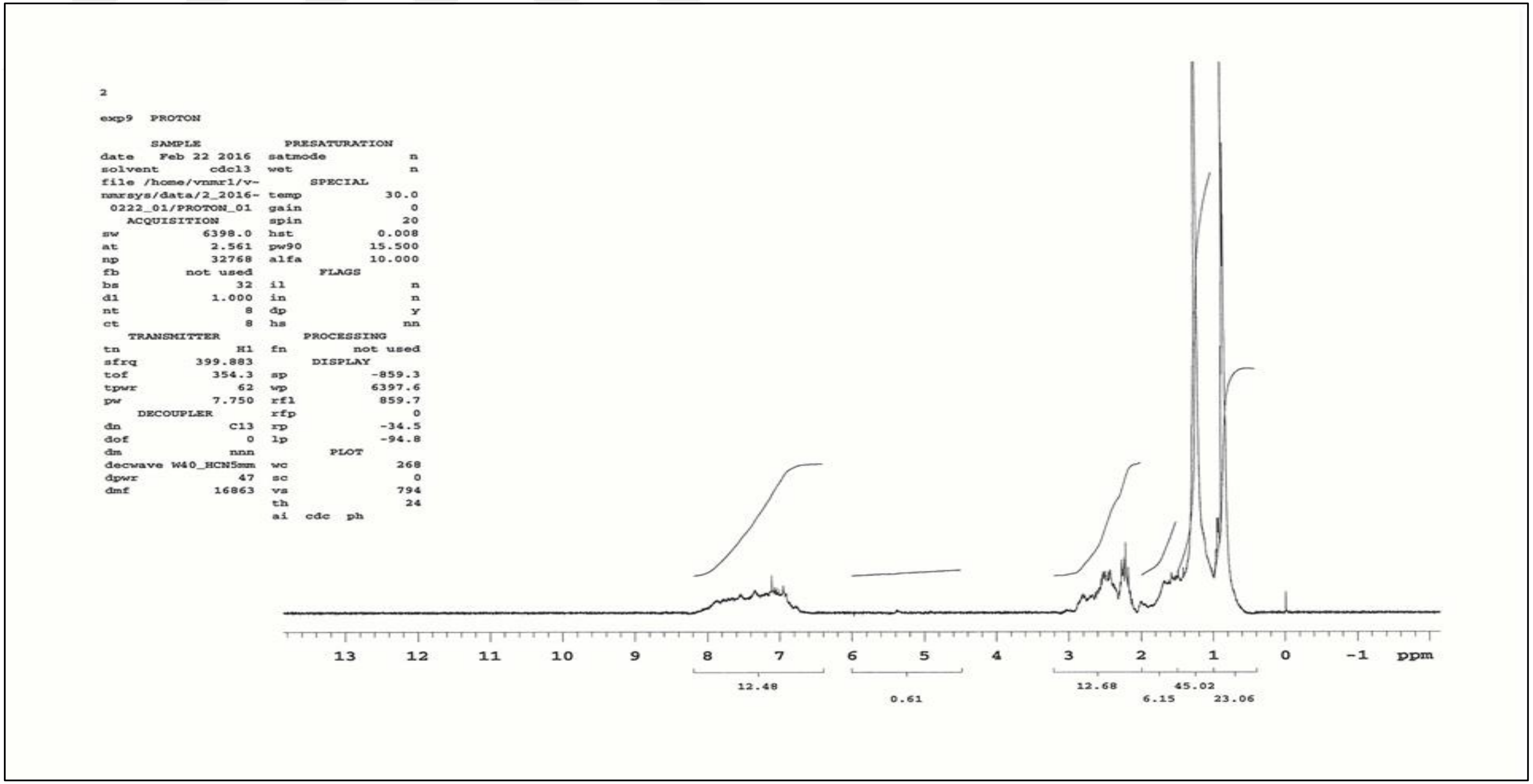
Appendix-13: ^{1}H NMR spectrum of HVGO hydrocracked at 450°C with catalyst



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np            32768  alfa          10.000
fb         not used          FLAGS
bs               32  il                 n
d1            1.000  in                 n
nt                8  dp                 y
ct                8  hs                nn
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tn               H1  fn          not used
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tof           354.3  sp            -859.3
tpwr             62  wp            6397.6
pw            7.750  rfl            859.7
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                     th                24
                     ai   cdc   ph
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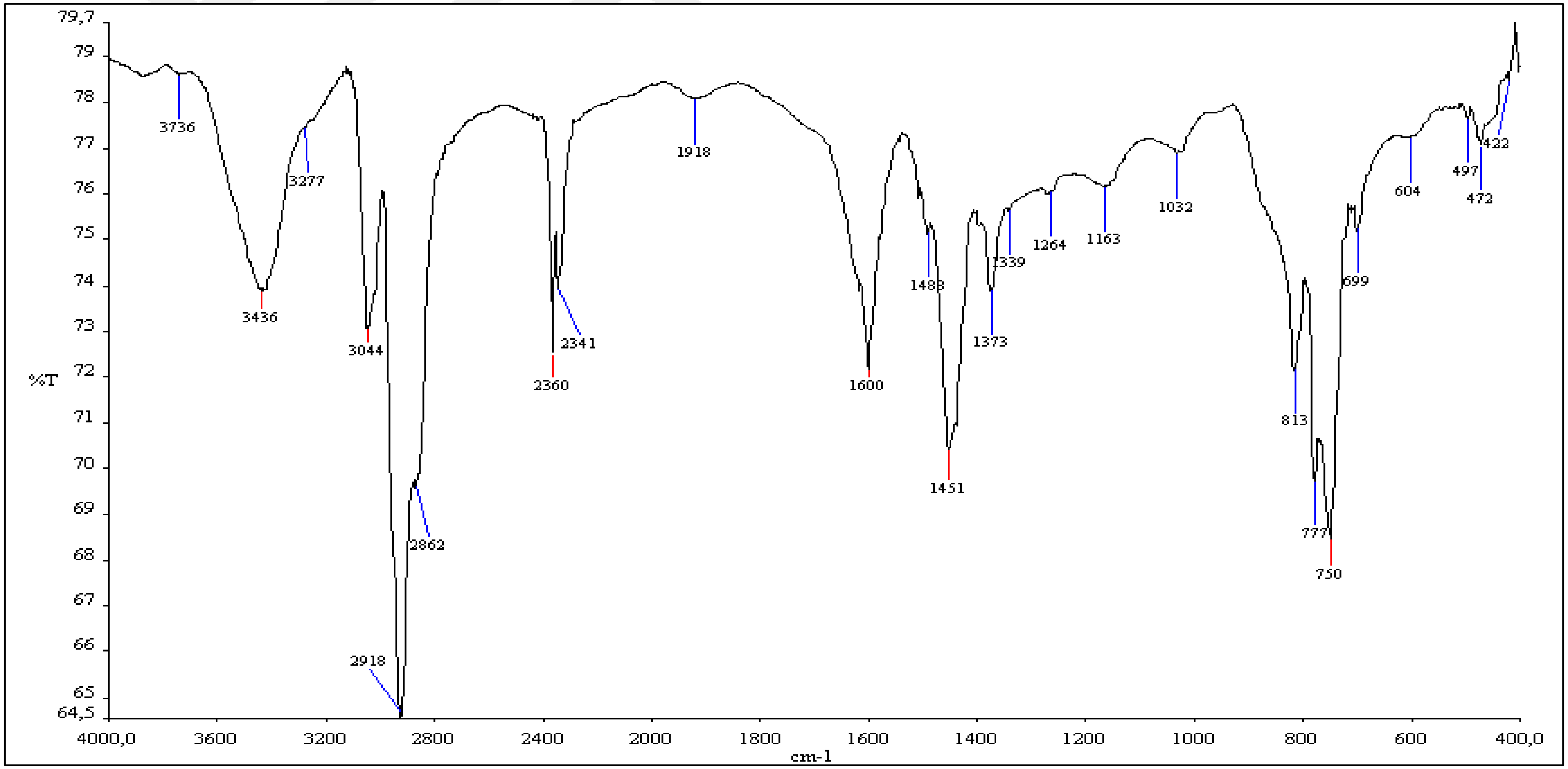
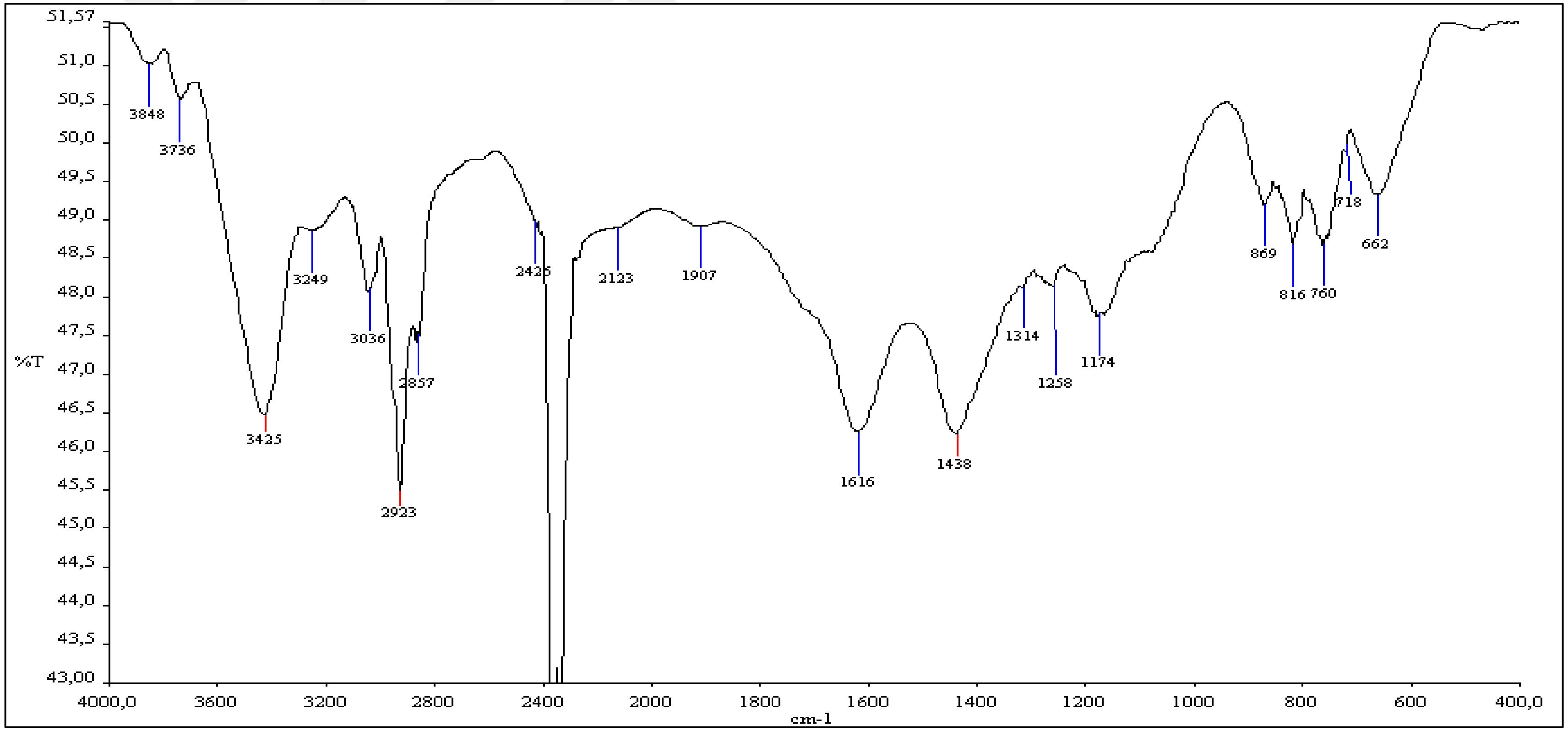
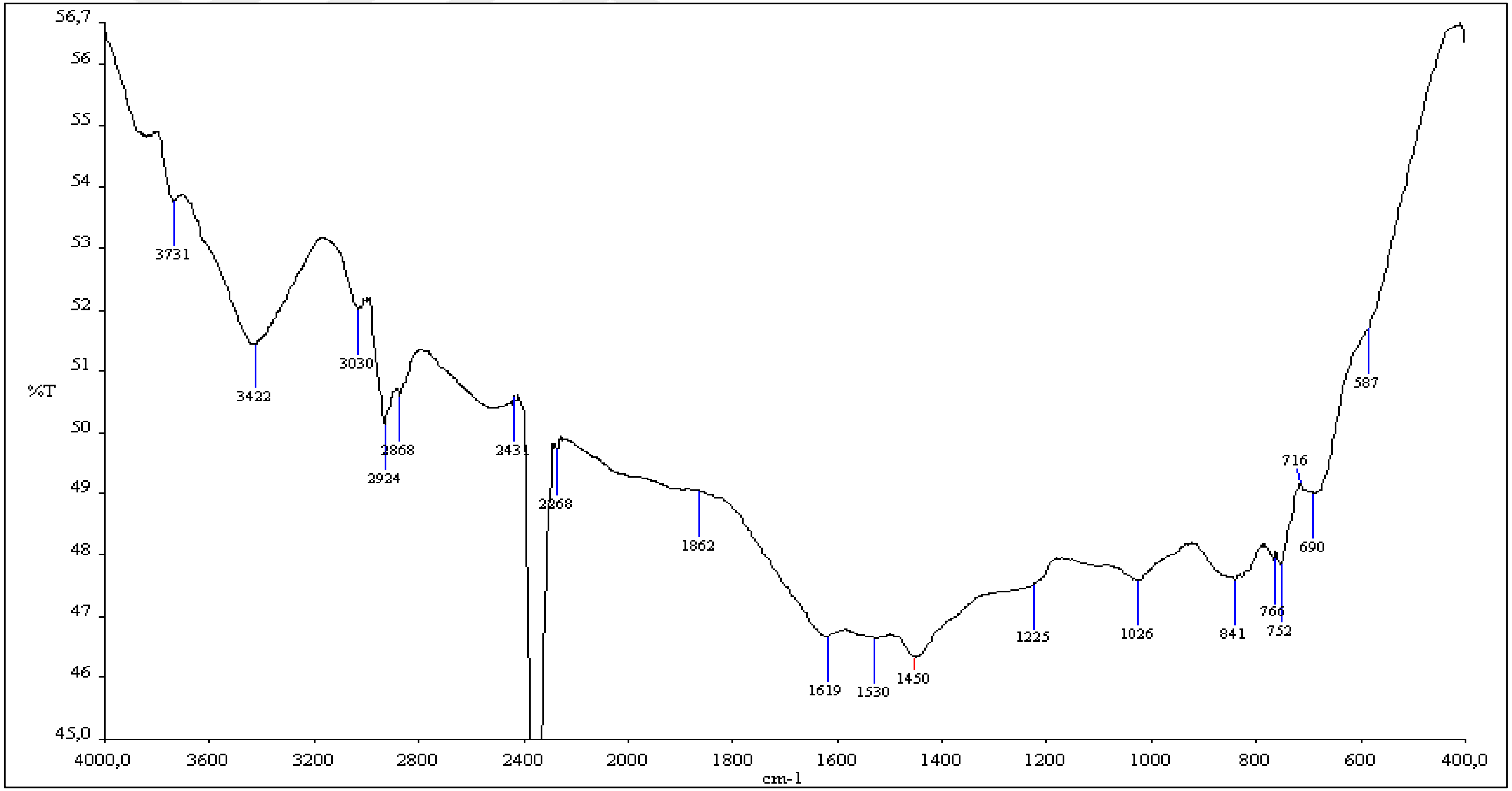
Appendix-14: FTIR spectrum of crude ARCFO



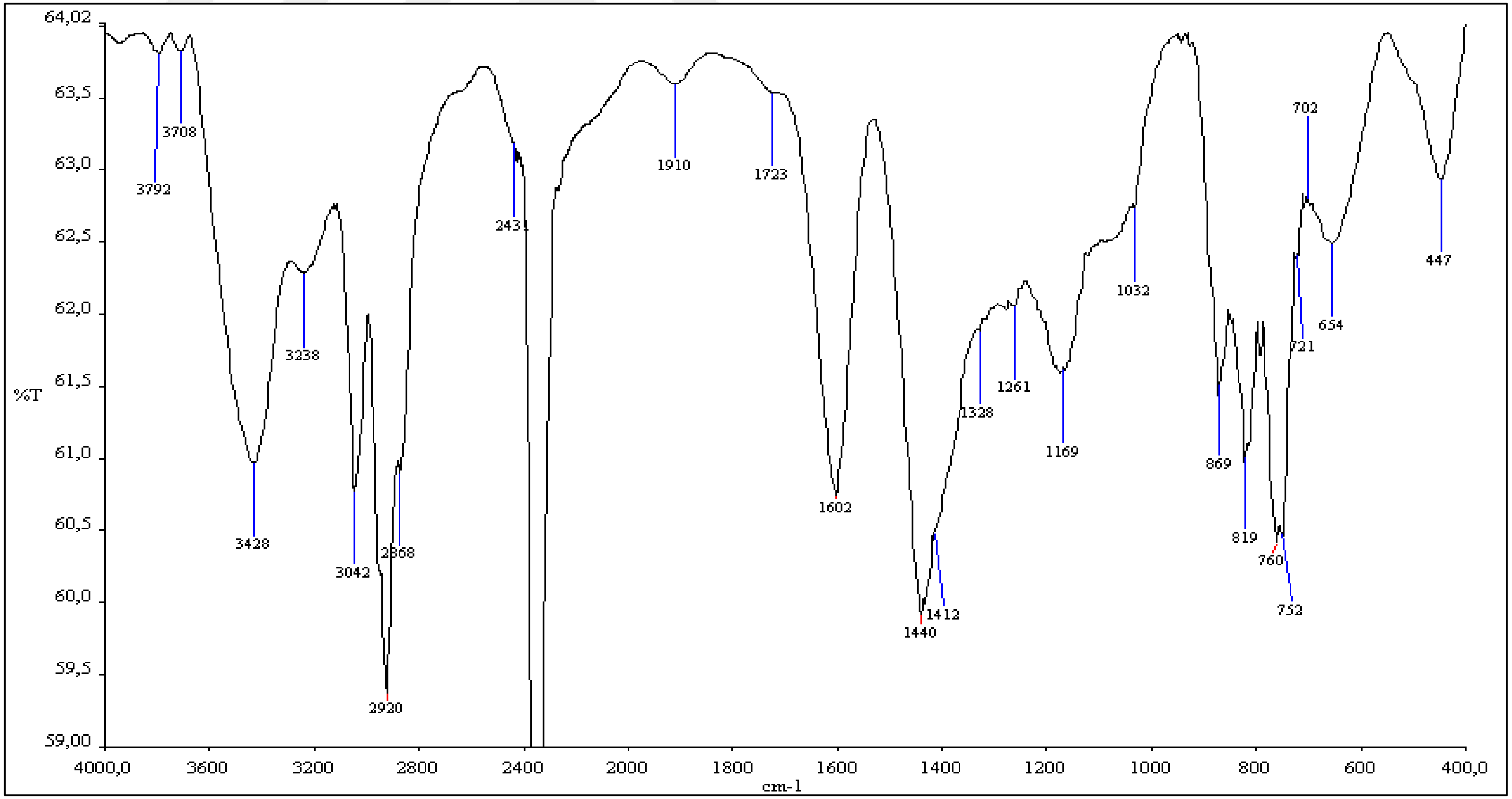
Appendix-15: FTIR spectrum of ARCFO hydrocracked thermal at 400°C



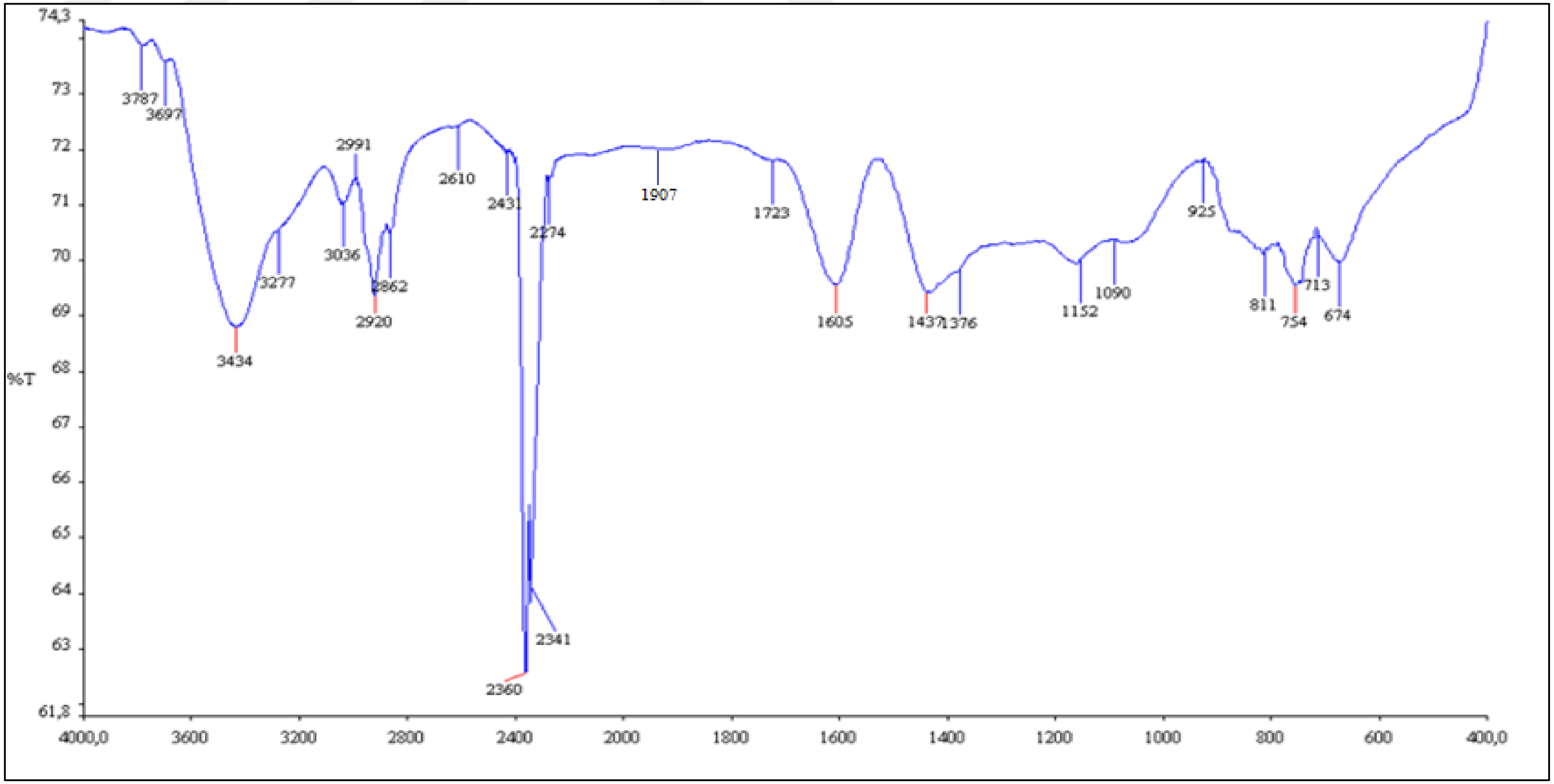
Appendix-16: FTIR spectrum of ARCFO hydrocracked at 400°C wıth catalyst



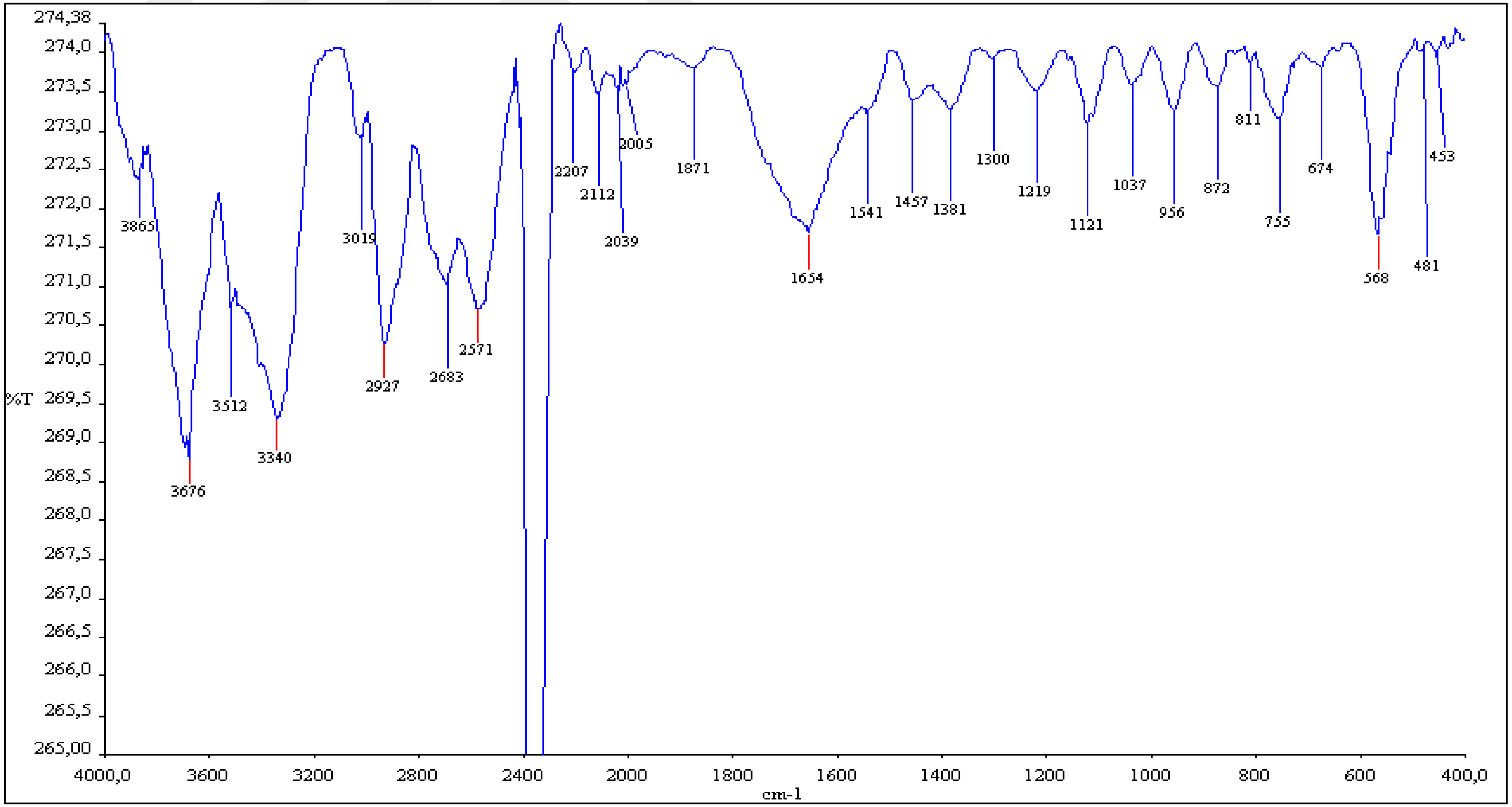
Appendix-17: FTIR spectrum of ARCFO hydrocracked thermal at 425°C



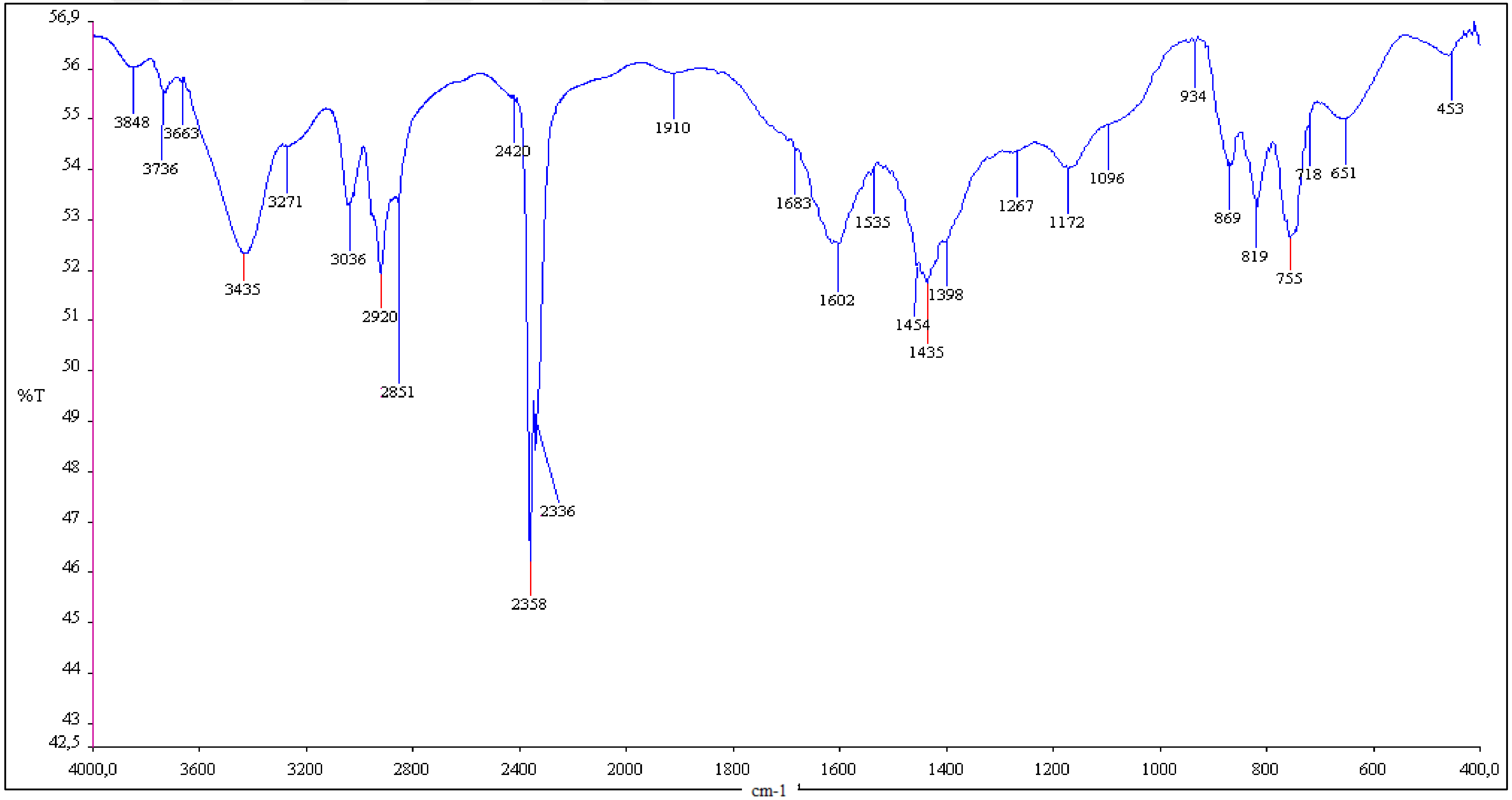
Appendix-18: FTIR spectrum of ARCFO hydrocracked at 425°C wıth catalyst



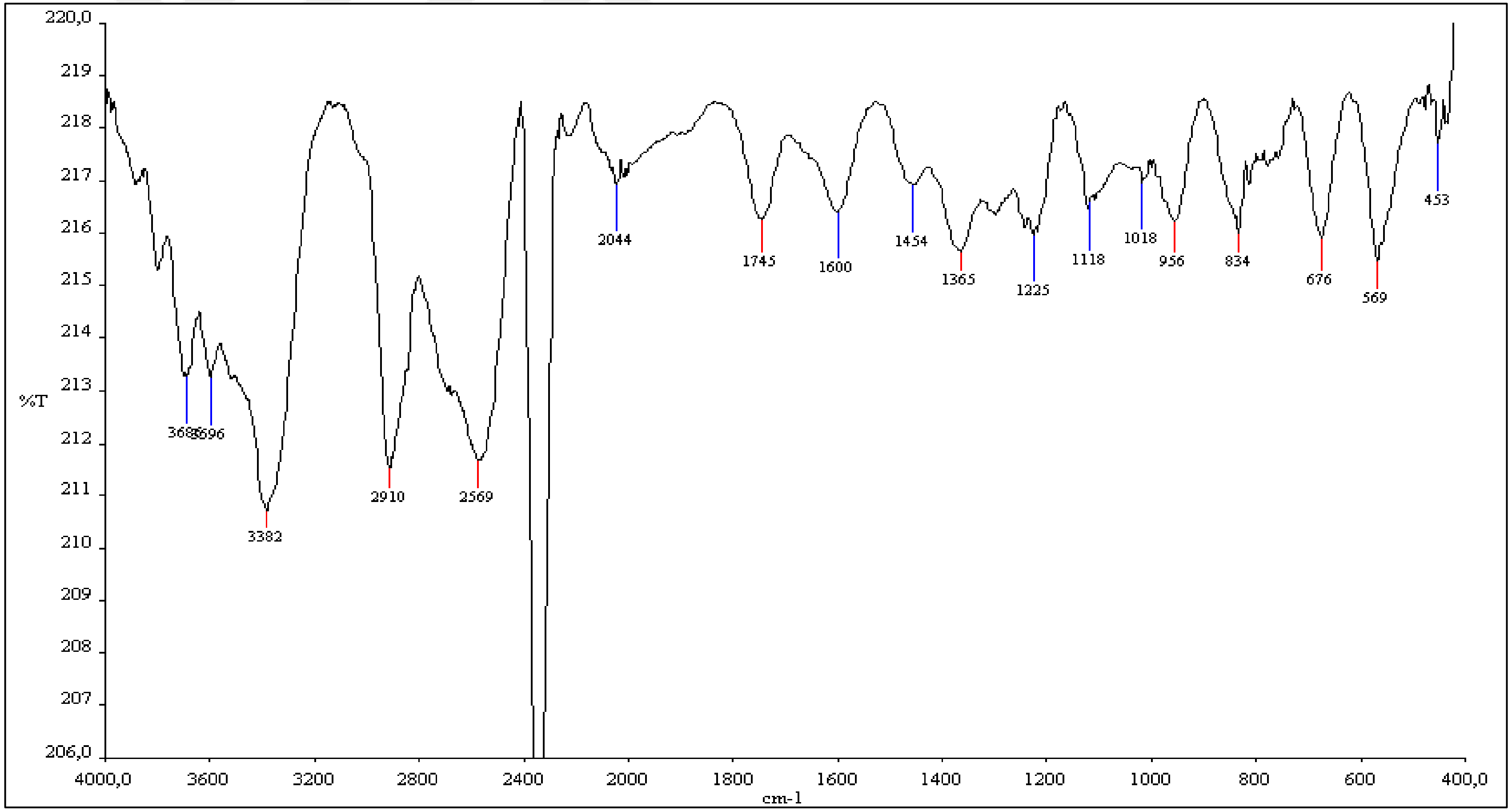
Appendix-19: FTIR spectrum of ARCFO hydrocracked thermal at 450°C



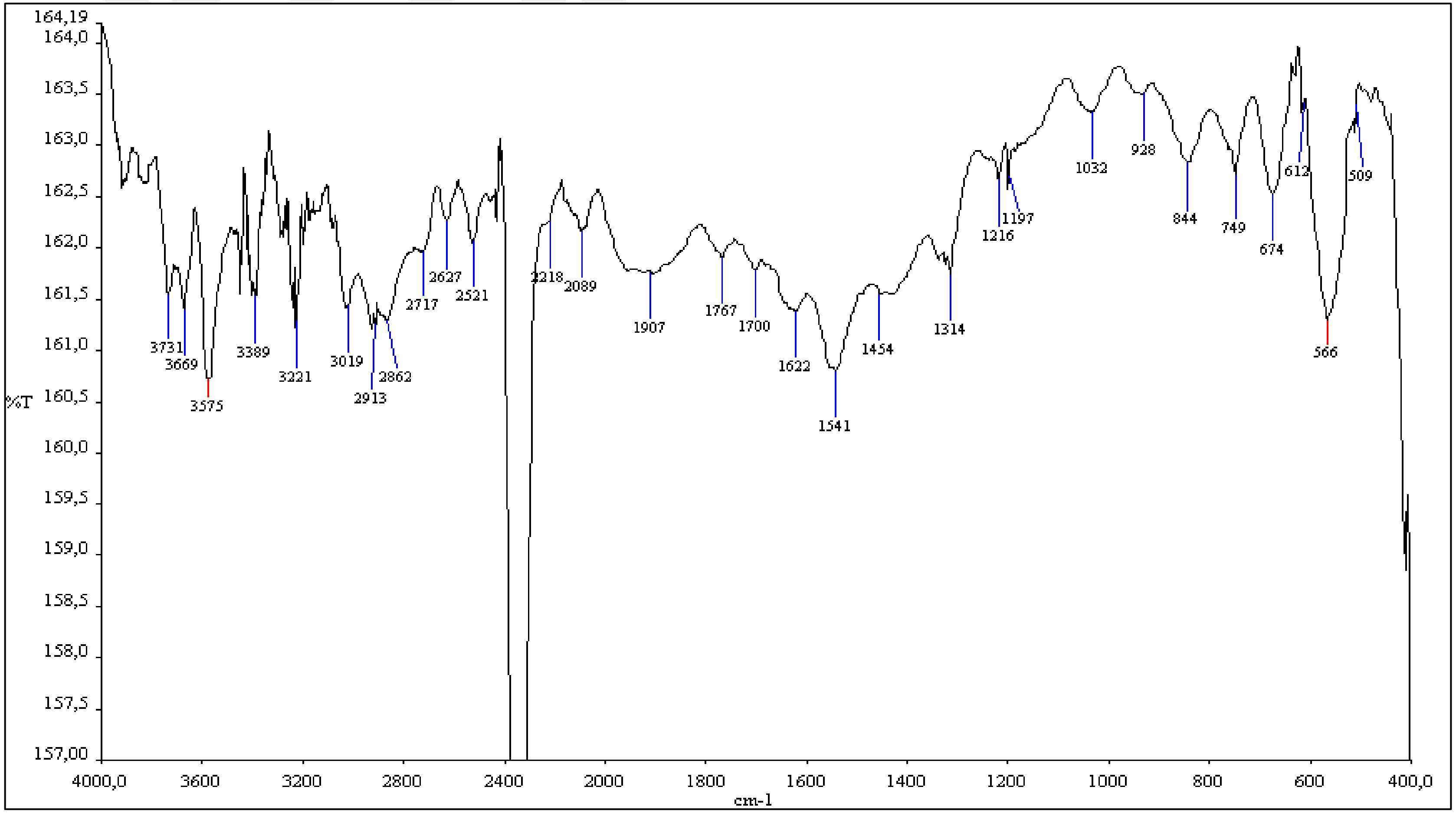
Appendix-20: FTIR spectrum of ARCFO hydrocracked at 450°C with catalyst



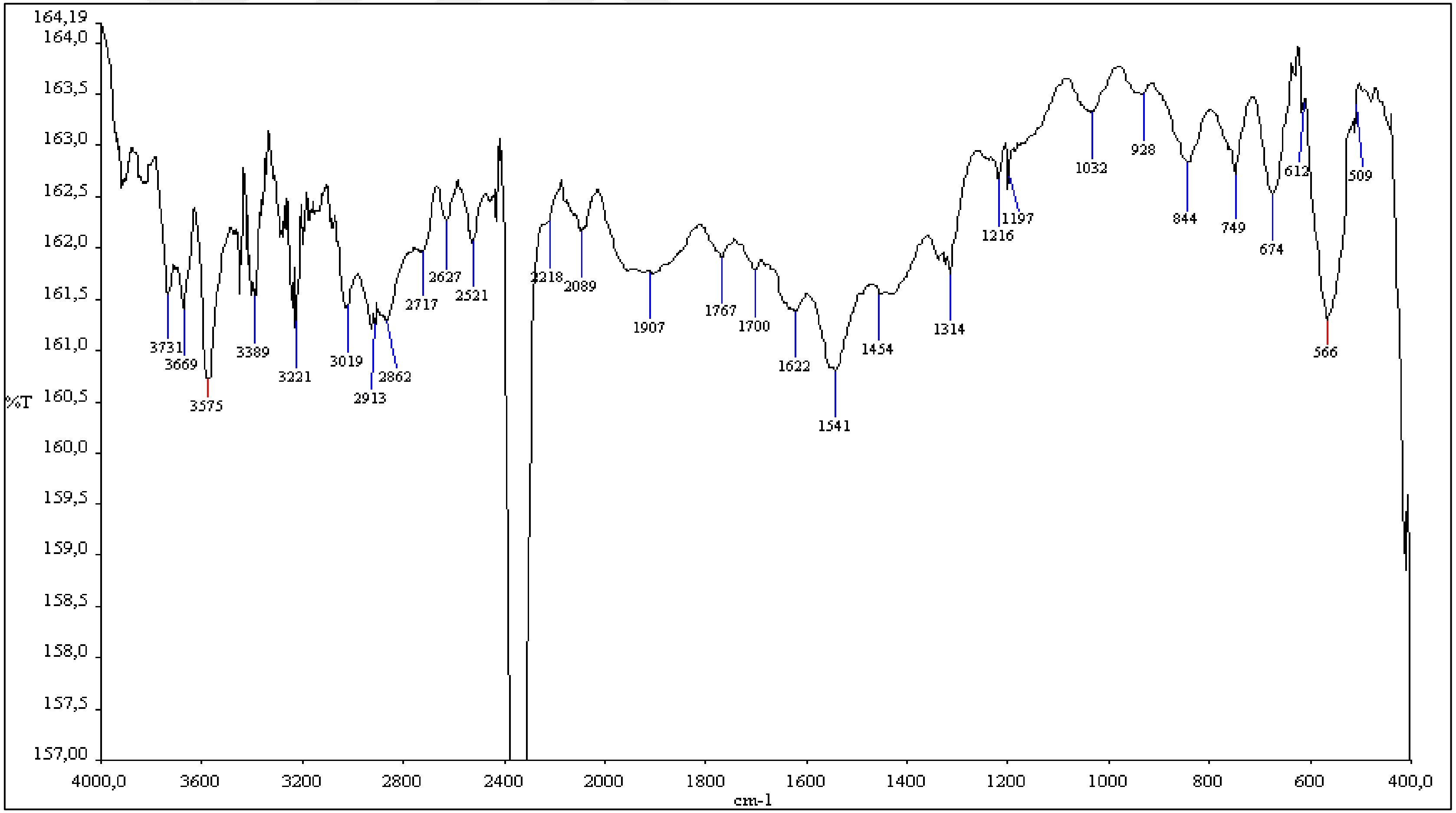
Appendix-21: FTIR spectrum of 25% ARCFO and 75% HVGO mixture hydrocracked thermal at 450°C



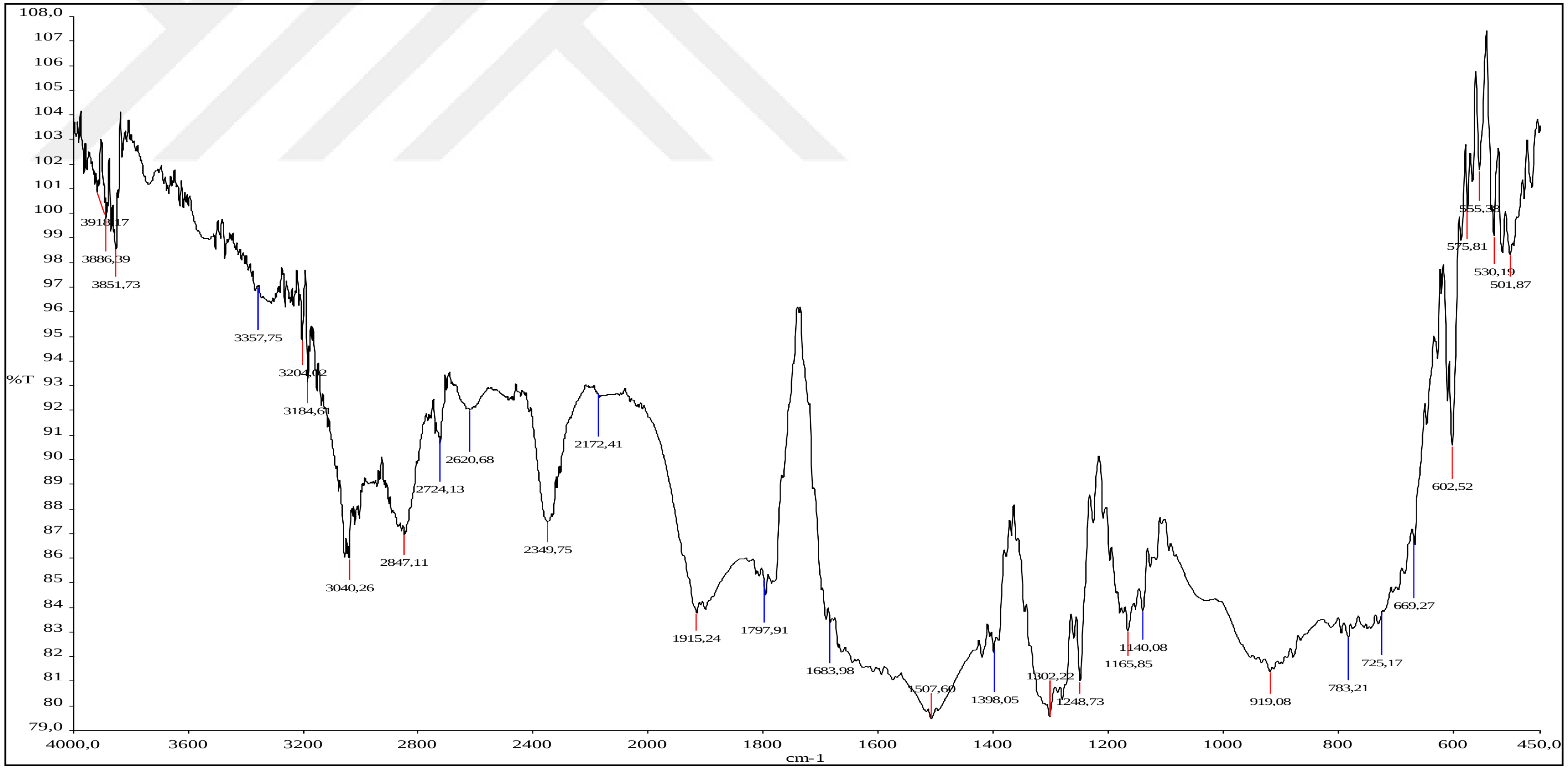
Appendix-22: FTIR spectrum of 25% ARCFO and 75% HVGO mixture hydrocracked at 450°C wıth catalyst



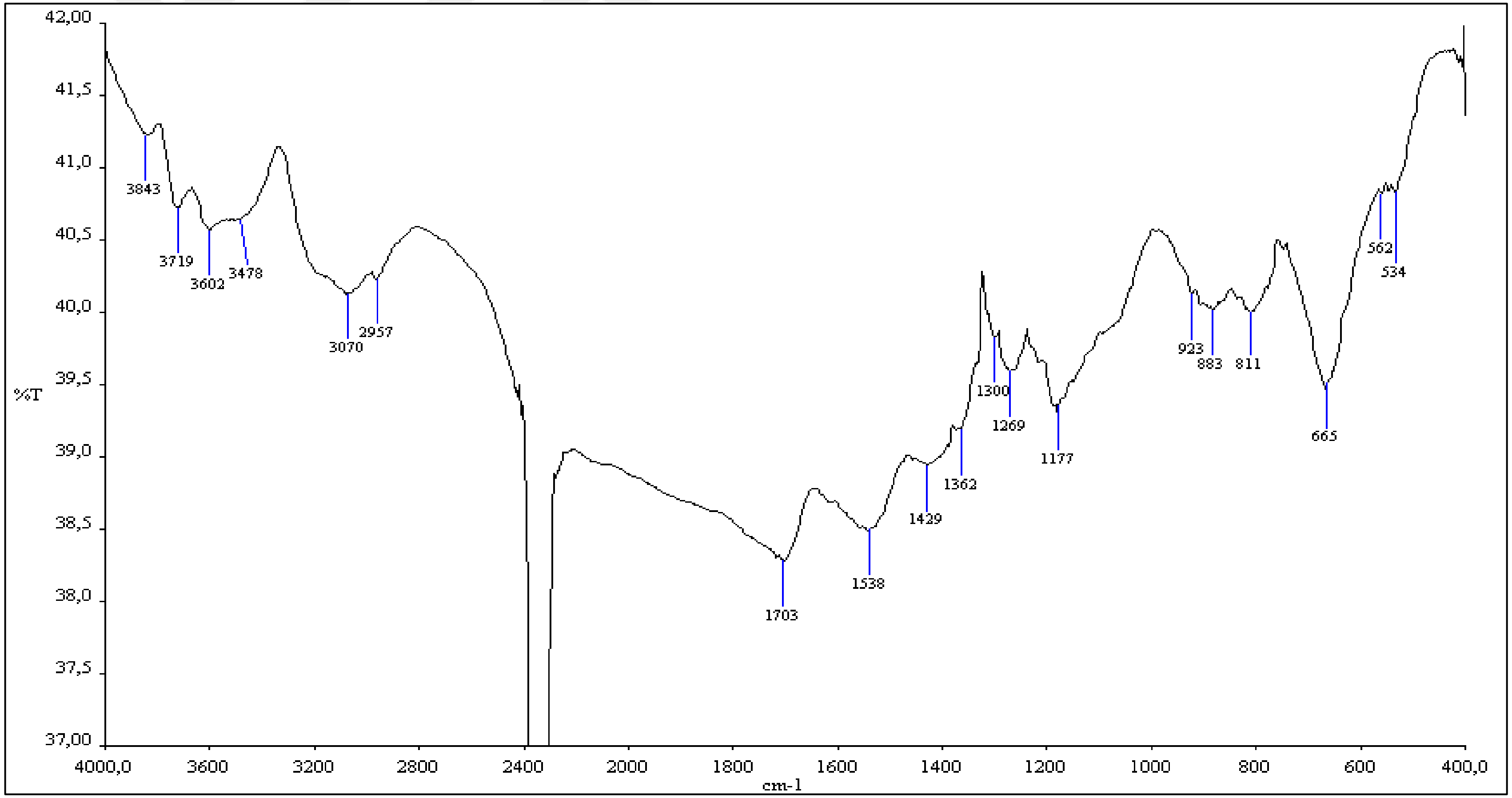
Appendix-23: FTIR spectrum of 50% ARCFO and 50% HVGO mixture hydrocracked thermal at 450°C



Appendix-24: FTIR spectrum of 50% ARCFO and 50% HVGO mixture hydrocracked at 450°C with catalyst



Appendix-25: FTIR spectrum of HVGO hydrocracked thermal at 450°C



Appendix-26: FTIR spectrum of HVGO hydrocracked at 450°C with catalyst