Ethylene Oligomerization to Olefins on Supported Nickel Catalyst

by

Abu Mohammed A. Sani

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

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DEDICATION

This thesis is dedicated to Allah (SWT), may He continue to shower His blessings and guidance upon us, and may He continue to stand for the oppressed and recompense the oppressors!

AKNOWLEDGEMENT

I am indeed grateful to Allah (SWT) for the guidance He bestowed upon me.

I would like to express my deep appreciation to Dr. Halim Hamid who served as my major advisor, Dr. Mohammed Al-Saleh the co-advisor and Dr. Esam Hamad a member of my Thesis Committee. This work would not have been possible without their constructive suggestions, criticisms and above all their patience.

I also wish to thank with all sincerity Dr. Sami Barri for the invaluable assistance and support he gave to me during this work. My feelings of gratitude go to the staff in Section I, Division I, RI, KFUPM for all the assistance rendered to me during this work. To mention few names; A.M. Aitani, M.A. Siddique, K. Alam and A. Ashraf.

To my friends, I must confess life would have been hell here without your constant encouragement, motivation and support. I am very happy and grateful being with you during this program, you really stood with me. You are great! I am whole heartedly grateful to my parents, brothers and sisters for their support and encouragement, may Allah(SWT) continue to assist and guide you. You are really wonderful and loving! To my sister Rabi, I am honestly happy and impressed with the spirit by which you kept in touch with me during the whole program. Kudos!

Most importantly, I must give credit to whom its due: Department of Chemical Engineering, King Fahd University of Petroleum and Minerals. I am indeed grateful for the chance and support given to me. My special thanks to the faculties of the department. Finally, I very much aknowledge the assistance given to me by the Section I, Div-I, RI in letting me use their set-up, equipments and chemicals.

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THESIS ABSTRACT

Name: Abu Mohammed A. Sani
Title: Ethylene Oligomerization to Olefins on Supported Nickel Catalyst
Field: Chemical Engineering
Date: June 1995

Ethylene oligomerization to olefins over supported nickel catalyst was studied in a fixed bed tubular reactor system. Nickel was supported on a prepared amorphous silica-alumina (ASA) by ion exchange and impregnation. Nitrogen was used for catalyst in-situ calcination, hydrogen for reduction and ethylene for reaction. Oligomerization experiments were carried out at various temperatures (100-300°C), space velocities (2-6 h^{-1} WHSV), 4 hours time-on stream for each run and a pressure of 500 psi. Catalyst performance, products distribution, and other side-by reactions were determined. The Ni-ASA (ion exchanged) was found to be more active than the Ni/ASA (impregnated) at the conditions operated. High olefins (oligomers) up to C_{16} were obtained at high temperatures (>200°C) and also at low temperature (150°C) by extending the run period. All the catalysts tested were found to exhibit cracking activity as a result of the support acidity (Si/Al ratio) and at high temperature yielding some traces of paraffins. Increasing the space velocity at high temperature decreased catalyst performance as a result of the reduction in the contact time and more ligther products were produced. Nickel was also supported on a prepared sodium silica-alumina (SSA) by ion exchange. This supported catalyst suppressed cracking activity by lowering the acidity of the support. Cobalt was used as a promoter on one of the prepared catalysts (Co/Ni-ASA) and it was found to be active. At low temperatures it produced about 12% paraffins. All the catalysts exhibited high selectivity to butene-1 at low temperatures (100-150°C).

MASTER OF SCIENCE DEGREE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS

Dhahran, Saudi Arabia

June 1995

خلاصة الرسالة

اسم الطالب الكامل : أبو محمد ساني

عنـوان الدراســة : تحويل الإيثيلين إلى الأليفينات باستخدام حفازات النيكل المدعومة

التخـصـــــص : هندسة كيميائية

تاريــخ الشهــادة : محرم ١٤١٦هـ (الموافق يونيو ١٩٩٥م)

تمت دراسة تحويل الإيثيلين إلى الأليفينات باستخدام حفاز النيكل المحمول في وحدة مفاعل أنبوبي . وتم تحميل النيكل على السيليكا ـ الألومينا غير المتبلرة بواسطة التبادل الأيوني والتشبع . واستخدام النيتروجين في عملية تكليس الحفاز والهيدروجين للإختزال والإيثيلين للتفاعل . وتم إجراء تجارب تحويل الإيثيلين عند درجات حرارة مختلفة (١٠٠ـ٣٠٠) درجة مئوية وسرعة الدفق (٢ ـ ٦ /ساعة) وبلغ زمن التفاعل (٤) ساعات عند ضغط يساوي (٥٠٠) باوند/البوصة المربعة . وتم كذلك تحديد أداء الحفاز وتوزيع المنتجات والتفاعلات الثانوية الأخرى . وأظهرت النتائج أن حفاز النيكل المعد بالتبادل الأيوني لديه نشاطاً حفزياً أكبر من ذلك المعد بالتشبع . وتم الحصول على أليفينات مرتفعة (حتى ١٦ ذرة كربون) عند درجات حرارة مرتفعة (أعلى من ٢٠٠ درجة مئوية) إضافة إلى درجة حرارة منخفضة (١٥٠ درجة مئوية) عند زيادة زمن التفاعل . وأظهرت النتائج كذلك أن الحفازات لديها نشاطاً حفزياً للتكسير نتيجة حمضية الحامل (معدل السيليكا/الألومينا) و إرتفاع درجة الحرارة مما ينتج بعض البرافينات . ولقد إنخفض الأداء الحفزي عند زيادة سرعة الدفق ودرجة الحرارة نتيجة الإنخفاض في الزمن التلامسي ونتج عن ذلك منتجات خفيفة . وتم كذلك تحميل النيكل على السيليكا ـ الألومينا المحتوية على الصوديوم بطريقة التبادل الأيوني . وأظهرت النتائج أن هذا الحفاز قلل من النشاط الحفزي التكسيري نتيجة الإنخفاض في حمضية الحامل . واستخدم الكوبلت في أحد الحفازات المعدة إلى جانب النيكل المحمول على السيليكا/الألومينا ووجد أن لديه نشاطاً حفزياً للتفاعل . وعند درجات حرارة منخفضة فقد نتج عن هذا الحفاز حوالي(١٢٪) برافينات . وأظهرت النتائج أن جميع الحفازات قيد الدراسة لديها إنتقائية عالية لبيوتين ـ ١ عند درجات حرارة منخفضة (١٠٠ـ١٥٠) درجة مئوية .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكه العربيه السعودية

محرم ١٤١٦هـ

Chapter 1

INTRODUCTION

1.1. BACKGROUND

A large variety of industrial products uses ethylene as their basic starting chemical raw material. Catalytic oligomerization of ethylene produces comonomers such as butene and other olefins in the gasoline and diesel ranges.

These intermediates (comonomers) in particular the linear alpha olefins are used with ethylene in the production of low linear density polyethylene (LLDPE), high density polyethylene (HDPE), and in the production of polyolefins, lube oil additives, fatty acids, tertiary amines, plasticizers for poly vinyl chloride (PVC), biodegradable detergents, preparation of alcohols after isomerizing to linear internal olefins, polystyrene, and polyesters (1-6). While branched olefins represent potential candidates for improving octane number (5). 2-butene is used in alkylation process and with other isomers of butene ($C4^{=}$) they can be converted to isobutylene which is useful as an intermediate for t-butyl alcohol and t-butyl methyl ether (7).

Table 1-1 presents the products of olefins with some of their uses and the advantages of using olefins in their production, their market demand was also given and the range of olefins required for their production (1,6).

TABLE 1-1: Products of Alpha-Olefins, their Uses, Demands and Advantages (1,6).

PRODUCTS	USES OF THE PRODUCTS	ADVANTAGES OF USING ALPHA OLEFINS	OLEFINS REQUIRED AND 1990 MARKET
Biodegradable surfactants	Laundry detergents	Minimal environmental impact on water ways in highly populated areas	C_{10}-C_{14} 750 Million Ib/Year
LLDPE	Plastic films	Less damage to goods in shipment and efficient disposal of refuse	C_4-C_8 890 M Ib/Yr. (M=Million)
Plasticizers esters	PVC	Usable over a wider temperature range in automobiles, thus less likely to crack in low temperature	C_4,C_8 & C_{10} 200 Million Ib/year
HDPE	Bleach bottles	High crack resistance (less breakage)	C_4-C_6 200 M Ib/year
Synthetic lubricants	Automobile fuel	Better fuel economy	200 M Ib/year
Polyolefins (olefins derivatives)	Paper and rubber seals in space shuttles	Longer lasting. They maintain sanitary conditions in hospitals	C4-C8
Surfactants	Enhanced oil recovery	Assist in extracting more crude oil from wells	C_{16}-C_{18} 100 M Ib/year

TABLE 1-1 (Continued)

LAB and oxo alcohol	Aldehydes and alcohols for the preparation of detergents	More biodegradable and highly foaming	C_{10}-C_{14} 200 M Ib/year (odd & even linear internal olefins)
Tertiary amines	Light duty liquid detergents, disinfectants, sanitizers and oil recovery	Kill bacteria, fungi and viruses involved in pneumonia, gonorrhea, diphtheria, influenza, polio & many contagious diseases	C_8-C_{18} 60 M Ib/year
Fatty acids	In plasticizers, metal salts, paint dryers, synthetic lubricants, surfactants, cosmetics, alkyd resins, cutting fluids	Consistent quality and availability	C_{10}-C_{14} 40 M Ib/year
Lubricants	Engines oils, gear lubricant, greases, hydraulic fluids	High quality and more stable base oil viscocity	C_4-C_8 120 M Ib/year

TABLE 1-1 (Continued)

Merceptance	Cotton defoliants, water repellent, rubber & detergents	Play important role in biological systems and in the application of chemistry to life	C_3-C_{12} 20 M Ib/year
Paper, fabric and leather	Paper, and gypsum board. ASA and Leather fanning agents	Fine quality ASA is used in petroleum additives and food additives	C_{16}-C_{20} 30 M Ib/Year
Miscellaneous, epoxides, chlorinated olefins, waxes, fuel additives, drag flow improvers	As modifiers for epoxy resins and as polyether for polyurethanes, as additives to the hydraulic oil for high pressure presses, wax applications, and as flow improver	Higher olefins have high melting points and exhibited good wax properties, as fuel additives they are efficient and antifouling, as drag flow reducers they reduce pipeline drag	C_4-C_{30+} 30 M Ib/year

As of 1995 the following companies (Table 1-2) are in the supply of alpha olefins based on ethylene (1,3,8-10). The figures under 1995 base capacity are the sum of the start-up capacities and the capacities that resulted due to expansions over the years.

TABLE 1-2: Companies in Supply of Alpha Olefins based on Ethylene (1,3,8-10).

LOCATION	COMPANY (market entry)	1995 ALPHA OLEFIN BASE CAPACITY	CATALYST FOR THE PROCESS (Homogeneous)
USA	Chevron (1966)	550 M Ib/year	$Al(C_2H_5)_3$ (Ziegler type)
	Ethyl (1970)	1002 M Ib/year	$Al(C_2H_5)_3$ (Ziegler type)
	Shell (1970)	1277 M Ib/year	Nickel complex (SHOP)
UK	Shell (1983)	595 M Ib/year	Nickel complex (SHOP)
	Ethyl (1990)	440 M Ib/year	$Al(C_2H_5)_3$ (Ziegler type)
Japan	Mitsubishi (1970)	77 M Ib/year	$Al(C_2H_5)_3$ (Ziegler type)
	Idemitsu (1989)	110 M Ib/year	Catalytic approach
Russia	Ethyl (1990)	165 M Ib/year	$Al(C_2H_5)_3$ (Ziegler type)
Czech Republic	Chevron (1991)	264 M Ib/year	$Al(C_2H_5)_3$ (Ziegler type)

It is obvious from the information so far mentioned that oligomerization or chain growth of ethylene to produce linear alpha-olefins and other types of olefins is likely to be the basis for such production for many decades. The trend of producing olefins from wax (paraffins) cracking went down for economical and quality reasons (1).

According to latest report by Colin A. Houston & Associates, Inc. (CAHA), Mamaroneck, N.Y.-based consultants, carried out in January 1995. Worldwide demand for alpha olefins is growing at an average annual rate of 6.2%. Consumption of alpha-olefins in direct end uses (excluding internal olefins) will be nearly 1.5 MMton in 1994 growing to 2.4 MMton by 2002 (8).

The demand growth rate for the shorter chain length C_6-C_{10} is growing 7.5% per year, while higher chain length C_{12+} are averaging 1.7% per year growth. The C_4-C_8 for use in polyolefins accounts for about half of all direct alpha-olefins consumption. HDPE and LLDPE are the major users, but newer materials are drawing attention such as very low density polyethylene (VLDPE), polyolefin elastomers (POE), and polyolefin plastomers (POP) because of their excellent growth prospects and high alpha-olefin content ranging up to 30% versus 8% for conventional LLDPE. Dow's plastomers (POPs) and elastomers (POEs) use high levels of exclusively C_8. Polyalphaolefin (PAO) uses C_{10} (8). Some of the companies producing alpha-olefin have came up either with new technology or a license technology. Ethyl is the leading supplier of alpha-olefin to the marchant market and has developed a technology that permits much more selective peaking of the chain length distribution than other producers via ethylene oligomerization.

Other companies producing olefins not based on ethylene are Gujarat-Godrej Innovative Chemicals (GGIC) in India in 1992 who produces a detergent range alpha-olefins from alcohols derived from natural oils. The impact on GGIC on alpha-olefin market will be minimal because the supplies contained too much higher olefins. Sasol in South Africa produces pentene and hexene from coal-derived synthesis gas, adding an unprecedented element of competition to comonomer markets worldwide (8).

There is a rapid increase in recovering but-1-ene from refineries especially in Asia in conjunction with new ethylene or MTBE plant, and is targeted to supply local polyethylene market. Butene-1 capacity is expected to reach 1 MMton by 2002 if all the planned new plants were built. This is likely not going to happen because most of the comonomers growth is in hexene and octene (8). The production of alpha-olefins from all sources is expected to reach 3 MMton by 2002. This forecast assumes that only producers who currently own alpha-olefin technology will construct new plants. Among likely projects by 2002 a plant in China using Shell technology, a new Chevron plant in Europe or Asia and a doubling of Sasol's capacity in South Africa (8).

Most of the catalysts used in the Industries for the catalytic oligomerization of ethylene to olefins are homogeneous Ziegler type consisting of aluminium trialkyls, Ziegler-Natta types consisting of aluminum trialkyls or alkyl halides and zirconium halides, and nickel complexes and nickel ylide type coordination compounds (1,11). The application of these homogeneous catalysts is going on but at the same time studies are being carried out in industries and academic institutions all around the world on the heterogeneous approach (support catalyst on an inorganic material) for ethylene oligomerization because of the inherent disadvantages of the homogeneous catalyst systems, which are (12,2):

- products may be contaminated with catalyst.
- products are difficult to separate.
- the ligands are expensive.
- the catalyst is relatively unstable.
- ethylene pressure requirements too high.
- the solvents used are degraded and
- unwanted polyethylene by-product.

Recent studies carried out by Espinoza *et al* (13-15) and Heveling *et al* (16-18) and Li-min *et al* (19) have shown that heterogeneous catalysis where by nickel catalyst is supported on silica, silica-alumina or zeolites produces olefins in the gasoline and diesel ranges. These olefins contain linear alpha-olefins, linear internal olefins and branched olefins (iso-olefins). The products are easy to separate from the catalyst, the process has lesser problems and better economy. Reactor corrosion is also minimized (12). The acid strength of the support also increases the catalyst activity (14).

Linear alpha olefins can be isomerized to linear internal olefins, the later can inturn disproportionate to short and long chain internal olefins (metathesis) and when the higher internal olefins are reacted with ethylene alpha olefins are obtained (part of SHOP process) (1,8,20,21).

Ethylene is produced by steam cracking of ethane and naphtha and in small quantities from the offgas in FCCU of refineries (22,23). Oligomerization of ethylene by heterogeneous catalyst is going to be studied in this work. The products will be tailored to get the desired olefins range for most applications.

1.2. OBJECTIVES

The present study has been initiated with the following objectives:

a) To prepare and characterize amorphous silica-alumina (ASA), then support nickel catalyst on the ASA and test it for the oligomerization of ethylene.

b) To find the effect of temperature in the range 100-300°C on the catalyst prepared at a space velocity of 2 h^{-1}WHSV and at a pressure of 500 psi.

c) To find the effect of space velocity using the optimum operating temperature. The range of space velocities will be between 2-6 h^{-1}WHSV. The operating pressure will be 500 psi.

In order to tailor the products distribution into the range C_4-C_{10} because of this range vast applications, the following will be carried out;

d) Sodium amorphous silica-alumina (SSA) will be prepared and characterized, nickel catalyst will be supported on it and tested for ethylene oligomerization reaction in the temperature range of 100-300°C at 2 h^{-1} WHSV and 500 psi.

e) Cobalt catalyst will be incorporated on one of the Ni supported on ASA and tested for ethylene oligomerization reaction in the temperature range of 100-300°C at 2 h^{-1} WHSV and 500 psi.

f) Performance comparison of the catalysts tested above for oligomerization of ethylene will be carried out.

Chapter 2

LITERATURE SURVEY

Catalytic oligomerization of ethylene is an ongoing research open to great improvements. It is an alternative to wax cracking. A process where olefins are produced from paraffins cracking with a yield of 35-40% ethylene and propylene and other odd and even numbered carbon chains ranging from C_5 to C_{20+} (1,24). It is also an alternative to naphtha steam cracking for the production of $C_4^{=}1$. The over riding of ethylene oligomerization over these processes is purely based on economics and quality (1). Most important in the ethylene oligomerization process is the development of the catalyst system which must have high activity and selectivity, less process problems and high ease of product separation leading to a better economy. A heterogeneous catalyst offers such advantages (12).

2.1 HETEROGENIZATION

Heterogeneous catalysis refers to a catalytic system where by a phase boundary separates the catalyst from the reactants. Some of the combinations are liquid catalyst-gas reactant, solid catalyst-liquid reactant, solid catalyst-gas reactant (which is going to be used in this study), and solid catalyst-liquid+gas reactants (25). Heterogenization of a catalyst is achieved by any of the following;

a) attaching a metal catalyst to a carrier via the formation of chemical bonds.
b) causing metal catalyst to become physically dispersed within the pore structure of a support (i.e. impregnation).
c) same as (b) but with relatively involatile solvent which remains in the solid, the catalyst is dispersed there (12).

Nickel is one of the catalyst used in the preparation of a heterogeneous system. It is about fifty times more reactive than chromium catalyst and can be obtained easily from its precursors (26). The nickel precursor can be a nickel complex or a nickel salt (2). However, the nickel complex with their zero valency are expensive and are thermally and oxidatively unstable and they are highly consumed (2). The supports that are normally used are acidic in nature mostly, alumina, silica, silica-alumina or zeolites (25).

2.2. NICKEL SALT

The nickel salt studied include inorganic (halides) and organic (carboxylic acids) divalent nickel salts. They are available at low cost. The simple divalent nickel has a +2 formal valence and bonded through ionic or electrovalent linkages to two singly charged anionic groups, e.g. halides or to one doubly charged anionic group, e.g. carbonate and not complexed with or coordinated to any other additional molecular or ionic species. They also contained water of crystallization in addition to one or two anionic groups. Example, $Ni(NO_3)_2.6H_2O$, $NiCl_2.6H_2O$ (2), e.t.c.

2.3. SUPPORTS

Organic polymers for example polystyrene cross-linked with divinyl benzene, have been used as catalyst supports, however, they have been found to have a problem of extensive rupture of structure during preparation (12). They are also not very active (27). Other inorganic supports include silica, alumina, silica-alumina and zeolites (12).

2.3.1. Silica-Alumina

Silica-alumina are amorphous form of dehydrated aluminosilicates. They are porous in nature and lack a definite geometry. They are acidic in nature and can be prepared using different silica/alumina ratios. A high SiO_2/Al_2O_3 ratio provides high temperature stability (28). Their preparation is mostly carried out in sodium form but this can be replaced by ion-exchange with various other cations including ammonium or by a hydrogen ion (28). Silica-alumina is going to be used as a support in this study.

2.3.2. Zeolites

Zeolites on the other hand, are highly crystalline aluminosilicates, having a uniform pore structure, with minimum channel aperture ranging from 0.3 to 1.0 nm. They are produced by dehydration of hydrated aluminosilicates. Their structure is composed of AlO_4 and SiO_4 tetrahedra interconnected through shared oxygen atoms forming a 3-Dimensional network (25,28). This arrangement made them acidic in nature thus liberating (Lewis acid) or accepting protons (Bronsted acid).

Zeolites are of different sizes depending on the cations present and the nature of the treatments such as calcination, leaching and other chemical treatments involved in its preparation. Zeolites are highly active and selective in a variety of acid-catalyzed reactions. The selective behavior of zeolites is associated with the very fine pore structure that allows certain molecules into the interior or only certain products out. This setting by pore structure on an allowable transition states is referred to as *spacio-selectivity* (which is not affected by crystal size) (28).

2.4. OLIGOMERIZATION REACTION

Oligomerization (chain growth) is a term used to describe the conversion of lower olefins such as ethylene and propylene to olefinic products of higher molecular weight, example, butene, hexene, octene, decene, e.t.c. These products are termed dimer, trimer, tetramer, etc. (11). True oligomerization means that the products are integral multiples of the monomer (16). In the oligomerization of alkenes by (non-acid) transition metal the alkenes with terminal double bonds (ethene and propene) have higher rates of reaction than internal alkenes (olefins) (29).

Under the same reaction conditions the ethylene and propylene conversion on the catalyst are the same. However, acid catalysis makes a significant difference with propylene. The rate of conversion of 1-butene was found to be half that of ethylene when averaged over the useful time on stream (13). Most butenes from ethylene oligomerization are present in their thermodynamic composition (75% 2-butene) (30). Acidic sites increases the rate of reaction and promotes double bond isomerization and the formation of branched and higher oligomers. The low reactivity of 1-butene and higher olefins is probably due to the size of the molecule and the presence of internal alkenes (olefins) (30).

2.5. ETHYLENE OLIGOMERIZATION MECHANISM

Transition-metal oxides and salts, supported on inorganic gels such as alumina and silica-alumina, oligomerize ethylene to alpha-olefins C_6-C_{10}. On the surfaces of these catalysts Bronsted acid and coordinative centers exist, which together are responsible for the olefin oligomerization. EPR investigations suggest that Ni(I) ions are the ethylene oligomerization centers in the NiO-Al_2O_3 and NiO-SiO_2-Al_2O_3 system (20,31,32).

The mechanism of olefin polymerization reactions was proposed by Natta soon after the discovery of coordination polymerization catalysts (33). It has now been substantiated that the oxidation state of the active metal in nickel supported on inorganic materials for alkene conversion is Ni^+ (34-37). The following steps are involved in the scheme proposed (38):

Initiation reaction involving Ni-H species:

$$Ni-H + CH_2 = CH_2 \xrightarrow{k_i} Ni-CH_2-CH_3$$

Chain propagation reactions:

$$Ni-(CH_2-CH_2)_nC_2H_5 + CH_2 = CH_2 \xrightarrow{k_p} Ni-(CH_2-CH_2)_{n+1}C_2H_5$$

Spontaneous chain termination through ß-elimination reactions:

$$Ni-(CH_2-CH_2)_nC_2H_5 \xrightarrow{k_t} Ni-H + CH_2 = CH(CH_2-CH_2)_{n-1}C_2H_5$$

Chain transfer with monomer:

$$Ni-(CH_2-CH_2)_nC_2H_5 + CH_2=CH_2 \rightarrow Ni-CH_2-CH_3 + CH_2=CH(CH_2-CH_2)_{n-1}C_2H_5$$

Chain transfer with Hydrogen:

$$Ni-(CH_2-CH_2)_nC_2H_5 + H_2 \rightarrow Ni-H + CH_3CH_2-(CH_2CH_2)_{n-1}-C_2H_5$$

Chain transfer with Aluminium alkyl (AlR_3):

$$Ni-(CH_2-CH_2)_nC_2H_5 + AlR_3 \rightarrow Ni-C_2H_5 + AlR_2-(CH_2CH_2)-C_2H_5$$

Detailed mechanisms for ethylene copolymerization of one and two alpha-olefin molecules were given by Kissin (18,39).

2.6. NICKEL SUPPORTED ON SILICA-ALUMINA

Amorphous support for nickel oligomerization catalysts were given extensive attention (40-42). It was found that reduction of nickel was essential to the activity of Ni/silica, Ni/alumina and Ni/silica-alumina in ethylene oligomerization (34,43,44). Since NiH is the proposed active species (34).

The physiochemical properties of the catalyst such as the nickel concentration, acidity of the support and the reaction conditions had an influence on the performance of the catalyst.

2.6.1. Increasing Nickel Content

In the study of oligomerization of ethylene over nickel exchanged silica-alumina, it was found that activity was due mainly to the presence of nickel. Beach and Kobylinski (45) tested the activity of 1.4 wt% Ni on silica-alumina for ethylene oligomerization at 500 psi and 150°C as 'Ni' concentration is increased, the catalyst activity decreased and the product distribution shifted to lighter products as the catalyst deactivated.

A study carried out by Espinoza *et al* (15) found the ethylene oligomerization activity to be approximately proportional to the Ni concentration. However, the activity per Ni site is higher at low Ni concentration than at higher Ni concentration because Ni exchanges selectively with sites of high acid strength. Increasing Ni concentration resulted into a marked shift to lighter products at the same level of ethylene conversion because of the electronic effects exerted on the Ni by the anionic sites present on the support. Other features they observed are the increase in deactivation rate as Ni content increases while on the other hand the activity recovery on regeneration decreases. The study was carried out in a tubular reactor with the catalyst having the following composition (Ni = 0.03-0.3%, Si/Al = 100, surface area (S_g) = 557m^2/g and pore radius (r) = 1.7 nm)

2.6.2. Increasing Acidity of a Support

The alumina content in silica-alumina is the one responsible for the formation of acid sites. Increasing aluminium content thus increases acidity. This acidity has tremendous effect in determining the selectivity of products in an ethylene oligomerization reaction.

Beach and Kobylinski (45) in their study of ethylene oligomerization using Ni on silica-alumina found the Si/Al ratio to be the dominant factor for the catalyst activity. Higher molecular weight olefins are formed as they increased the Si/Al ratio. At low Si/Al ratio the catalyst was selective for the formation of butenes. Peuckert and Keim (46) studied ethylene oligomerization reaction over Ni supported on silica-alumina (Sg = $102m^2/g$) at various temperatures (50-75°C) and a pressure of 100 bar (1470 psi). Catalyst activity was found to be low. However, increasing the acidity of the support brought about increase in the activity of the catalyst with the formation of internal olefins, cracking and branching products.

By using supports of different acid strength, Espinoza *et al* (14) were able to established the same results as that of Peuckert and Keim. In addition they observed for their system (Ni = 0.27wt%, Si/Al = 100, S_g = $557m^2/g$, r = 1.7 nm) the deactivation rates were moderately fast but not strongly affected by the acid strength and that the supports with stronger acidity enhances more Ni activity with the reaction becoming selective to cracking.

Heveling *et al* (18) investigated the oligomerization of ethylene to gasoline and diesel range products in a fixed bed flow reactor using Ni supported on amorphous silica-alumina (Si/Al = 36, S_g = $450m^2/g$). The catalyst was highly active and requires no pre-reduction. Two regions of high catalytic activity were observed one at low temperature 120°C due to the Ni and the other at high temperature 300°C where the acidity of the support contributed a lot. Cracking products were obtained as a result of the support acidity.

2.6.3. Reaction Conditions

Reaction parameters, such as temperature, pressure and space velocity are the determinant factors of catalyst activity, stability, and deactivation. Process pressure has been found to be a critical aspect (18). Lapidus *et al* (32) and Elev *et al* (47) studied ethylene conversion over Ni on silica-alumina at moderately low temperatures (100-150°C) and high pressure 508 psi, a rapid deactivation of catalyst was observed as the temperature and pressure were increased. For Ni supported on silica-alumina with S_g = 102m^2/g and operated at 50-75°C at 100 bar (1470 psi), Peuckert and Keim (46) observed the catalyst activity to be low.

Espinoza *et al* (13) studied the oligomerization of ethylene over Ni exchanged silica-alumina having S_g = 557m^2/g and Si/Al = 50. The effect of operating conditions were examined. Temperatures were varied from 300-380°C, pressure from 25-377 psi and a space velocity 0.15-12 h^{-1} WHSV. It was found that the rate of deactivation of the catalyst increased with increasing temperature and pressure while the space velocity has no effect on it. The activity, however, increased with increasing the temperature the pressure and the space velocity. With increasing pressure there was also an optimum performance.

The effect of temperature on the performance of Ni supported on silica-alumina (S_g = 450m^2/g, Si/Al = 36) investigated by Heveling *et al* (16) showed a complex behavior as there was a maximum at 120°C and above 300°C. The space velocity used was 2 h^{-1} MHSV for the entire study while the pressure was varied from 157-500 psi. The catalyst activity was found to increase at relatively high pressure and low temperature. High temperature also caused high cracking activity. The deactivation was also rapid at low pressure and high temperature.

2.7. NICKEL SUPPORTED ON ZEOLITES

Catalysts that rely on their acid sites for reactivity involve carbonium ions mechanism. Acid sites also increases formation of branched products. Reactivity of ethylene over zeolites (Y, X and ZSM-5) is low. However, incorporating an active transition metal, Ni into Y-zeolite led to a more active catalyst, with high yield of branched alkenes (olefins) (17).

Ethylene oligomerization carried out over Ni/Y-zeolite gave 1-butene as primary product which rapidly isomerizes to *cis* and *trans*-2-butene at 250°C and 441 psi (48,34). Diaz *et al* (49) for the same conditions got oligomers up to C_{12}. Forni *et al* (50) treated Ni/X-zeolite with amine to suppress the acidity, 1-butene dimerizes to octenes of high linearity at 170°C and 441 psi.

Heveling *et al* (17) examined Ni/Y-zeolite at 40-360°C using a pressure of 508 psi and varying the nickel content from 1.13 to 3.7wt% for ethylene oligomerization reaction to diesel range products (C_4-C_{18}). The catalyst was found to be more active at high pressure and low temperature. But, it deactivates rapidly and the activity recovery was low. Internal olefins were formed at high temperature. The effect of raising nickel content was an increase in activity and the formation of heavier products. They also found the first 0.5% nickel exchanged into the zeolite do not contribute to catalysis. At high temperature (>200°C) acid sites marginally catalyzed ethylene conversion but were considered to be primarily responsible for the isomerization, oligomerization and cracking of primary products.

Ng and Creaser (51) investigated the kinetics of ethylene oligomerization on Ni exchanged Y-zeolite in the temperature range of 50-70°C and a pressure range of 115-615 psi. They found the catalyst was effective in ethylene dimerization to 1-butene. However, it does deactivated rapidly due to the formation of oligomers. A threshold Ni loading point at which the activity per Ni site is increased was found. As a result of the migration of Ni^{2+} to the inactive sites of the zeolite. Ni was found to be the active site for ethylene dimerization while isomerization of 1-butene is caused primarily by the protonic acid sites on the zeolite support. This behavior was confirmed after the addition of picolinic acid which increases the support acidity.

Kobelkova *et al* (52,53) carried out ethylene oligomerization over H-ZSM-5 and H-Y and Meclin *et al* (54) on ZSM-5 at 27-100°C. The catalysts were found to have low activity and all sorts of hydrocarbons were obtained (olefins, paraffins and aromatics). Oligomerization of ethylene on ZSM-5 at high temperatures 300-390°C gave heavier products (55-59). Li-min and Burton (19) using ZSM-5 of low acidity at 100°C observed low activity. However, addition of methanol increased the total ethylene conversion, but, altered the selectivity. Dimerization to C_4 was dominant reaction. Same observation was made with carbon 14 isotope (^{14}C).

Garwood *et al* (22) studied the conversion of lower olefins that are obtained from FCC offgas in a multistage system with reactor quenching means. The first adiabatic catalytic bed reactor contained an acidic zeolite solid catalyst (ZSM-5) and the second a metallic zeolite catalyst (Ni/ZSM-5). Interstage quench means was incorporated for injecting water in the feed to the first reactor and into the effluent from the first reactor to the second one. Under the following conditions 90-415 psi, 0.4-0.6 h^{-1} WHSV and 4.4-157°C. The feed contained light gases and

ethylene (12.6 mol%) It was converted to all sorts of hydrocarbons (paraffins, olefins, diolefins, triolefins, aromatics e.t.c.).

2.8. KINETICS STUDY

Reikert (60) in his kinetic study of ethylene oligomerization over NiY, experimentally distinguished the rates of sorption, diffusion and reaction. By considering the sorption and diffusion steps the reaction was found to be second order with respect to ethylene concentration. The apparent activation energy was 17 kJ/mol. and the true activation energy was 88 kJ/mol.

The study by Espinoza *et al* (13) on ethylene oligomerization over Ni exchanged silica-alumina considered the effects of operating conditions (120-380°C, 23-310 psi and 0.5-12 h^{-1} MHSV) and found that the reaction was first order by considering the effect of pressure at 6 and 12 h^{-1} WHSV at 300°C based on an isothermal integral flow reactor model. The apparent activation energy of 37 kJ/mol was obtained from the Arrhenius plot at constant space velocity (6 h^{-1} WHSV) and pressure of 167 psi.

Heveling *et al* (17) carried out a kinetic study for the catalyst NiY at temperature ranging from 40-360°C using a tubular reactor. Based on the application of an isothermal integral flow reactor model at 150°C and 2 h^{-1} MHSV, first order kinetics were found with respect to nickel content in the low temperature region.

Ng and Creaser (51) carried out kinetic studies on ethylene oligomerization over Ni exchanged zeolite-Y in the temperature range of 50-70°C and a pressure range of 115-615 psi in a tubular flow reactor operating in differential mode. First order dependence on ethylene was observed and the apparent activation energy decreased from 58.6 to 42.1 kJ/mol as the time of the catalyst on stream was increased.

2.9. EFFECT OF A PROMOTER

Incorporating a certain element with Ni supported on silica-alumina or zeolites as a promoter has worked in some cases. Glockner and Barnett (4) sulfided NiO impregnated on silica-alumina (3.6% Ni, 0.29wt% S) and using an autoclave at 415 psi and 150°C carried out ethylene oligomerization and obtained oligomers with 85.4% C_4 and 9.6% C_6 selectivity.

Nubel (7) incorporated ZnO with NiO supported on HAMS-IB crystalline borosilicate molecular sieve composited of an amorphous silica-alumina at 190°C and 350 psi. The catalyst performance and the selectivity to higher oligomers increased. The catalyst deactivation over three days period was insignificant.

Chapter 3

CATALYST PREPARATION, MATERIALS REQUIRED EXPERIMENTAL SET-UP AND PROCEDURE

3.1. CATALYST PREPARATION

3.1.1. Support preparation

An aqueous mixture of tetrapropylammonium aluminate was gelled with silicic acid stirred well, dried at 90°C and calcined at 530°C to get the silica-alumina (19). Procedure for preparing TPA aluminate is given in Appendix A-1. For the silica-alumina with sodium, NaOH was added to the mixture according to the composition reported by Landau *et al* (61). The mixture was left under stirring untill its pH stabilized then dried at 90°C and calcinated at 500°C. Calculations of the chemicals composition used are reported in Appendix A-2.

3.1.2. Nickel Ion-exchange

The prepared support was calcined at 500°C then cooled down in a dessicator. Solution of the nickel precursor 1M was prepared from nickel nitrate. The support was added to the solution and refluxed with stirring for 4-6 hours , followed by filtration, washing and drying at 90°C over-night and finally calcined at 500°C (stage-wise) for 3 hours (19,62,63). Calculations for the ion exchange are presented in Appendix A-3.

3.1.3. Nickel Impregnation

The support was calcined at 500°C then cooled down in a dessicator. Solution of the nickel precursor was prepared from nickel nitrate, based on the calculation presented in Appendix A-3. The support was added to the solution and put in a rotary evaporator at 90°C. After the water had evaporated the catalyst was removed and dried at 90°C over-night and finally calcined at 500°C (stage-wise) for 3 hours to decompose the nickel nitrate to NiO (62-64).

3.1.4. Promoter Impregnation

Cobalt was used as a promoter for the supported nickel catalyst. After Ni had been supported on the amorphous silica-alumina, a solution of cobalt precursor was prepared from cobalt nitrate. The catalyst and cobalt precursor were put in a rotary evaporator at 90°C. After the water had evaporated the catalyst was removed and dried at 90°C over-night and finally calcined at 500°C (stage-wise) for 3 hours to decompose the cobalt nitrate to CoO (62-64).

3.2. EXPERIMENTAL SET-UP

Figure 3-1 shows the process diagram of the experimental set-up used in the study. The set-up was constructed by the Research Institute, Div-I, KFUPM. The set-up is made up of three parts: feed section, reaction system and product separation section. The reaction was carried out in a tubular stainless steel (fixed bed) reactor. The schematic of the reactor is shown in Figure 3-2. Table 3-1 lists the reaction parameters and their operating condition ranges.

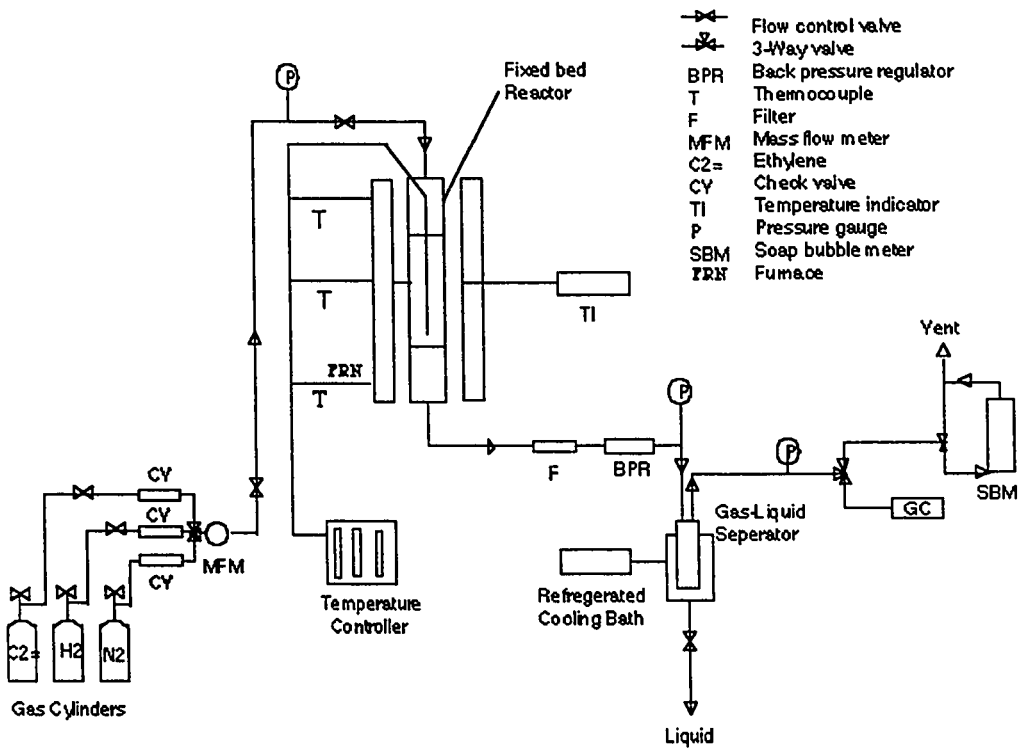
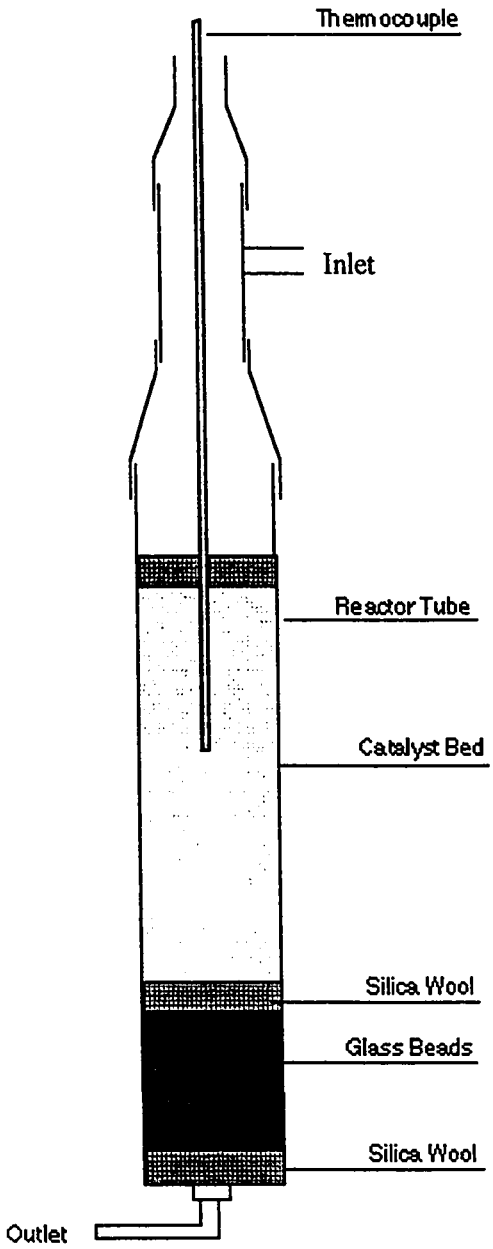


Figure 3-1: Experimental Set-up



Reactor dimensions
OD = 1.27cm
Thickness = 0.2cm
Height = 34cm
Volume = 27cc

Figure 3-2: Schematic of the Fixed Bed Reactor

TABLE 3-1: Design Basis of the Experimental Set-up.

PARAMETER	DESIGN BASIS
Ethylene flowrate (cc/min)	0-1000
Nitrogen flowrate (cc/min)	0-1000
Hydrogen flowrate (cc/min)	0-1000
Furnace Temperature (°C).	up to 750
Space Velocity (per hour)	1-20
Pressure (psi)	0-800

3.2.1. Feed Section

From the feed section, the feed under controlled pressure and flowrate is supplied to the reaction system. The feed section consisted of ethylene, hydrogen and nitrogen cylinders, and a Brook's mass flowmeter. All the gases were supplied at a regulated flowrate using Brooks mass flowmeter. Nitrogen was used for purging the system, hydrogen for reduction and ethylene for the reaction. The various gas lines to the reactor were constructed of 1/4" stainless steel tubing.

3.2.2. Reactor Section

A tubular stainless steel 1.27 cm (0.5") O.D. tube having a thickness of 0.2 cm and a height of 34 cm and volume of 27 cc was used as the reactor. The catalyst sample was placed in the reactor and held in position using silica wool and glass beads supports to provide a fixed bed operation and another silica wool at the top to avoid pressure losses. A thermocouple located at the catalyst bed center was used to measure the temperature of the reaction and a three-zone electric furnace was used for its control (65).

3.2.3. Product Separation Section

Reaction products were separated into liquid and gaseous fractions. The section consisted of a cooling system comprising a refrigeration circulator which contained a mixture of ethylene glycol and water as the circulating medium. The unit has got a capacity of 1 liter and was operated at 0°C. The condensed products taken at various sampling times through flow-drain valves located at the bottoms of the cooler. Gaseous products were sampled through rubber tubing to an on-line gas chromatography (65).

3.3 EXPERIMENTAL PROCEDURE

The experimental procedure is presented in Table 3-2.

TABLE 3-2: Experimental Procedure.

STEP	ACTIVITY
1	**CALCINATION IN AIR** -Prior to catalyst loading into the reactor, the sample was calcined at 500°C in the presence of air for 4 hours (62,66).
2	**REACTOR PACKING** -Catalyst sample (1 gm) was loaded at the center of the reactor with the help of glass beads and glass wool as supports (Figure 3-2). -Leak test at high pressure (>500 psi) to ensure the unit is free from leak and it can withstand the reaction pressure.
3	**CATALYST CALCINATION** -100 cc/min Nitrogen stream was used for 1 hr at 300°C (stage-wise) and 500 psi in-situ to clean up residual calcination products and any other impurities.
4	**REDUCTION** -Hydrogen was used for reduction at 300°C and 500 psi under 100 cc/min stream for 3 hrs to make the nickel active by changing it from NiO to NiH. -In situ activation prevents contamination with air and other gases which might oxidize or poison the nickel (67).

TABLE 3-2: Experimental Procedure. (CONTINUED)

5	**RUN START** -Reactor heated-up to the required temperature using different temperature settings (100-300°C). -Product coolers started-up and set to 0°C. -Gas chromatograph started-up. -Ethylene was fed at controlled rate (2-6 h^{-1} WHSV, at 500 psi). -N_2 was fed over night when reaction was not carried out. -Operating conditions were revisited to ensure the activity of the catalyst at those conditions is constant. -Gaseous product flowrate was measured with a 100 ml bubble meter, a stop watch and an intelligent flow meter
6	**SAMPLING** -Gaseous product were injected into GC at specific intervals (2-4 hrs). -liquid product was collected from the bottom of the separator and its weight determined. It was then injected into capillary GC.
7	**RUN STOP AND SHUT DOWN** -Run stop when catalyst deactivated or screening completed. -Shutdown and reactor unloading was followed. -Spent catalyst was analyzed for coke deposition. -All observations and readings from the start to the end were recorded.

TABLE 3-3: Operating Conditions

TEMPERATURE	PRESSURE	SPACE VELOCITY	RUN TIME
Effect Of Temperature			
100°C	500 psi	2 h^{-1} WHSV	4 hours
150°C	500 psi	2 h^{-1} WHSV	4 hours
200°C	500 psi	2 h^{-1} WHSV	4 hours
250°C	500 psi	2 h^{-1} WHSV	4 hours
300°C	500 psi	2 h^{-1} WHSV	4 hours
Effect Of Space Velocity			
300°C	500 psi	2 h^{-1} WHSV	4 hours
300°C	500 psi	4 h^{-1} WHSV	4 hours
300°C	500 psi	6 h^{-1} WHSV	4 hours

3.4. MATERIALS USED

Catalyst precursors;

$Ni(NO_3)_2.6H_2O$

$Co(NO_3)_2.6H_2O$

Gases;

Ethylene

Nitrogen

Hydrogen

Helium and Air

Chemicals;

Tetrapropylammonium Bromide

Silicic acid

Aluminium powder

NaOH

IRA400 (anionic resin)

Ethylene glycol

3.5. CATALYST CHARACTERIZATION TECHNIQUES

In order to determine the performance of any catalyst its physical, chemical, thermal and structural properties have to be known. Some of the characterization studies that can help in correlating the various catalyst parameters are; chemical composition, thermal stability, crystallinity, surface area, pore volume, pore size distribution and particle surface morphology. Appendix B contains some results of the characterization studies selected.

3.5.1. Chemical Composition

The nature of products formed over a catalyst are dependent on the chemical composition of the catalyst. Properties such as silica/alumina ratio, exchangeable cations, and promoter loadings are all determined from the chemical analysis. This information help in evaluating catalyst performance and also how to optimize it.

Sodium analysis was done by flame photometer. The instrument was calibrated with standard Na solution of 0, 4, and 10 ml. Ni analysis was performed by UV-visible spectrophotometer using dimethylglyoxime method. The photometeric measurement was made at 540 nm wavelength using 1cm cell. The instrument was calibrated with three standards covering the ranges of Ni content in the samples. Inductively Coupled Plasma (ICP) is an atomic emission spectroscopic technique where radio-frequency power is coupled to a specially designed quartz torch establishing the plasma in Argon. The species introduced into the high temperature plasma source are excited and each element emits radiation of a particular wavelength. This emission intensity was measured by a spectrometer that facilitates the elemental determination at the trace level.

For the ICP analysis, ICP model ARL-3580 (made in UK) was used, it was equipped with various channels that can allow the simultaneous determination of 48 elements shown in Table A-4 in Appendix A.

3.5.2. Thermal Stability

Since oligomerization reactions are carried out at moderate temperatures, the catalyst should maintain thermal stability over the ranges of operating temperature. In thermal analysis, the catalysts were subjected to a controlled temperature program so as to determine the changes in properties. Two techniques were employed (1) thermogravitymetry (TG) and (2) Differential Thermal Analysis (DTA).

In TG, change in the mass of the catalyst sample was measured as a function of temperature. DTA is a means of determining the amount of heat evolved or absorbed by the material and the temperature at which such changes takes place. The temperature difference between a substance and a reference material is measured as both the substance and a reference material are subjected to a controlled heating program. Other studies that can be made from thermal analysis are dehydration, desorption, solid-state and solid-gas reactions, vaporization, fusion, phase transformation and crystalline transition. Simultaneous Thermal Analyzer STA-429 (made in West Germany) was used.

3.5.3. Pore Volume and Pore Size Distribution

Knowledge of pore volume can help predict the effective diffusivity in a porous catalyst and also the calculation of the ease of access of reactant molecules to the interior of a catalyst pellet by diffusion (28). Catalyst pores are generally visualized to be an array of randomly oriented cylindrical capillaries of different shapes, sizes and lengths. Pores in zeolites plays an important role in the determination of zeolite shape selectivity. They act as channels through which reactants gain access to the catalytic sites and products diffuse out from the framework structure. With their knowledge the different reactions taking place within the framework structure can be known.

Two different methods in used are physical adsorption of a gas, which is applicable to pores less than 60 nm in diameter and mercury porosimetry, applicable to pores larger than 3.5nm. The true pore structure is of almost infinite complexity. However, if pores are fairly close in size, a useful concept of determining the pore size is by the average pore radius defined as (28);

$$\bar{r} = 2V_g / S_g$$

V_g = pore volume per gram

The high pressure mercury penetration is based on the fact that mercury has a significant surface tension and does not wet most catalyst surfaces. This means that the pressure required to force mercury into the cavities of a porous material depends on the pore sizes of the substance. At equilibrium, the external force applied on the mercury becomes equal to the force resisting entrance caused by the surface tension of the mercury. The following equation relates pore radius to the applied pressure for a cylindrical pore having a given size (28):

$$r = \frac{-2\sigma\cos\theta}{p}$$

where,

r = pore radius (A)

p = applied pressure (psi)

θ = contact angle between mercury and pore wall (deg)

σ = surface tension of mercury (psi)

Pore sizes that are very small can be detected depending on the maximum pressure to which mercury can be subjected by a particular equipment.

The nitrogen adsorption method is based on the principle that the pressure at which vapor condenses or evaporates is determined by the curvature of the meniscus of the condensed liquid in the pores. Kelvin's equation expresses that:

$$In\, p/p_o = \frac{-2\sigma v_m \cos\theta}{r_k RT}$$

Critical radius r_c is related to the relative pressure by (28):

$$r_c = \frac{-2\sigma v_m}{RT\,(In\, p/p_o)} + t$$

t = adsorbed layer of thickness t

For the equipment used, Porosimeter 2000 (made in Italy) the maximum capacity of the porosimeter was 2000 bars, and under the operating conditions, the smallest pore size measurable by the apparatus was 37A.

3.6. ANALYTICAL METHODS

The products from the reaction were separated into two, gaseous and liquid. The gaseous product was analyzed using Gas Chromatograph (GC) Hewlett Packard model HP-5880A. Three separate columns were used: a 29ft Bis(-2-methoxy ethyl) Adipate and DC 200 column to separate C_5, C_4, and C_3 hydrocarbons, 6ft Porapak Q column to separate C_2's and a 10ft Molecular Sieve 13X to separate C_1. All columns in the 5880A-HP GC are 1/8 inch OD stainless steel. One of the gas chromatograms is presented in Appendix A-5.

The liquid product was analyzed using Flame Ionization Detector (FID) and also GC mass spectrometer so as to identify the products. For the GC-MS the samples were analyzed using HX100 mass spectrometer equipped with a Carlo Erba HRGC 5300 gas chromatograph. The chromatograph was equipped with a split/splitless injector at 220°C. The column was HP-1 (methyl silicone on fused silica), 50M x 0.31mM i.d. with a 0.52μM film thickness. Helium was used as the carrier gas at 1mL/min. The oven temperature was programmed from 30°C to 220°C at 10°/min. with a 10-minute initial time and 10-minute final time. Ion source temperature was set at 250°C. Electron energy: 70 eV; ion current: 100 μA; and acceleration voltage: 5kV. The mass spectra was obtained by scanning from 35 to 450 amu. A JMS-D5000 System control was used for data acquisition and processing. Some of the liquid chromatograms and some parts of the report from GC-MS are presented in Appendices A-6 and A-7 respectively.

Chapter 4

RESULTS AND DISCUSSION

4.1. CATALYSTS PREPARATION AND CHARACTERIZATION

4.1.1. Catalyst Preparation

In the preparation of the support, silicic acid was used as the source of silica while TPA aluminate was used as the source of Alumina. TPA aluminate was prepared from TPA bromide, aluminium powder, IRA400 (anionic resin) and sodium hydroxide. The procedure of preparing TPA aluminate is presented in Appendix A-1 and that of the supports and the catalysts are presented in section 3-1. For the preparation of the support with sodium, the pH dropped from 12.3 and stabilized at 11.3 after 1 day of stirring at room temperature. Two supports and a total of seven catalysts were prepared. Table 4-1 presents the compositions of the main components in the catalysts prepared. The ICP analysis of all the elements present in one of the catalysts is presented in Appendix A-8.

4.1.2. Chemical Analysis

From the chemical analysis of the supports it can be inferred that sodium has suppressed the acidity of sodium silica-alumina (SSA) when the Si/Al ratio of the two supports were compared (Table 4-1). The support with sodium was first ion

exchange with ammonium nitrate three times to reduce the sodium concentration. Around 1% sodium was left in the support and then nickel ion exchange was carried out.

TABLE 4-1: Catalysts Composition.

TAG	NAME	wt% Na	wt% Ni	Si/Al
		Support		
A	ASA	0.015	0.0	37.5
S	SSA	6.420	0.0	21.8
		Catalyst		
C	Ni-ASA	0.012	0.42	37.5
K	Ni-ASA	0.005	0.40	37.5
J	Ni/ASA	0.007	3.70	37.5
D	Ni-SSA	1.180	0.43	21.8
G	Ni-SSA	1.010	0.11	21.8
F	Co-ASA	0.005	0.40	37.5
L	Co/Ni-ASA	0.005	0.40	37.5
		L: 3.78 wt% Co		

For the catalysts **C**, and **K**, nickel was ion exchange (represented by "-") on **ASA.** Catalysts **D** and **G** were ion exchange on **SSA.** Catalysts **J,** nickel was impregnated (represented by "/") on **ASA**. For catalyst **F,** cobalt was ion exchange on **ASA**. The catalyst **L** was first ion exchange ("-") with Ni and then impregnated ("/") with cobalt on **ASA**.

Around 0.4% Ni was exchange after carrying out the exchange three times for most of the catalysts except catalyst G where 1.1% Ni was exchanged. This confirmed that saturation was reached. The sodium found in the amorphous silica-alumina were the traces from the sodium hydroxide used in the preparation of TPA aluminate. For the nickel and cobalt impregnated catalysts about 3.84% loading was expected based on the calculation carried out before the preparation (Appendix A-3), however, about 3.7% was found from the analysis. The ICP analysis presented in Appendix A-8 shows traces of some element which might have come from the chemicals or the equipments used

4.1.3. Thermal Analysis

The figures from the thermal analysis are presented in Appendix A-9. All the catalysts analyzed were found to be stable up to a temperature of 1200°C. The low valley peak from DTA around 100°C indicates an endothermic peak (loss of absorbed water). The amount of water lost at DTA was calculated, for Ni-ASA (C) = 7.0%, for Ni-SSA (D) = 2.0% and for Co/Ni-ASA (L) = 6.8%. No phase transformation was observed.

4.1.4. Pore Size Distribution

For the pore size distribution only the supports prepared were analyzed. The results from the analysis is presented in Appendix A-10. The maximum capacity of the porosimeter was 2000 bars, so under the conditions operated, the smallest pore size measurable by the apparatus was 37A. Small pores were detected in the SSA.

4.2. REPRODUCIBILITY AND SCREENING STUDIES OF NICKEL SUPPORTED ON AMORPHOUS SILICA-ALUMINA (Ni-ASA)

To ensure that the catalysts were active, reproducibility studies was carried out on Ni exchanged on amorphous silica-alumina (Ni-ASA) both at low and at high temperatures (150 and 300°C). The results served as a reliable test for the reaction set-up, sampling and analytical procedures. Adequate attention was observed so as to ensure replication of identical experimental conditions. This takes care of possible causes of deviation in the results. Figure 4-1 shows the plot of the two runs carried out and the data is presented in Table 4-2. In both cases there was not much deviation in the data collected as all the points are within the same region, thus establishing a reasonable limit of confidence.

TABLE 4-2: Reproducibility run for Ni-ASA at 500 psi, 2 h^{-1} WHSV and 4 hours run.

Temperature °C	Conversion	Conversion
150	54.0	55.0
300	90.0	91.5

After establishing the reliability of the set-up and the activity of the catalyst, performance studies were then carried out on all the catalysts prepared. Sample calculation for the conversion and yield is presented in Appendix A-11.

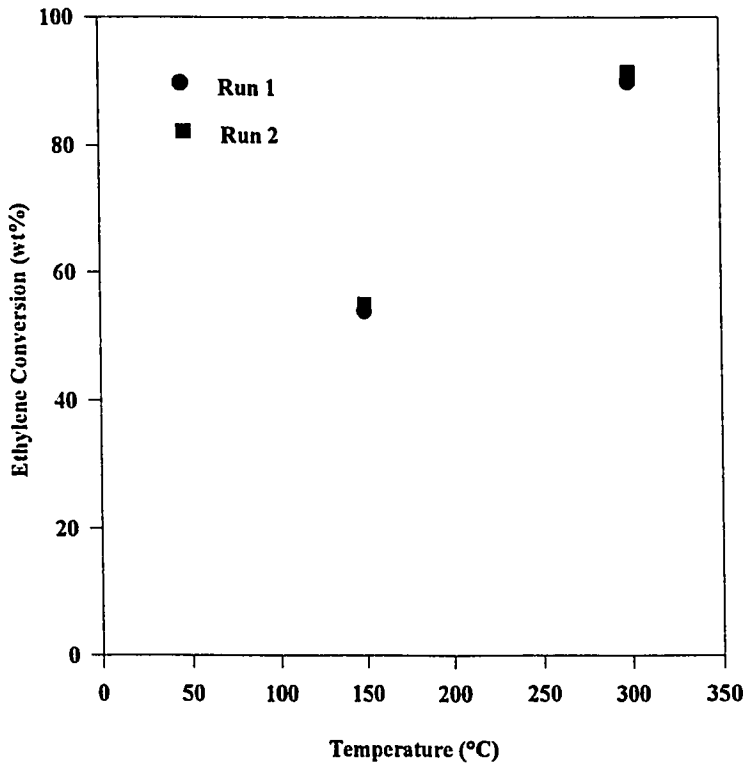


Figure 4-1: Reproducibility run for Nickel Supported on Amorphous Silica-Alumina (Ni-ASA, 0.42 wt% Ni) at 2 h^{-1} WHSV and 500 psi for ethylne conversion

4.3. EFFECT OF TEMPERATURE ON THE PERFORMANCE OF NICKEL SUPPORTED ON AMORPHOUS SILICA-ALUMINA (NiASA)

Temperature has profound effect on catalyst activity. In oligomerization reaction of ethylene, temperature determines, the extent of the reaction (conversion), the types of products and their distribution, cracking activity and skeletal isomerization of dimers. Tables 4-3 to 4-5 present the results of the (NiASA) catalysts for the overall evaluation of their runs in terms of conversion, products distribution yield (olefins, cracking and paraffins products) and butenes distribution at different temperatures (100-300°C).

Figure 4-2 presents a plot of temperature versus conversion profile of the ion exchanged catalysts Ni-ASA (C; Ni = 0.42% and K; Ni = 0.40%) and the impregnated catalyst Ni/ASA (J; Ni = 3.7%). The data plotted was based on the following operating conditions; a pressure of 500 psi, a space velocity of 2 h^{-1} WHSV of ethylene flow, 4 hours time on stream for each setting and a temperature range of 100-300°C (using 50°C interval). The selection of these conditions were based on the literature survey related to ethylene oligomerization on supported nickel catalyst (13-18,51). These conditions were reported as favorable. The amount of catalyst used for each run was 1g and the cooler temperature was maintained at 0°C in all cases.

TABLE 4-3: Effect of Temperature on Ethylene Oligomerization using **Ni-ASA (C**-0.42 wt% Ni exchanged) at 2 h^{-1}WHSV, 500 psi and 4 hours run.

PARAMETER	TEMPERATURE				
	100 °C	150 °C	200 °C	250 °C	300 °C
$C_2^=$ Conversion (%)	12.1	55.0	56.2	81.8	91.5
Mass Balance (%)	95.7	94.3	84.9	96.9	87.3
Olefins Product Distribution (%)					
$C_4^=$	99.7	99.7	74.7	52.4	21.1
$C_6^=$	0.0	0.0	9.7	18.9	15.6
$C_8^=$	0.0	0.0	8.6	19.9	24.8
$C_{10}^=$	0.0	0.0	4.4	7.5	16.4
$C_{12}^=$	0.0	0.0	1.4	0.0	10.2
$C_{14}^=$	0.0	0.0	0.0	0.0	0.8
$C_{16}^=$	0.0	0.0	0.0	0.0	0.0
Cracking Products *	0.0	0.0	0.3	0.1	8.5
Total olefins	**99.7**	**99.7**	**99.1**	**98.7**	**97.4**
Paraffins Prodt (%)#	0.3	0.3	0.9	1.2	2.6
Butenes Distribution (%)					
$C_4^=1$	41.2	23.9	12.8	14.8	17.5
Trans-$C_4^=2$	28.1	40.4	52.2	51.4	49.4
Cis-$C_4^=2$	30.8	35.7	35.0	33.8	33.0

* Cracking Products: All Odd Numbered Olefins
\# Paraffins Products; C_1-C_5 Alkanes

TABLE 4-4: Effect of Temperature on Ethylene Oligomerization using **Ni-ASA** (**K**-0.4 wt% Ni exchanged) at 2 h^{-1} WHSV, 500 psi and 4 hours run.

PARAMETER	TEMPERATURE				
	100 °C	150 °C	200 °C	250 °C	300 °C
$C_2^=$ Conversion (%)	10.7	11.9	46.8	71.4	95.7
Mass Balance (%)	96.4	95.6	93.2	91.5	87.4
Olefins Product Distribution (%)					
$C_4^=$	96.7	99.3	71.9	50.8	26.4
$C_6^=$	0.0	0.0	4.8	8.6	13.2
$C_8^=$	0.0	0.0	7.6	12.7	21.6
$C_{10}^=$	0.0	0.0	5.6	8.7	11.9
$C_{12}^=$	0.0	0.0	3.4	7.3	8.5
$C_{14}^=$	0.0	0.0	1.4	2.3	2.3
$C_{16}^=$	0.0	0.0	0.7	0.6	0.9
Cracking Products	0.0	0.4	3.8	6.6	14.0
Total olefins	**96.7**	**99.7**	**99.2**	**97.6**	**98.8**
Paraffins Prodt (%)	3.3	0.3	0.8	2.4	1.2
Butenes Distribution (%)					
$C_4^=1$	44.9	15.8	12.0	16.9	21.4
Trans-$C_4^=2$	26.2	48.4	53.9	49.6	46.1
Cis-$C_4^=2$	28.9	35.8	34.1	33.5	32.5

TABLE 4-5: Effect of Temperature on Ethylene Oligomerization using **Ni/ASA (J-3.7 wt% Ni impregnated) at 2 h^{-1}WHSV, 500 psi and 4 hours run.**

PARAMETER	TEMPERATURE				
	100 °C	150 °C	200 °C	250 °C	300 °C
$C_2^=$ Conversion (%)	1.0	8.2	40.0	68.0	84.5
Mass Balance (%)	97.3	97.3	95.2	92.7	91.0
Olefins Product Distribution (%)					
$C_4^=$	99.5	99.9	99.8	52.1	48.5
$C_6^=$	0.0	0.0	0.0	10.2	16.0
$C_8^=$	0.0	0.0	0.0	15.1	16.3
$C_{10}^=$	0.0	0.0	0.0	9.1	8.1
$C_{12}^=$	0.0	0.0	0.0	4.2	4.3
$C_{14}^=$	0.0	0.0	0.0	1.5	0.6
$C_{16}^=$	0.0	0.0	0.0	0.5	0.1
Cracking Products	0.0	0.0	0.0	6.2	4.6
Total olefins	**99.5**	**99.9**	**99.8**	**98.9**	**98.5**
Paraffins Prodt (%)	0.5	0.1	0.2	1.1	1.5
Butenes Distribution (%)					
$C_4^=1$	77.3	14.2	12.0	14.5	19.0
Trans-$C_4^=2$	8.9	47.7	54.0	51.1	47.3
Cis-$C_4^=2$	13.8	38.1	34.0	34.4	33.7

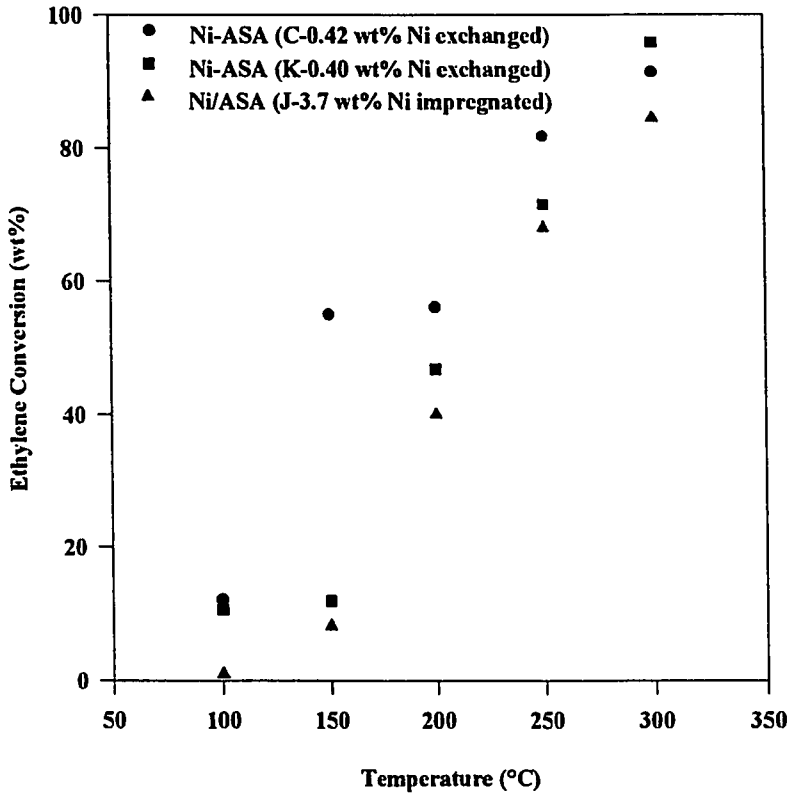


Figure 4-2: Effect of Temperature on the Performance of Nickel Supported on Amorphous Silica-Alumina (NiASA) at 2 h^{-1} WHSV and 500 psi for Ethylene Conversion.

These catalysts, C and K, were found to be very active and two regions of activity were observed as reported by Heveling *et al* (17,18) one at low temperature (100-150°C) and the other at high temperature (250-300°C). The low temperature activity was attributed to the Ni catalyst itself while the high temperature was due to the combination of the Ni and the support. The later point was substantiated considering the amount of cracking products obtained, which are due mainly to the acidity of the support and the high temperature. Cracking products are presented in Tables 4-3 to 4-5.

The three catalysts reported in Figure 4-2 show similar behavior. The slight differences could be attributed to the amount of sodium in the catalyst (Table 4-1 presents the Na content in each of the catalysts), while for the Ni/ASA (impregnated) the differences are possibly due to the high nickel content. The ion exchanged Ni-ASA was slightly more active than the impregnated Ni/ASA this could be due the fact that the bonding between Ni and the support in the impregnated catalyst was not that strong. Another important factor could be the dispersion of the catalyst on the carrier, such as the formation of larger clusters of Ni atoms. That is many more Ni atoms were deposited on top of each other, so that the dispersion of the Ni on the surface was less uniform than with the 0.42 wt% Ni ion exchanged.

The life time activity of these types of catalyst has been reported in the literature by Heveling *et al* (17,18). So, it was not determined in this case. However, over the one week period that they were studied there was not much sign of deactivation. This observation was further confirmed by the fact that almost identical conversion levels were obtained when one reaction was carried out with gradual increase from 100-300°C and onother with gradual decrease from 300°C to

100°C. The amount of carbon deposited on the catalysts for the period of the studies was about 1% in most of the cases studied. Mass balances are presented in Tables 4-3 to 4-5. The recovery was high in the neighborhood of 90 to 95%.

4.4. EFFECT OF TEMPERATURE ON THE PRODUCTS DISTRIBUTION OF NICKEL SUPPORTED ON AMORPHOUS SILICA-ALUMINA (NiASA)

4.4.1. Olefins Product Distribution of NiASA

Olefins product distribution were in the range of C_4 to C_{16}. Tables 4-3 to 4-5 present the data of olefins distribution for NiASA catalysts. The plots are presented in Figures 4-3 to 4-5. The distributions are similar to the one reported by Heveling *et al* (18). However, within the time on stream considered (4 hours) higher olefins were not formed at lower temperatures 100-150°C. But, when the reaction was allowed to run for a much longer period, higher oligomers up to C_{16} were obtained. Figure 4-6 presents the distribution of Ni-ASA at 150°C after 14 hours time on stream. The conversion when calculated was still about the same as that of 4 hrs. This further confirmed steady state was reached even before 4 hours.

At lower temperatures butenes (C_4) were the predominant products. Figures 4-3 to 4-6 present that behavior. At higher temperatures butenes products were almost the same as C_8. This further confirmed the oligomerization of the C_4 produced already and the copolymerization of C_2 and C_6 to form C_8, C_{10} and C_{12} were also produced in appreciable quantities.

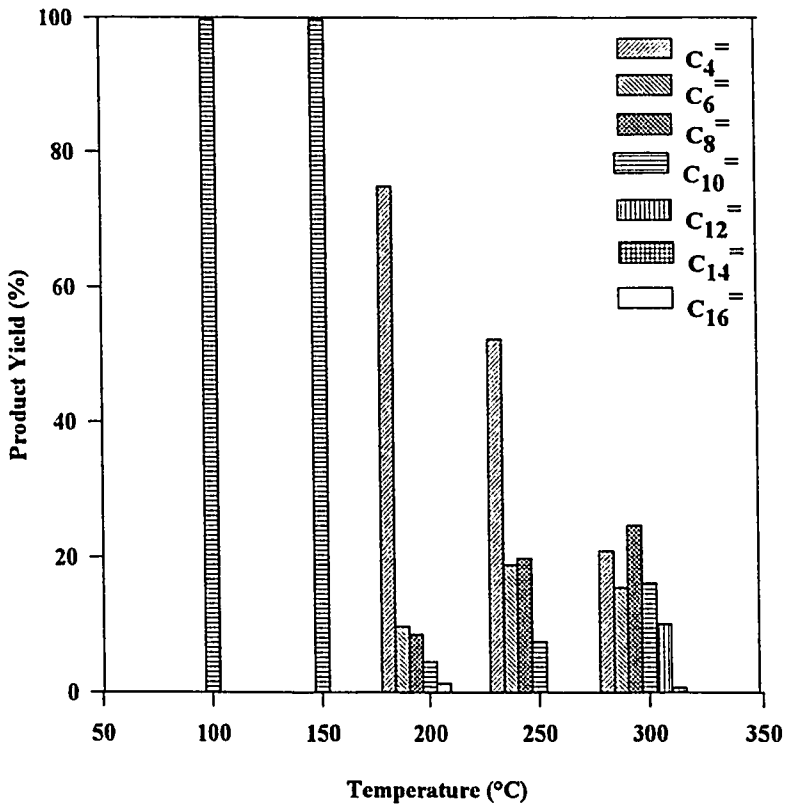


Figure 4-3: Olefins Product Distribution versus Temperature of Ni-ASA (C-0.42 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

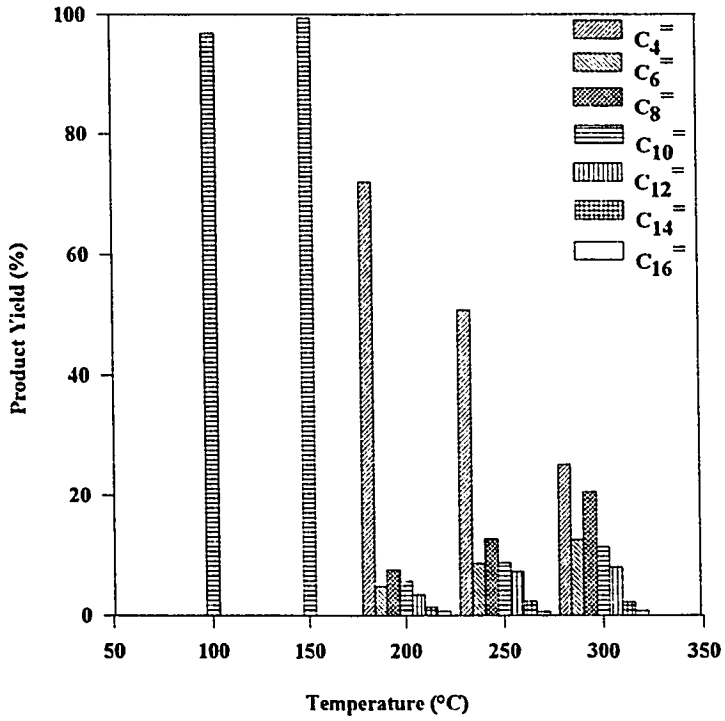


Figure 4-4: Olefins Product Distribution versus Temperature for Ni-ASA (K-0.40 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

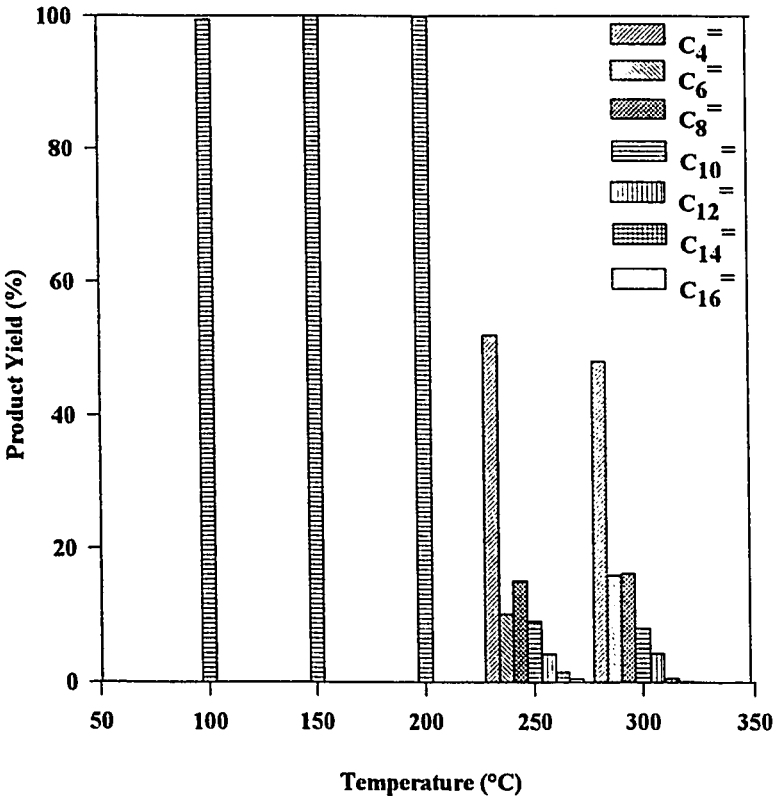


Figure 4-5: Olefins Product Distribution versus Temperature for Ni/ASA (J-3.70 wt% Ni impregnated) at 2 h^{-1} WHSV and 500 psi.

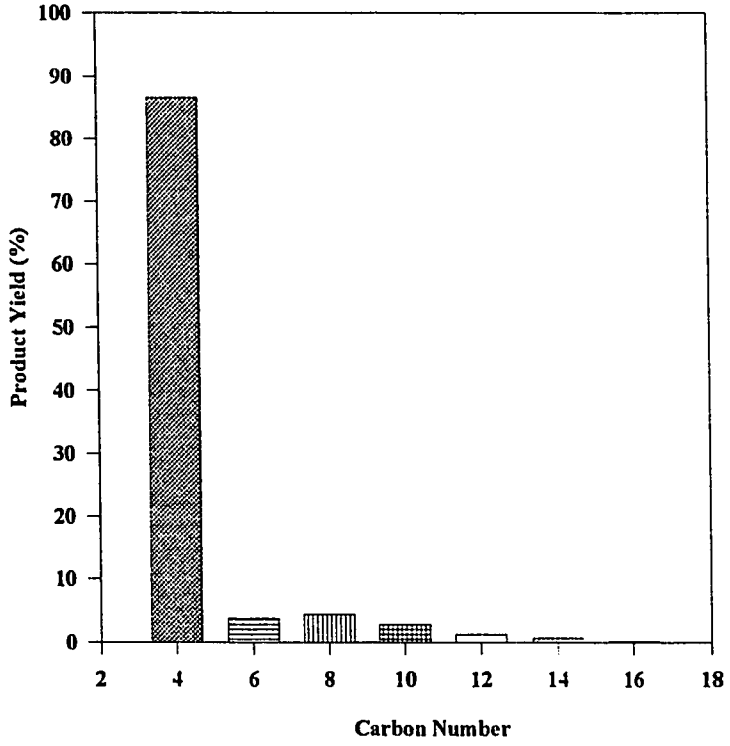


Figure 4-6: Olefins Product Distribution at 150°C, 2 h^{-1} WHSV, 500 psi and 14 hours run for Ni-ASA (C-0.42 wt % Ni exchanged)

4.4.2. Cracking Products of NiASA

Cracking of primary products (higher oligomers) is another prominent reaction taking place in the oligomerization of ethylene. Cracking products refers to all odd numbered olefins ($C_3^=$ to $C_{15}^=$). The major factors causing cracking reaction are the support acidity and high temperature.

Cracking activity was quite pronounced with these catalysts (C, K and J) Tables 4-3 to 4-5 present cracking products at different temperatures. The effect of cracking activity was well pronounced at high temperature (>200°C). For the catalyst Ni-ASA (K; 0.40 wt% Ni) Table 4-4 up to 14.0% of the products yield at 300°C were cracking products. This behavior may be attributed to the acidity of the support which dominated the reaction at high temperature. Similar behavior was observed by Heveling *et al* (18) in their studies.

Another feature observed in Tables 4-4 and 4-5 was that the supported Ni by ion exchange (K; 0.40 wt% Ni) gave more cracking products than the impregnated one (J; Ni/ASA, 3.7 wt% Ni). Possible explanation could be the impregnated catalyst has formed a cluster of Ni atoms which might have blocked the acid sites of the support. These sites are responsible for most of the high oligomers cracking. This observation was again in conformity with that of Espinoza *et al* (15).

4.4.3. Parrafins Product of NiASA

Paraffins product refers to all saturated hydrocarbons (alkanes) produced during the reaction. They are normally produced with the gaseous products (C_1-C_5). During oligomerization reaction, silica-alumina support causes cracking (67) of the products. Traces of parafffins obtained are probably from these cracked products.

Parrafins product yield of NiASA catalysts are presented in Tables 4-3 to 4-5. The products were more at 100 and 250°C. For the catalyst Ni-ASA (K; 0.40 wt% Ni) the products were 3.3% at 100°C and 2.4% at 250°C this behavior could be attributed to the cracking activity, since for the impregnated catalyst Ni/ASA (J; 3.7 wt% Ni) where the cracking activity was less compared to Ni-ASA (K) the paraffins yield was just 1.1% at 250°C.

4.4.4. Butenes Distribution of NiASA

Butenes ($C_4^=$) are the predominant products in the ethylene oligomerization and the source of producing higher olefins. Generally $C_4^=1$ is the initial dimer (34,47,51,69,70), however, the support acidity and the nickel catalyst brings about skeletal isomerization and the result is isomerization of butene-1 ($C_4^=1$) to *trans* and *cis*-butenes ($C_4^=2$).

Tables 4-3 to 4-5 present the data for butenes distribution at different temperatures for the catalysts NiASA. Plots of these distributions are presented in Figures 4-7 to 4-9. $C4^{=}1$ was the predominant product at low temperature (100°C) as observed by Ng and Creaser (51) and by other authors (34,47,69,70), but, it isomerized to *trans* and *cis* at higher temperatures through primarily protonic acid sites of the support.

Another feature observed in Tables 4-3 to 4-5 was the isomerization of $C4^{=}1$ to *trans*-$C4^{=}2$ was higher at 200°C for all the catalysts and for *cis*-$C4^{=}2$ it was at 150°C. In Table 4-3 *Trans*-$C4^{=}2$ was 52.2% at 200°C and 49.4% at 300°C, while *Cis*-$C4^{=}2$ was 34.9% at 200°C and 33.0% at 300°C. The sudden increase in $C4^{=}1$ at 250-300°C as compared to 200°C was the result of high cracking activity at those temperatures and so, more lower olefins were available in the system. Since $C4^{=}1$ is the initial dimer, subsequent oligomerization of the lower olefins increases its yield.

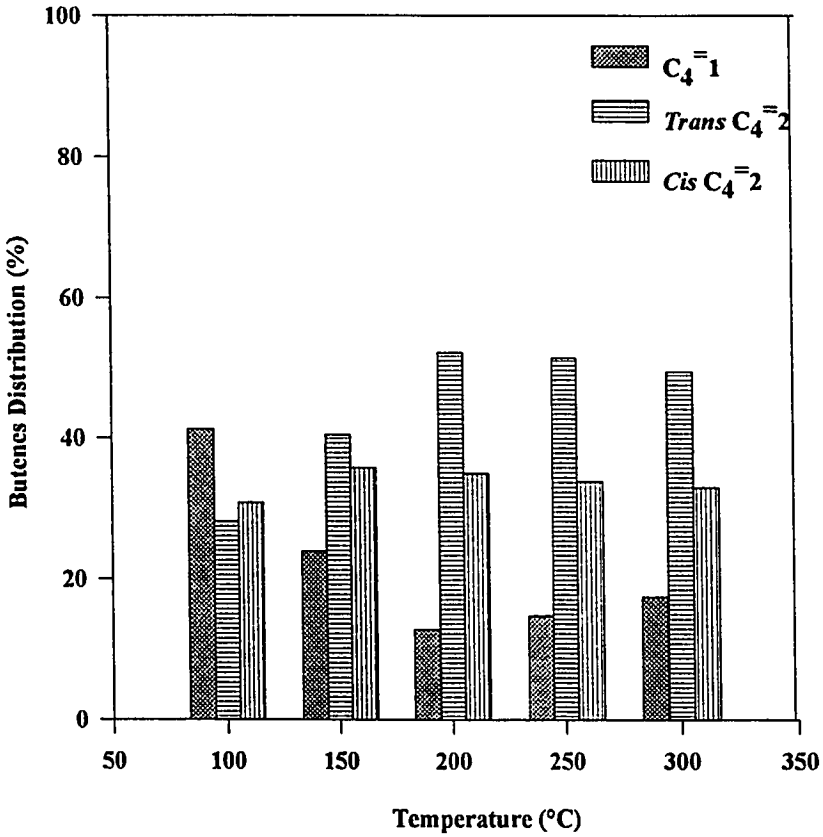


Figure 4-7: Butenes Distribution versus Temperature for Ni-ASA (C-0.42 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

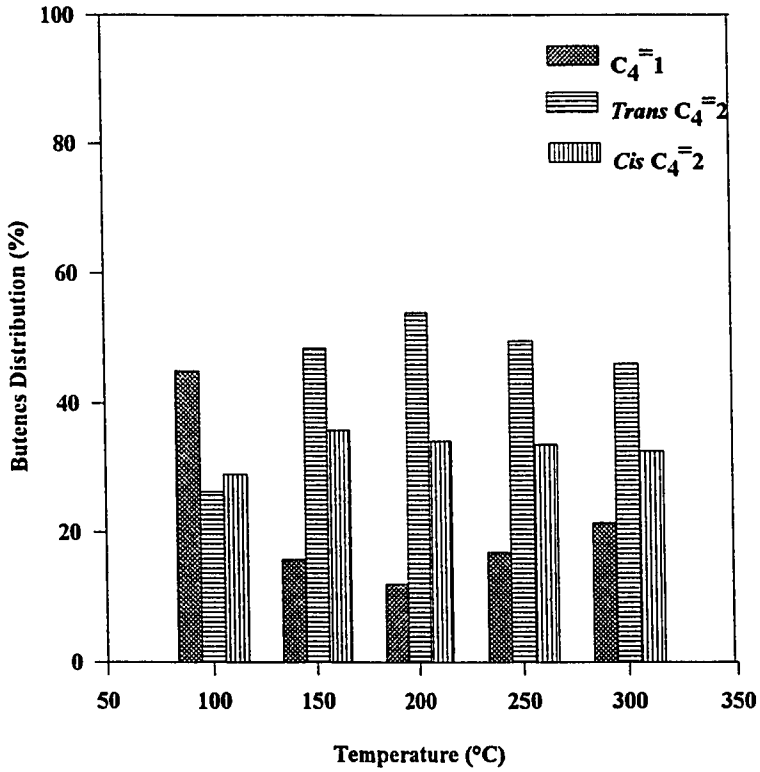


Figure 4-8: Butenes Distribution versus Temperature for Ni-ASA (K-0.40 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

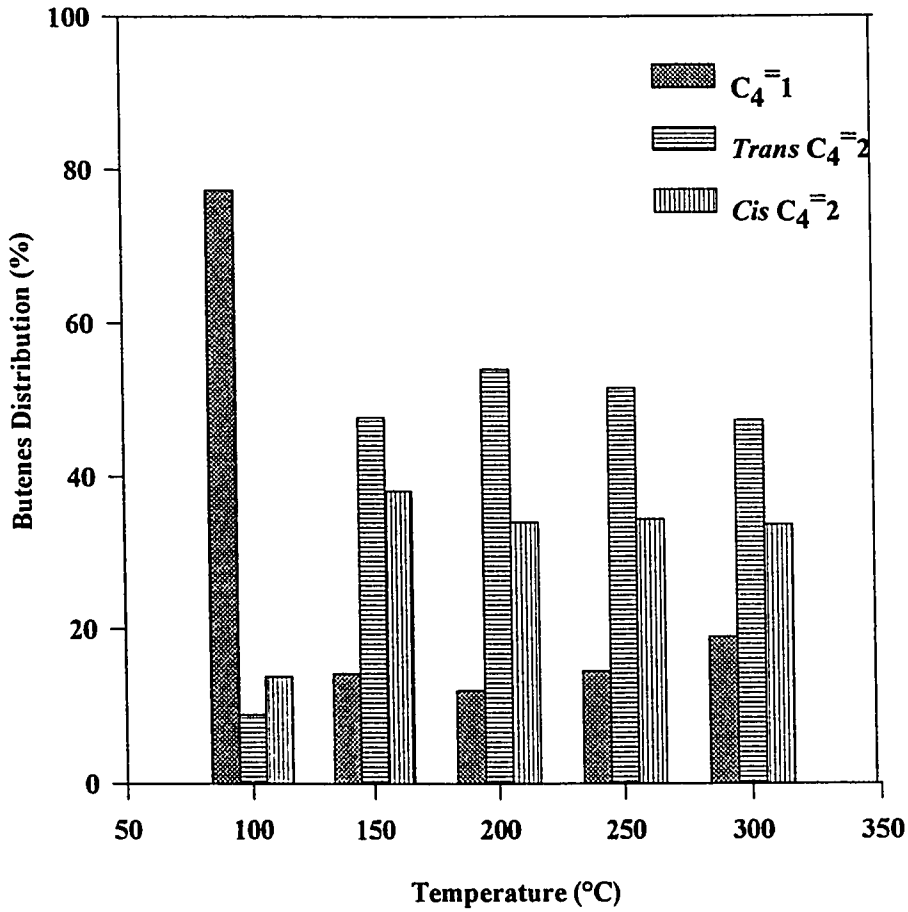


Figure 4-9: Butenes Distribution versus Temperature for Ni/ASA (J-3.70 wt% Ni impregnated) at 2 h^{-1} WHSV and 500 psi.

4.5. EFFECT OF SPACE VELOCITY ON THE PERFORMANCE OF NICKEL SUPPORTED ON AMORPHOUS SILICA-ALUMINA (Ni-ASA)

The effect of space velocity was studied on the catalyst Ni-ASA (K) at 300°C because of the high conversion obtained (95.7%) at 2 h^{-1} WHSV, 500 psi and 4 hrs time on stream, Table 4-4. As the space velocity was increased from 2 to 4 h^{-1} WHSV the conversion decreased to 81.0% and to even much lower value of 72.1% at a space velocity of 6 h^{-1} WHSV. This was eminent, since high velocity reduces contact time as a result not enough residence time was given to the molecules. The data is presented in Table 4-6. Figure 4-10 presents the plot of ethylene conversion versus the space velocity. An almost linear relation was observed.

4.6. EFFECT OF SPACE VELOCITY ON THE PRODUCTS DISTRIBUTION OF NICKEL SUPPORTED ON AMORPHOUS SILICA-ALUMINA (Ni-ASA)

4.6.1. Olefins Product Distribution of Ni-ASA

Increasing the space velocity from 2 to 6 h^{-1} WHSV affected the olefins product distribution significantly. Light olefin (butene) dominated the distribution. This behavior was the result of reduction in the residence time of the molecules. As more feed was coming into the system the initial oligomers formed desorp and leave the system. Table 4-6 presents the distribution of olefins at different space velocities. The plot for the distribution is presented in Figure 4-11.

TABLE 4-6: Effect of Space Velocity on Ethylene Oligomerization using **Ni-ASA (K-0.4 wt% Ni exchanged)** at 300°C, 500 psi and 4 hours run.

PARAMETER	SPACE VELOCITY		
	2 h^{-1} WHSV	4 h^{-1} WHSV	6 h^{-1} WHSV
$C_2^=$ Conversion (%)	95.7	81.0	72.1
Mass Balance (%)	87.4	88.3	86.6
Olefins Product Distribution (%)			
$C_4^=$	26.4	67.3	76.1
$C_6^=$	13.2	13.9	10.9
$C_8^=$	21.6	11.6	5.6
$C_{10}^=$	11.9	3.7	2.5
$C_{12}^=$	8.5	0.0	1.1
$C_{14}^=$	2.3	0.0	0.1
$C_{16}^=$	0.9	0.0	0.0
Cracking Products	14.0	0.8	1.8
Total olefins	**98.8**	**97.3**	**98.1**
Paraffins Prodt (%)	1.2	2.7	1.9
Butenes Distribution (%)			
$C_4^=1$	21.4	19.7	19.4
Trans-$C_4^=2$	46.1	46.7	46.1
Cis-$C_4^=2$	32.5	33.6	34.5

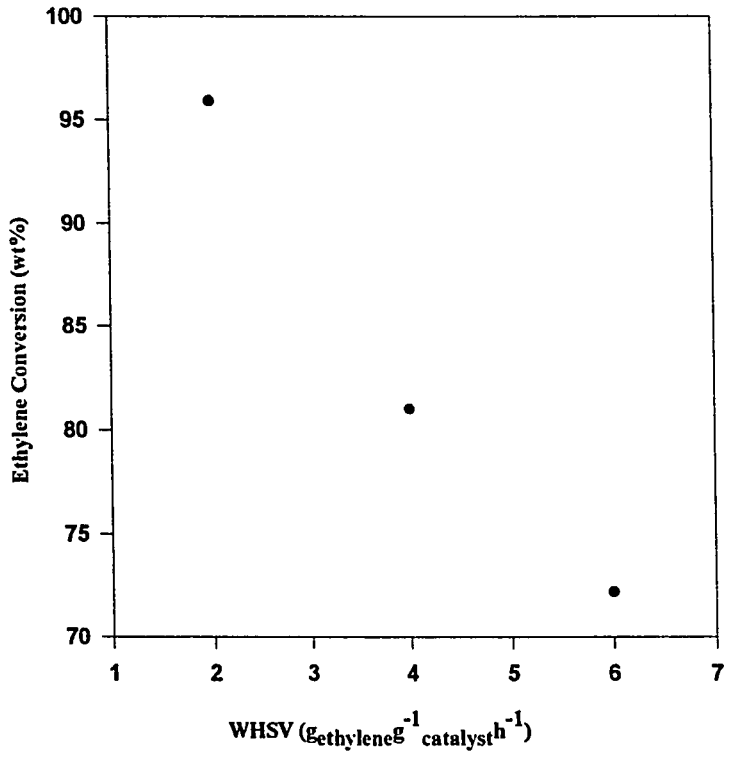


Figure 4-10: Effect of Space Velocity on the on the Performance of Ni-ASA (K-0.4 wt% Ni exchanged) for Ethylene Conversion at 300°C and 500 psi.

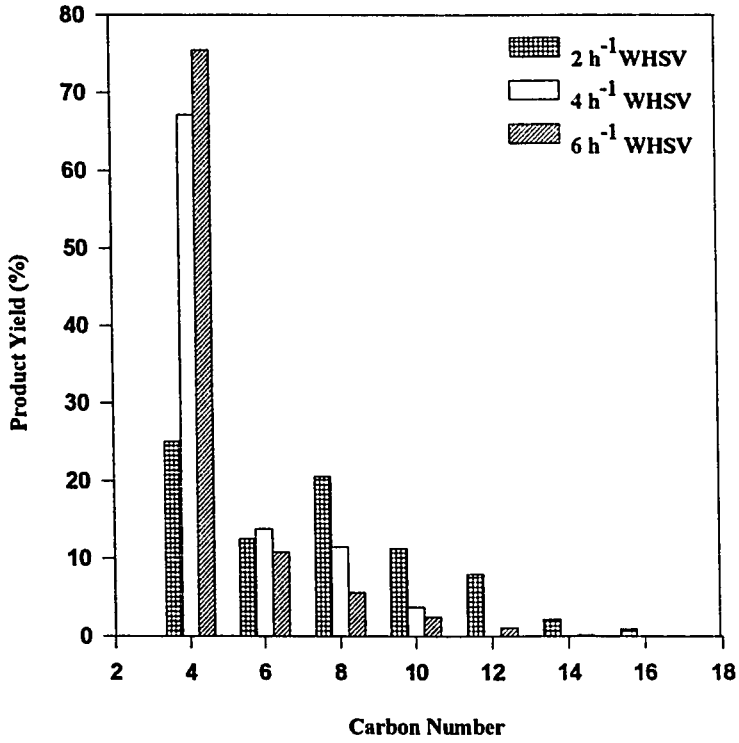


Figure 4-11: Effect of Space Velocity on the Olefins Product Distribution of Ni-ASA (K-0.4 wt% Ni exchanged) for Ethylene Conversion at 300°C and 500 psi.

4.6.2. Cracking Products of Ni-ASA

Cracking products (activity) decreased as the space velocity was increased from 2 to 6 h^{-1} WHSV. From a value of 14.0% at 2 h^{-1} WHSV to 0.8% at 4 h^{-1} WHSV and 1.8% at 6 h^{-1} WHSV at the same 300°C. This indicated that the longer the products stayed in the system the more cracking activity would prevailed. The data of the cracking activity is presented in Table 4-6.

4.6.3. Paraffins Product of Ni-ASA

Under the effect of temperature the paraffins product gave no specific pattern of behavior, however, considering the effect of space velocity the paraffins product decreased from a value of 2.7% at 4 h^{-1} WHSV to 1.9% as the space velocity was increased to 6 h^{-1} WHSV. This is because increase in space velocity would decrease the residence time of the products in the system as a result cracking activity which is the source of paraffins was reduced. The data of the paraffins product is presented in Table 4-6.

4.6.4. Butenes Distribution of NiASA

Figure 4-12 presents a bar chart of the butenes distribution and the data is presented in Table 4-6. Virtually there is not much difference in the distributions at different space velocities. This is a clear indication of how fast the isomerization equilibrium was attained at high temperature regardless of the residence time.

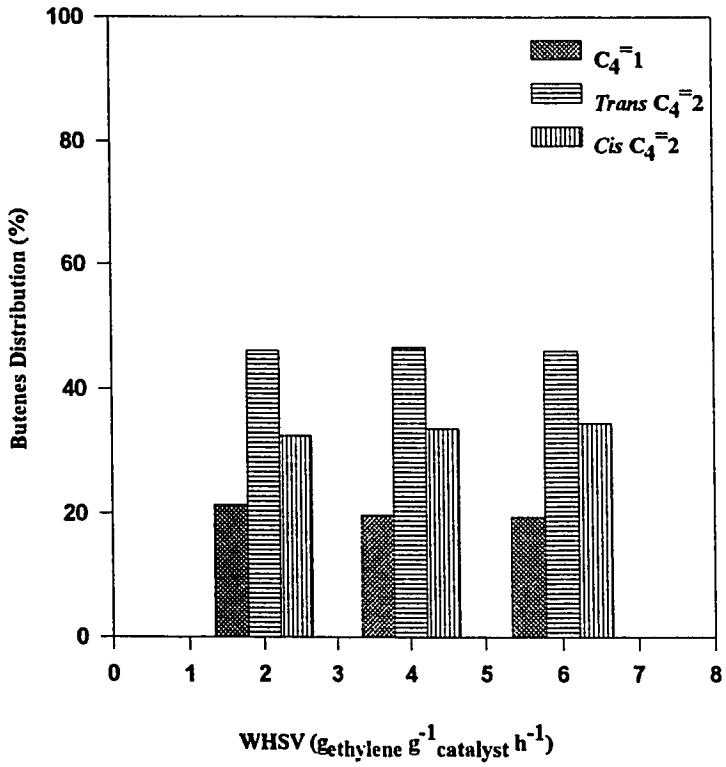


Figure 4-12: Effect of Space Velocities on the Butenes Distribution of Ni-ASA (K-0.4 wt% Ni exchanged) at 300°C and 500 psi.

4.7. PRELIMINARY STUDY ON THE EFFECT OF SPACE VELOCITY ON THE REACTION RATES OF NICKEL SUPPORTED ON AMORPHOUS SILICA-ALUMINA (Ni-ASA)

Reaction rates are concentration and temperature dependent (1,71). So as the reactant composition in the system changes during the passage through the reactor, large variations are encountered. Due to this large variation we choose an integral flow reactor to account for these variations. The following kinetics relation holds:

$$\frac{W}{F_o} = \int_0^X \frac{dX}{-r'}$$

Applying differential analysis, the above equation can be rearranged to the following:

$$-r' = \frac{dX}{d(W/F_o)}$$

A plot of X (extent of reaction) versus W/F_O (reciprocal of space velocity) was done for Ni-ASA (K). The equation above shows that the rate of reaction (-r') at any value of X is simply the slope of this curve. Figure 4-13 presents the plot. Hence for a number of X values, the slope of the curve (-r') was determined. The corresponding concentration C was calculated as follows;

$$C = C_o \frac{1-X}{1+\varepsilon X}$$

Assuming constant volume and ideal gas behavior;

$$C = C_o(1-X)$$

and

$$C_o = \frac{P}{RT}$$

$$= 500 \text{ psi} \times 6894.8/(8.314 \times 573)/1000$$

$$= 0.724 \text{ mol/liter}$$

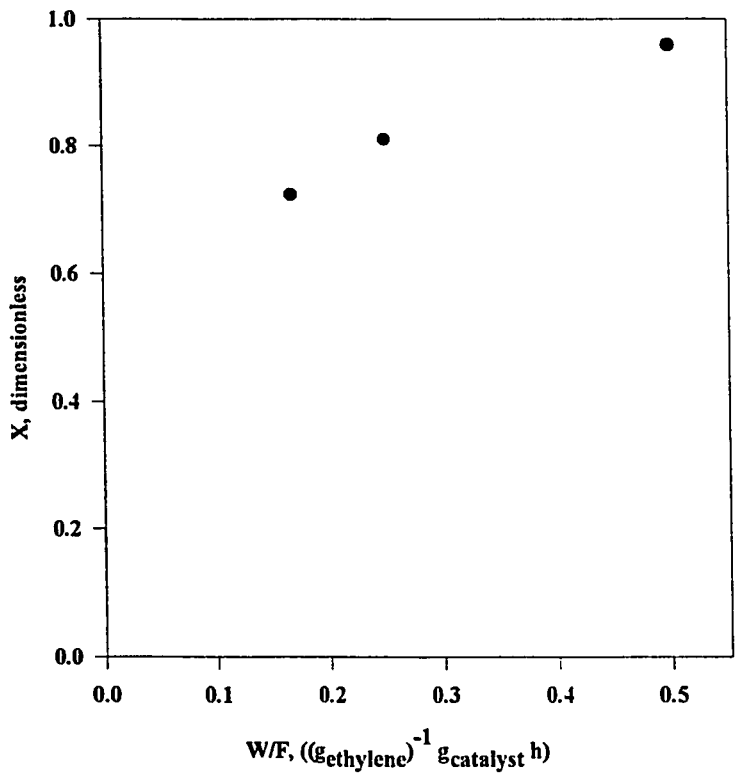


Figure 4-13: Differential Analysis for Ni-ASA (K-0.4 wt % Ni exchanged) at 300°C and 500 psi for different Space Velocities.

TABLE 4-7: Calculated Values of Extent of Reaction (X), Concentration (C), Reciprocal of Space Velocity (W/F_0) and Reaction Rate (-r').

X	C (mol/liter)	W/F_0 ($g_{cat}.h/g_{feed}$)	-r' ($g_{feed}/(g_{cat}.h)$)	-r' (mol/(g_{cat}.h))
0.957	0.030	0.50	0.22	0.01
0.810	0.137	0.25	0.83	0.03
0.721	0.203	0.17	1.33	0.05

From the nth order relation

$$r' = kC^n$$

A plot of Log -r' versus Log C, Figure 4-14 gives a straight line with slope (n) ~ 1.0. Thus the reaction was first order. Figure 4-15 presents the plot of -r' versus C, a straight line was obtained from which the slope (rate constant) was calculated; k = 0.25 liter/(g_{cat}. h)

In order to carry out integral analysis, first order was assumed and substituting r' = kC and $C = C_0(1-X)$ into the main integral relation and integrating yields the following;

$$\frac{W}{F_o} = -(1/kc_o)\ln(1-X)$$

A plot of -In(1-X) versus W/F_0, Figure 4-16 gives a straight line passing through the origin, thus confirming the first order nature of the reaction at 300°C and 500 psi for different space velocities. The rate constant k was calculated from the slope; k = 0.27 liter/(gcat. h). The value of the rate constant calculated from the differential and integral analysis were both in agreement.

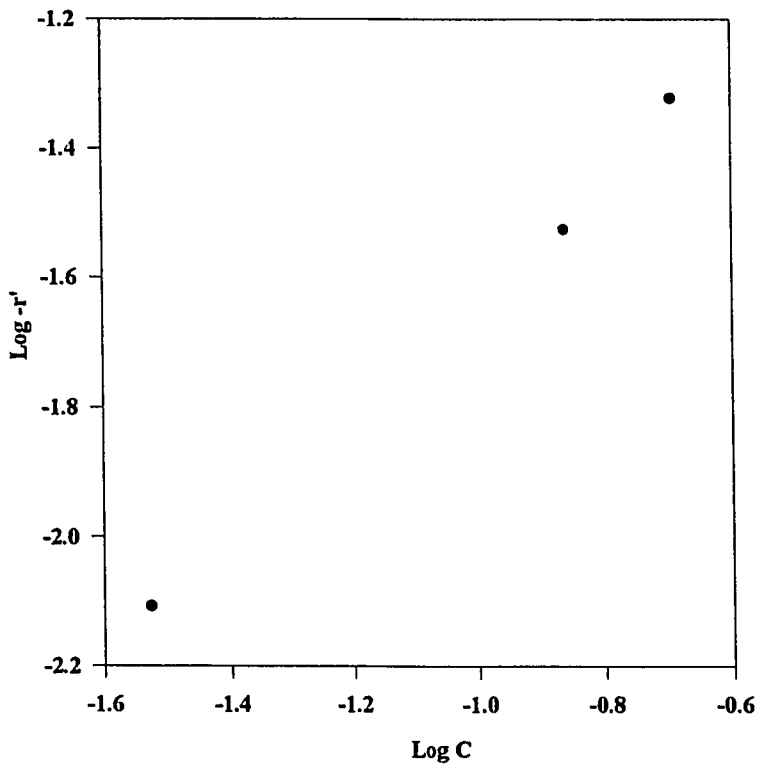


Figure 4-14: Determination of the Reaction Order for Ni-ASA (K-0.4 wt% Ni exchanged) at 300°C and 500 psi.

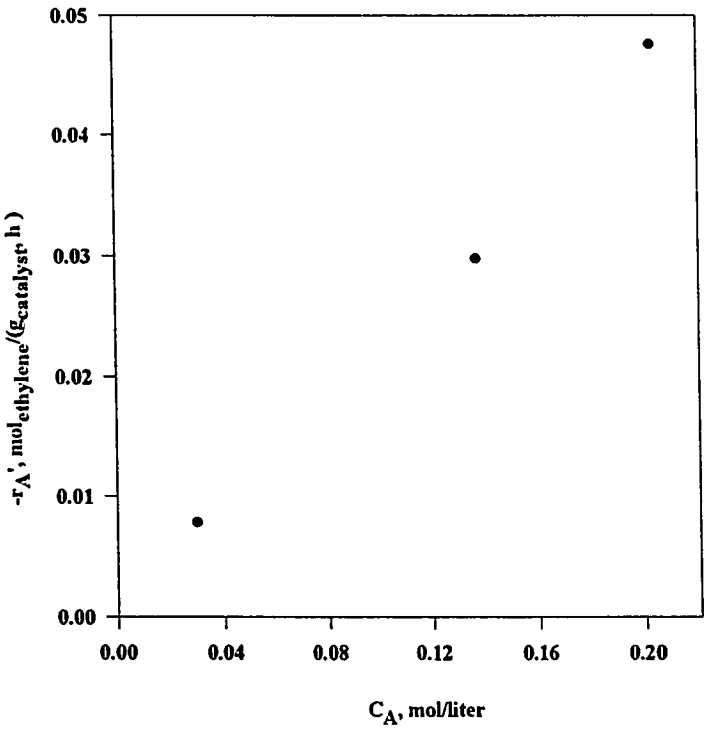


Figure 4-15: Demonstration of First-Order Kineteics by Differential Analysis for Ni-ASA (K-0.4 wt% Ni exchanged) at 300°C and 500 psi.

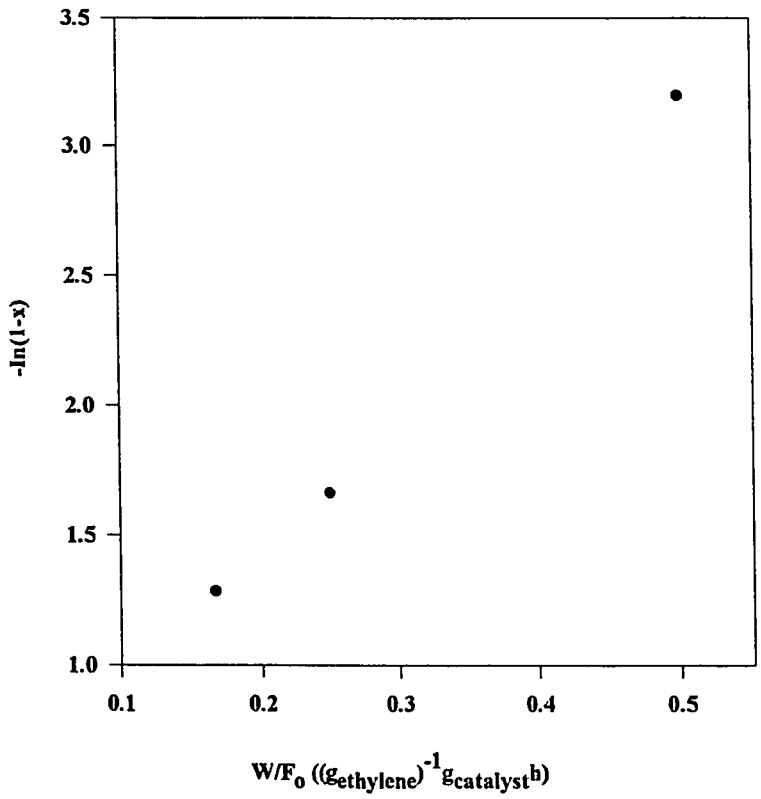


Figure 4-16: Demostration of First-Order Kinetics by Integral Analysis for Ni-ASA (K-0.4 wt % Ni exchanged) for Ethylene Conversion at 300°C and 500 psi.

4.8. EFFECT ON TEMPERATURE ON THE PERFORMANCE OF NICKEL SUPPORTED ON SODIUM SILICA-ALUMINA (NiSSA)

Figure 4-17 presents a plot of temperature vs. conversion profile for the ion exchanged catalysts Ni-SSA (D; Ni = 0.43 wt%, Na = 1.18 wt% and G; Ni = 1.1 wt%, Na = 1.01 wt%). The data plotted was based on the following operating conditions, 500 psi pressure, 2 h^{-1} WHSV of ethylene flow, 4 hours time on stream for each setting and a temperature range of 100-300°C (using 50°C interval).

These catalysts D and G were found to be slightly less active than those without sodium (NiASA). There was not much activity at low temperatures this can be attributed to the presence of sodium in large amounts thus hindering the chances of ethylene molecules getting on to the nickel sites, since for different nickel concentration (D and G) about the same behavior was observed. The activity at high temperature was due mainly to the combination of Ni and the support. Tables 4-8 and 4-9 present the conversions, olefins products, cracking products, paraffins products mass balances and the butenes distribution of these catalysts.

TABLE 4-8: Effect of Temperature on Ethylene Oligomerization using **Ni-SSA (D**-0.43 wt% Ni exchanged) at 2 h^{-1}WHSV, 500 psi and 4 hours run.

PARAMETER	TEMPERATURE				
	100 °C	150 °C	200 °C	250 °C	300 °C
$C_2^=$ Conversion (%)	3.4	13.7	14.9	47.1	71.3
Mass Balance (%)	95.0	96.4	89.7	93.5	89.5
Olefins Product Distribution (%)					
$C_4^=$	99.7	98.6	99.9	94.1	65.8
$C_6^=$	0.0	0.0	0.0	1.3	13.3
$C_8^=$	0.0	0.0	0.0	1.6	9.6
$C_{10}^=$	0.0	0.0	0.0	0.8	4.2
$C_{12}^=$	0.0	0.0	0.0	0.5	2.5
$C_{14}^=$	0.0	0.0	0.0	0.1	0.5
$C_{16}^=$	0.0	0.0	0.0	0.02	0.03
Cracking Products	0.0	0.1	0.0	0.5	2.6
Total olefins	**99.7**	**98.7**	**99.9**	**98.9**	**98.5**
Paraffins Prodt (%)	0.3	1.3	0.0	1.1	1.5
Butenes Distribution (%)					
$C_4^=1$	21.6	18.9	28.5	16.0	18.5
Trans-$C_4^=2$	43.5	46.4	36.2	48.3	46.8
Cis-$C_4^=2$	34.8	34.7	35.3	35.7	34.7

TABLE 4-9: Effect of Temperature on Ethylene Oligomerization using **Ni-SSA (G-**1.10 wt% Ni exchanged) at 2 h^{-1}WHSV, 500 psi and 4 hours run.

PARAMETER	TEMPERATURE				
	100 °C	150 °C	200 °C	250 °C	300 °C
$C_2^=$ Conversion (%)	0.8	10.0	25.0	60.0	71.4
Mass Balance (%)	97.2	94.0	94.8	95.1	86.3
Olefins Product Distribution (%)					
$C_4^=$	96.6	98.1	99.6	71.8	66.7
$C_6^=$	0.0	0.0	0.0	8.7	12.1
$C_8^=$	0.0	0.0	0.0	8.7	11.6
$C_{10}^=$	0.0	0.0	0.0	4.8	5.7
$C_{12}^=$	0.0	0.0	0.0	2.6	1.4
$C_{14}^=$	0.0	0.0	0.0	1.0	0.0
$C_{16}^=$	0.0	0.0	0.0	0.2	0.4
Cracking Products	0.0	0.0	0.0	1.5	0.9
Total olefins	**96.6**	**98.1**	**99.6**	**99.3**	**98.8**
Paraffins Prodt (%)	3.4	1.9	0.4	0.7	1.2
Butenes Distribution (%)					
$C_4^=1$	77.9	53.5	15.2	14.7	17.9
Trans-$C_4^=2$	9.1	19.2	47.6	50.2	47.3
Cis-$C_4^=2$	13.0	27.3	37.2	35.1	34.8

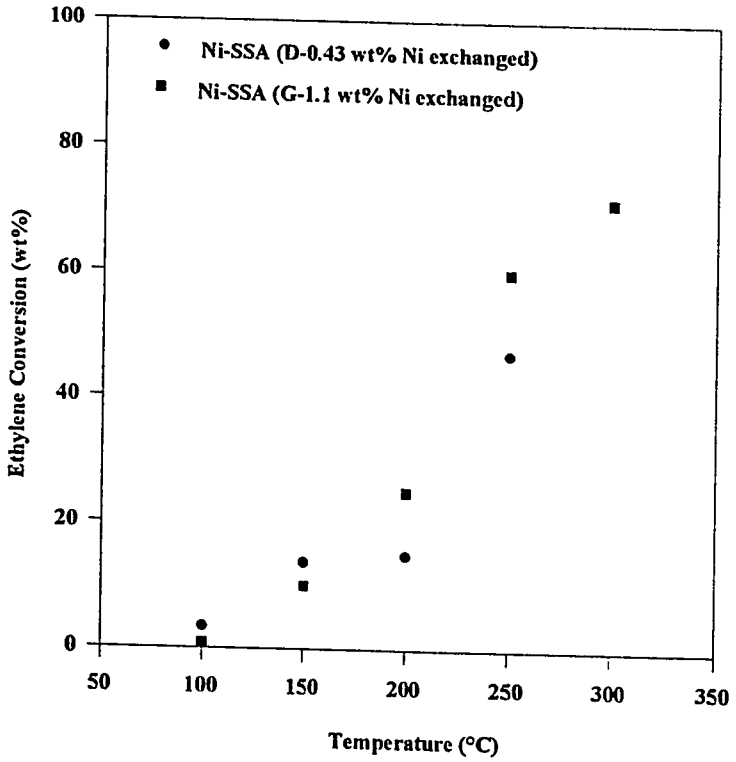


Figure 4-17: Effect of Temperature on the Performance of Nickel Supported on Sodium Silica-Alumina (NiSSA) at 2 h^{-1} WHSV and 500 psi for Ethylene Conversion.

4.9. EFFECT OF TEMPERATURE ON THE PRODUCTS DISTRIBUTION OF NICKEL SUPPORTED ON SODIUM SILICA-ALUMINA (NiSSA)

4.9.1. Olefins Product Distribution of NiSSA

Olefins product distribution were in the range of C_4 to C_{16}. Tables 4-8 and 4-9 present the data for olefins distribution. Plots of olefins products distribution for Ni supported on Sodium Silica-Alumina (SSA) are presented in Figures 4-18 and 4-19. Butenes dominated even at high temperatures. This effect was probably due to the presence of Na since the trend was not exactly like that in Ni-ASA.

Figure 4-19 as compared to 4-18 shows a slight increase in the formation of higher oligomers at 250°C this behavior could be ascribed to the amount of Na which was more (1.18%) in Figure 4-18 than in Figure 4-19 (1.01%). Thus it can be deduced that Na hinders the formation of higher oligomers for the conditions operated.

The catalyst G was slightly more active than D possibly due to the high Ni content in G (1.1% Ni) than in D (0.43% Ni). However, at 300°C the catalyst activity obtained was the same, indicating the pronounced effect of high temperature and support acidity over the the nickel catalyst. Mass balances were in the neighborhood of 90 to 95% indicating a good recovery. Data of mass balances are presented in Tables 4-8 and 4-9.

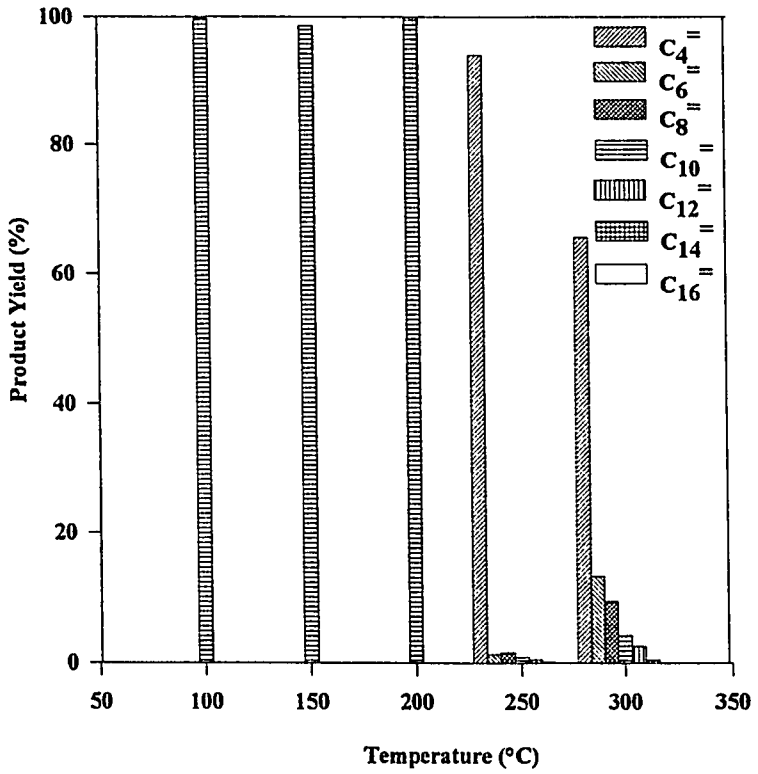


Figure 4-18: Olefins Product Distribution versus Temperature for Ni-SSA (D-0.43 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

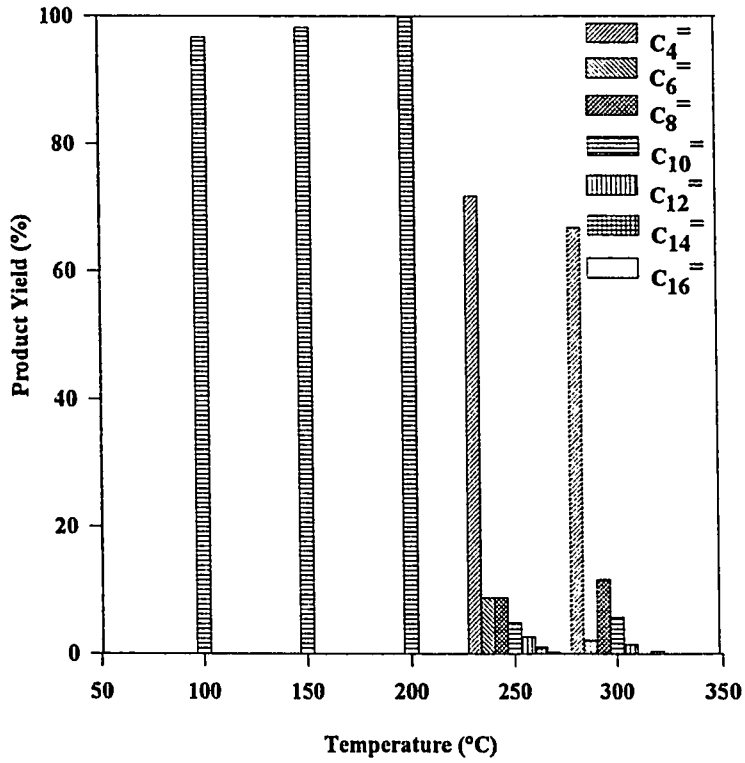


Figure 4-19: Olefins Product Distribution versus Temperature for Ni-SSA (G-1.1 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

4.9.2. Cracking Products of NiSSA

Cracking products refers to all odd numbered olefins ($C_3^=$ to $C_{15}^=$). The major factors causing cracking reaction are the support acidity and high temperature. Cracking activity however was not much in these catalysts (D and G) as presented in Tables 4-8 and 4-9. The highest was for D (0.43 wt% Ni, 1.18 wt% Na) at 300°C and was 2.6%.

The low cracking activity of these catalyst was due to the high content of Na which must have occupied the acidic sites of the support. The low Si/Al ratio (Si/Al = 21.8) Table 4-1, strenghing this observation. The cracking products of these catalysts (D and G) were less than those of the catalysts (C, K and J).

4.9.3. Parrafins Products of NiSSA

Paraffins products were normally produced with the gaseous products (C_1-C_5). Paraffins products of these catalysts were small both at 100 and at 300°C. The reason was the lowering of the support acidity by sodium as such cracking activity was reduced and so less chances of getting paraffins. Paraffins products are presented in Tables 4-8 and 4-9.

4.9.4. Butenes Distribution of NiSSA

The butenes distribution for these catalysts are presented in Figures 4-20 and 4-21 and the data is presented in Tables 4-8 and 4-9. The distribution showed high isomerization activity for the catalyst D at low temperature which progressively reduced, it is possible that sodium was affecting nickel catalyst which was responsible for isomerization at low temperatures.

The catalyst G produced a lot of $C_4^{=}1$ at low temperature possibly due to high Ni content, but, it rapidly isomerized as the temperature was increased. As the temperature reached 250°C the acidity of the support came into effect and the isomerization continued to increase. The slight increase in $C_4^{=}1$ yield at 250 and 300°C was the result of cracking activity which increases the ethylene (from cracking products) in the system, thus, more dimerization activity.

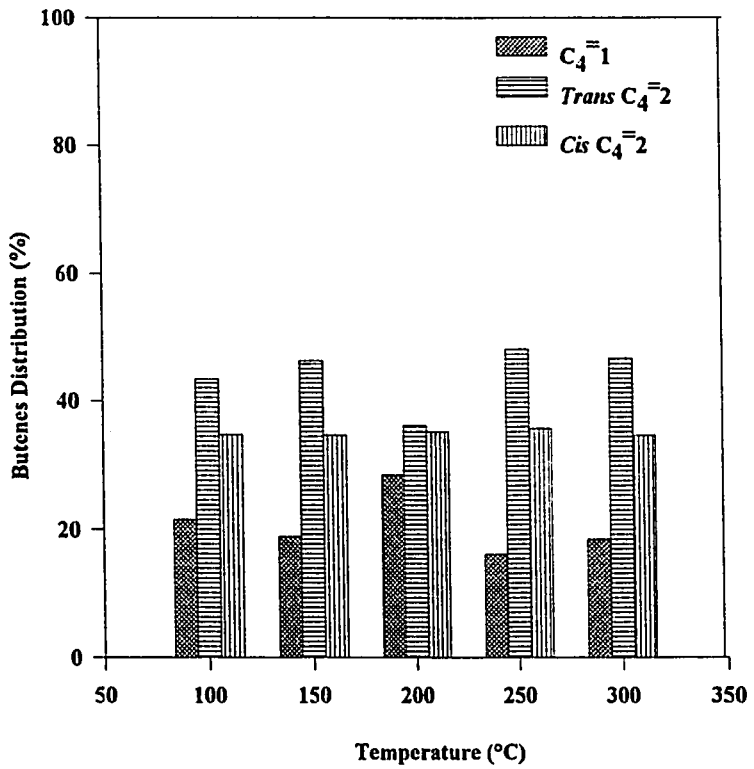


Figure 4-20: Butenes Distribution versus Temperature for Ni-SSA (D-0.43 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

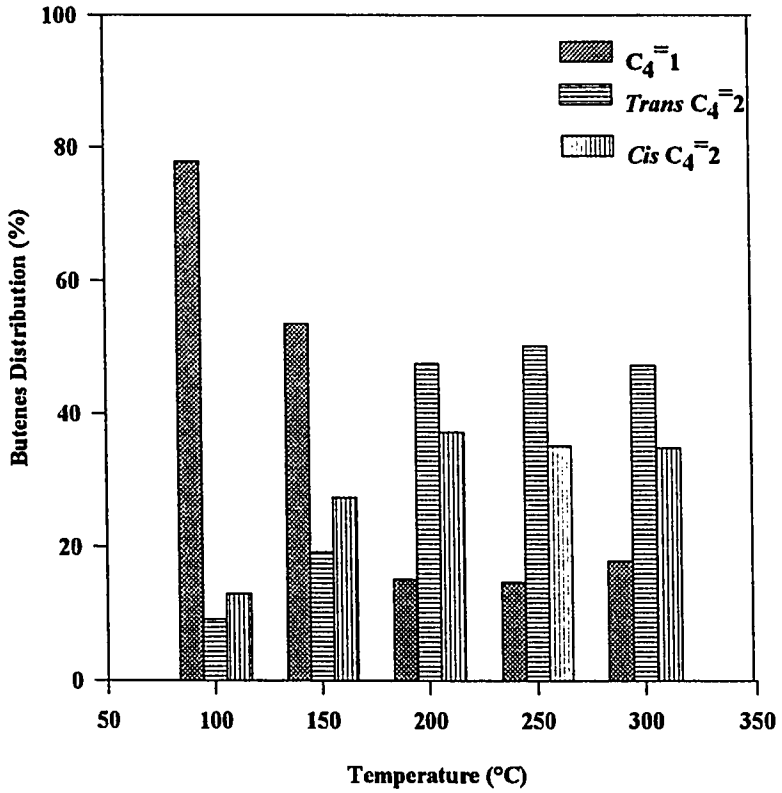


Figure 4-21: Butenes Distribution versus Temperature for Ni-SSA (G-1.1 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

4.10. EFFECT OF TEMPERATURE ON THE PERFORMANCE OF COBALT IMPREGNATED ON NICKEL SUPPORTED ON AMORPHOUS SILICA-ALUMINA (Co/Ni-ASA)

Cobalt was used as a promoter on Nickel ion exchanged on amorphous silica-alumina. The cobalt was incorporated by impregnation. Figure 4-22 presents a plot of temperature versus conversion profile for the catalyst (Co/Ni-ASA; Co = 3.78 wt%, Ni = 0.40 wt%, Si/Al = 37.5). The data plotted is presented in Table 4-10 and it was based on the following operating conditions, a pressure of 500 psi, 2 h^{-1} WHSV of ethylene flow, 4 hours time on stream for each setting and a temperature range of 100-300°C (using 50°C interval).

The catalyst was found to be active though less than the NiASA. The activity was not much at low temperature, possibly cobalt had formed clusters which might have blocked the nickel sites, thus the ethylene molecules were prevented from reaching the active sites. Remarkably at high temperature 250-300°C the catalyst activity was high even though the conversion level remains almost the same. This behavior could be due to the presence of cobalt, since for the catalyst without cobalt Figure 4-2 the trend increases as temperature increases from 250 to 300°C. The mass balance data presented in Table 4-10 was in the neighborhood of 90 to 95% indicating a high recovey from the system.

Cobalt was also ion exchanged on amorphous silica-alumina (F; Co-ASA). It was found to be non active at low temperatures (<200°C), at high temperature 300°C about 4% ethylene conversion was obtained after operating at 500 psi, 2 h^{-1} WHSV and 4 hours period. It was likely that activity was more from the support (ASA) than the catalyst (Ni), since the support is active at high temperatures (18).

TABLE 4-10: Effect of Temperature on Ethylene Oligomerization using **Co/Ni-ASA** (**L**-3.78 wt% Co, impregnated; 0.4 wt% Ni exchanged) at 2 h^{-1} WHSV, 500 psi and 4 hours run.

PARAMETER	TEMPERATURE				
	100 °C	150 °C	200 °C	250 °C	300 °C
$C_2^=$ Conversion (%)	1.2	4.1	38.4	58.4	584
Mass Balance (%)	97.4	91.8	87.6	87.4	87.5
Olefins Product Distribution (%)					
$C_4^=$	87.3	99.9	90.0	65.7	53.3
$C_6^=$	0.0	0.0	1.9	11.3	17.0
$C_8^=$	0.0	0.0	3.0	11.4	14.2
$C_{10}^=$	0.0	0.0	1.7	5.0	6.3
$C_{12}^=$	0.0	0.0	0.8	3.1	3.5
$C_{14}^=$	0.0	0.0	0.4	0.5	0.8
$C_{16}^=$	0.0	0.0	0.5	0.1	0.3
Cracking Products	0.0	0.0	0.8	1.9	3.5
Total olefins	**87.3**	**99.9**	**99.1**	**99.0**	**98.9**
Paraffins Prodt (%)	12.7	0.0	0.9	1.0	1.1
Butenes Distribution (%)					
$C_4^=1$	59.2	15.0	14.8	17.4	21.7
Trans-$C_4^=2$	17.3	48.9	50.3	48.5	43.9
Cis-$C_4^=2$	23.5	36.1	34.9	34.1	34.4

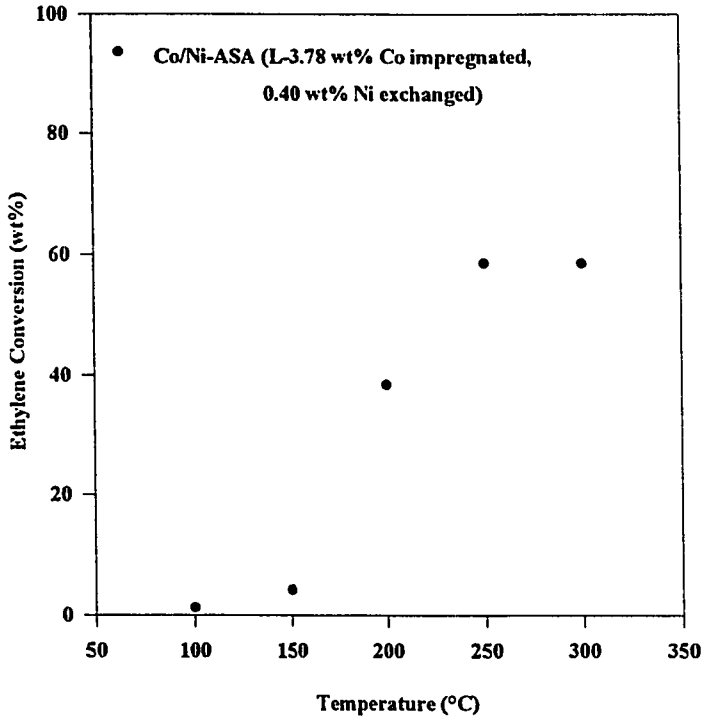


Figure 4-22: Effect of Temperature on the Performance of Cobalt over Nickel Supported on Amorphous Silica-Alumina (Co/Ni-ASA) at 2 h^{-1} WHSV and 500 psi for Ethylene Conversion

4.11. EFFECT OF TEMPERATURE ON THE PRODUCTS DISTRIBUTION OF COBALT IMPREGNATED ON NICKEL SUPPORTED ON AMORPHOUS SILICA-ALUMINA (Co/Ni-ASA)

4.11.1. Olefins Product Distribution of Co/Ni-ASA

Olefins product distribution were in the range of C_4 to C_{16}. Table 4-10 presents the data of olefins distribution. Effect of cobalt as a promoter on the olefins product distribution is presented on Figure 4-23. Butenes dominated both at low and at high temperature. However, high oligomers were formed in substantial amounts at high temperatures. The distribution shown at 200°C on Figure 4-23 was similar to that shown for Ni-ASA (C) at 150°C, Figure 4-6 for the catalyst Ni-ASA. Thus, its obvious from these figures that cobalt exerted no significant effect in the olefins product distribution.

4.11.2. Cracking Products of Co/Ni-ASA

The major factors causing cracking reaction are the support acidity and high temperature. Cobalt was also known as a hydrocracking catalyst (67). Cracking products were relatively low as compared to the catalysts Ni-ASA. From 0.8% at 200°C they increased to 3.5% at 300°C. Although, the cracking product were expected to go higher than this, because of the hydrocracking nature of cobalt (67). Possible explanation could be that, cobalt atoms had formed clusters, as a result only few sites of cobalt were active.

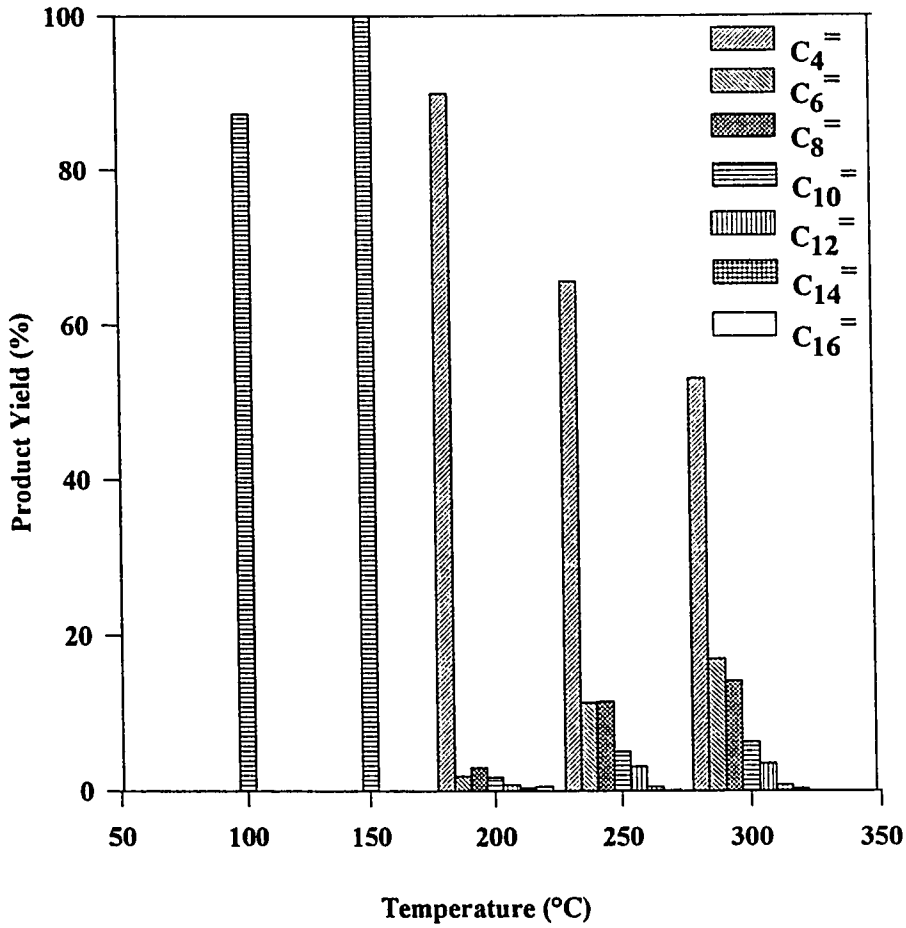


Figure 4-23: Olefins Product Distribution versus Temperature for Co/Ni-ASA

(L-3.78 wt% Co impregnated, 0.40 wt% Ni exchanged)

at 2 h^{-1} WHSV and 500 psi.

4.11.3. Parrafins Products of Co/Ni-ASA

The paraffins products are presented in Table 4-10. There was substantial amount at 100°C (12.7%). Probable explanation could be, cobalt has contributed to the cracking activity at low temperature and more paraffins were produced in the cracked product. However, at high temperature (>150°C) settings the paraffins produced were just around 1.0% though the cracking products have increased as indicated in Table 4-10.

4.11.4. Butenes Distribution of Co/Ni-ASA

Figure 4-24 presents the butenes distribution of the catalyst and the data is presented in Table 4-10. The promoter (Co) has not changed the butenes distribution significantly from that of Ni-ASA. At low temperature $C4^{=}1$ dominated and it isomerized to *trans*-$C4^{=}2$ and c*is*-$C4^{=}2$ at high temperatures. More *trans*-$C4^{=}2$ was obtained at 200°C and more *cis*-$C4^{=}2$ at 150°C just like the case of Ni-ASA. In effect presence of Co has no significant effect on the butenes distribution.

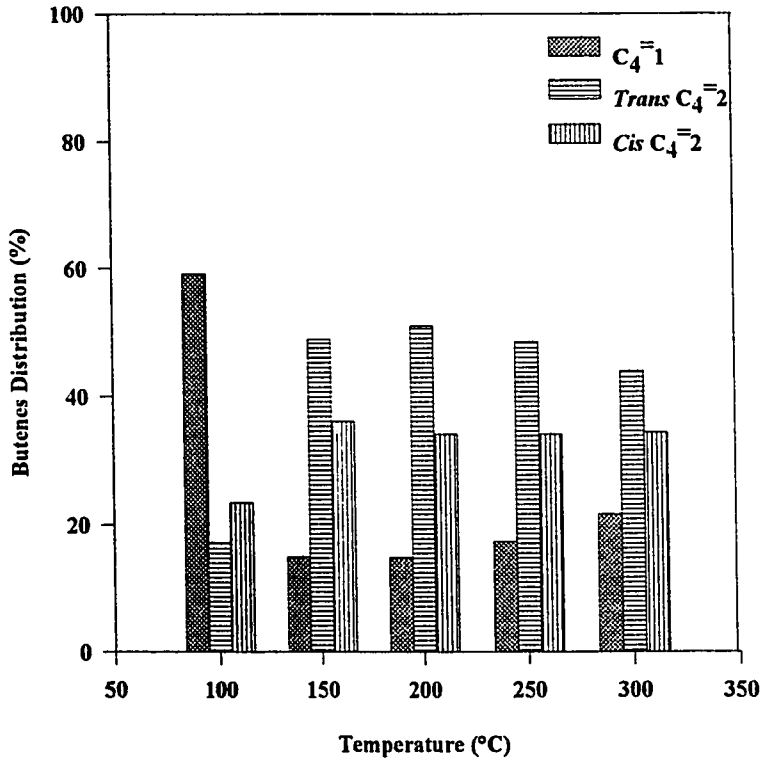


Figure 4-24: Butenes Distribution versus Temperature for Co/Ni-ASA (L-3.78 wt% Co impregnated, 0.4 wt% Ni exchanged) at 2 h^{-1} WHSV and 500 psi.

4.12. COMPARISON OF THE CATALYSTS TESTED

All the catalysts prepared and tested were found to be active for ethylene oligomerization. NiASA catalysts were more active than the NiSSA and Co/Ni-ASA. The catalysts activity increases with increase in temperature for the conditions operated except Co/Ni-ASA where the conversion did not change at 250 and 300°C.

The catalysts exhibited high selectivity to butene at low temperature and heavier products were obtained at temperatures greater than 200°C. Cracking and paraffin products were obtained both at low and high temperatures operated. Cracking products for Co/Ni-ASA were less as compared to Ni-ASA. In Table 4-4 cracking products for Ni-ASA (K) at 250 and 300°C were 6.6 and 14.0% respectively. While for Co/Ni-ASA, Table 4-10 cracking products at 250 and 300°C were 1.9 and 3.5% respectively. It is quite possible that Co has suppressed the acidity of the supports by blocking the acid sites and as well has formed clusters thus lacked uniformity.

For the paraffins products no specific pattern was obtained some catalysts yielded more at low temperatures such as Co/Ni-ASA probably due to the presence of cobalt, while other at high temperatures such as Ni-ASA. The butenes distribution for NiASA and the promoted catalyst (Co/Ni-ASA) were almost the same. $C_4^{=}1$ the initial dimer and it isomerizes to give *trans* and *cis* butene-2. This behavior increases as the temperature increases. However, a slight increase in the yield of $C_4^{=}1$ was observed as the temperature passed 250°C this was the result of increase of ethylene in the system from the cracking products. The butene distribution for NiSSA was slightly different at low temperature as sodium caused $C_4^{=}1$ yield to increases as the temperature was progressively increases.

4.13. COMPARISON OF THE CATALYSTS TESTED WITH THOSE REPORTED IN THE LITERATURE

TABLE 4-11: Comparative Study with Literature

SUBJECT	THIS STUDY	LITERATURE	COMMENTS
	Effect of Temperature		
Catalyst activity	Ni-ASA, 0.42% Ni Ni/ASA, 3.70% Ni	Ni-ASA, 0.73% Ni Ni/ASA, 3.84% Ni	Similar catalyst. activity
	Ni-SSA, 0.43% Ni Ni-SSA, 1.1% Ni	--	Catalysts found to be active
	Co/Ni-ASA, 3.78% Co and 0.4% Ni	--	Catalyst with Co as a promoter was more active at high temp.
Production of olefins	C_4-C_{16}	C_4-C_{18}	Higher olefins and similar distribution for all the catalyst at high temp.
	C_4-C_{16}	C_4-C_{18}	High olefins at low temperature after increasing the time on stream
Cracking products	Cracking increases with increasing temperature	Cracking increases with increasing temperature	High temp. and support acidity responsible
Paraffins products	Paraffins obtained	--	Obtained probably from the cracked products
Distribution of butenes	Studied both at low and high temperature	Studied at low temperature	Isomerization activity dominates
	Cobalt as a promoter	--	Co has no much effect on butenes distribution

TABLE 4-11 Comparative Study with Literature (Continued)

SUBJECT	THIS STUDY	LITERATURE	COMMENTS
Effect of Space Velocity			
Catalyst activity	Catalyst performance decreased as space velocity increases	Catalyst activity reached optimum then decreased as space vel. increases	Reduction in contact time responsible
Production of olefins	Products shifted to lighter olefins as space velocity increases	Products shifted to lighter olefins as space velocity increases	Reduction in residence time
Paraffins products	Paraffins obtained at low and high space vel.	--	Products decreases as space velocity increases
Cracking products	Cracking activity decreased with increase in space velocity	--	The longer the residence time the more the cracking activity
Distribution of butenes	No much difference in the distribution at different space velocities	--	Isomerization equilibrium was fast regardless of the residence time
Preliminary study on the Reaction rate	Effect of space velocity gave first order kinetics	Effect of pressure gave first order kinetics	Same pattern of behavior obtained

4.14. APPLICABILITY OF THE PRESENT STUDY

The application of olefins in the production of variety of goods has been presented in Table 1-1. In this study no specific application was considered. However, the vast olefins obtained fall in the most applicable range, C_4-C_{14}. The products from this study were mostly combination of linear alpha, linear internal and branched olefins, as indicated in from the GC-MS, Appendix A-7.

Provided the selectivity can be directed to more linear alpha olefins, the catalysts prepared and at the conditions operated, they can all be used in the production of biodegradable detergents, LLPDE, plasticizers esters, HDPE, polyolefins, tertiary amines, fatty acids, lubricants and some other miscellaneous products.

On the other hand directing the selectivity to more linear internal olefins, will eventually yield C_4-C_{14} which can inturn be used in the production of linear alkyl benzene (LAB) and oxo alcohol.

One possible way of directing the selectivity to one direction is by incorporating an element or compound that has tendency to draw electrons towards itself or away. This way the doble bond of the products can shift to the beginning or to the center of the products. Good control of catalyst, time and temperature can also help in preventing rapid isomerization of linear alpha olefins to linear internal olefins.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

1. All the catalysts prepared, Ni supported on amorphous silica-alumina and on sodium silica-alumina were found to be active for ethylene oligomerization in a fixed-bed tubular flow reactor system.

2. The Ni-ASA (ion exchanged) catalyst was found to be more active than the Ni/ASA (impregnated) because of the weak bonding and possible cluster formation of nickel in the later.

3. High olefins (oligomers) were obtained at high temperatures (>200°C) for all the catalysts tested. Ni-ASA at low temperature (150°C) gave high oligomers after extending the time on stream to 14 hours without much change in the conversion.

4. The high cracking activity of the catalysts was the result of the support acidity (Si/Al ratio) and high temperature operation. The presence of Na in Ni-SSA suppressed cracking activity by lowering the acidity of the support.

5. Cobalt as a promoter on Ni-ASA catalyst was found to be active. However, more paraffins were produced at low temperature this was due probably to the cracking nature of cobalt.

6. With the exception of Ni-SSA (D) all the other catalysts exhibited high selectivity to butene-1 ($C_4^{=}1$) at low temperature.

7. High space velocity decreased ethylene conversion as a result of the reduction in the contact time.

8. From the preliminary studies of the reaction rate, first order kinetics was found for the catalyst Ni-ASA (K) at 300°C and 500 psi based on the effect of space velocity.

5.2 RECOMMENDATIONS

1. The high cracking activity are related to the support acidity (Si/Al ratio) and high temperature. It would be interesting to explore further this area by reducing the acidity of the support and operating at low temperature.

2. Cobalt as a promoter on supported nickel catalyst showed promising behavior for ethylene oligomerization reaction. It can be further investigated by changing its content and by a stage wise impregnation so as to ensure a uniform distribution on the support.

3. The effect of support acidity can be further reduced by suppressing it with different amounts of sodium.

4. Further kinetics studies could be carried out over the entire temperature range to find the exact behavior of the catalysts with relation to kinetics.

5. It will also be interesting to incorporate electron withdrawing element or compound on the catalysts, so as see the effect on products distribution..

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A-1: Procedure of Preparing TPA Aluminate

A. Resin Exchange:

$RCl + NaOH \Longrightarrow ROH + NaCl$ (R implies resin)

1. NaOH; 1 Litre of 0.5M (20g in 1 litre), RCl; 75g:
   Stir for 30 min. then filter.
2. Filter cake + 1 litre of 0.5M NaOH;
   Stir for 30 minutes then filter.
3. Repeat 2 five times.
4. Wash the filter cake with 2 litres of distilled water on the filter paper.

B. TPA Bromide Exchange:

1. Make a solution; 20g of TPA Br + 200mL of Distilled Water.
2. Add the ROH (75g) from A to the TPA Br solution.
   $ROH + TPA\ Br \Longrightarrow RBr + TPA\ OH$
3. Stir for 30 minutes then filter and wash well with distilled water.
4. Evaporate the solution if necessary to recover 500ml of TPA OH

C. TPA-OH Exchange

1. Repeat A followed by addition of TPA OH solution from B
2. Stir for 30 minutes filter and test for any bromide left.
3. The test: add HNO_3 to small amount of the solution test for acidity then add $AgNO_3$ if white ppt. formed, then bromide is present.
4. Repeat part C. several times till it becomes clear that, no more bromide is left or atleast the amount left is of insignificant effect.

D. Aluminium Exchange

1. Assuming no lost in the TPA-OH that means 20g or 0.075moles are now available.
2. Take 1g of Al powder add to 20ml of Toluene.
   Stir well, Filter and Vacuum dry at 90°C.
3. Evaporate the TPA-OH to 200ml.
4. Put the 1g of Al into 250ml conical flask. Then add the TPA-OH solution.
5. Reflux for several hours to dissolve Al.

$$2Al + 2TPA\text{-}OH + 2H_2O \Longrightarrow 2TPA\text{-}ALO_2 + 3H_2$$

A-2: Supports Preparation

The silicic acid used was dry and has got the formula $H_2SiO_3.nH_2O$ ($SiO_2.nH_2O$), in order to find the exact amount of water, certain amount was taken and calcined at 600°C and at 900°C stage-wise each for 6 hours.

$$SiO_2.nH_2O \longrightarrow SiO_2 + nH_2O$$

2g 0.42g

Amount of water in silicic acid = 0.42 x 100/2 = 21%

Thus, $n.18/(60 + n.18) = 0.21$

and $n = 0.886 \sim 1.0$

We thus have,

$$SiO_2.H_2O \Longrightarrow SiO_2 + H_2O$$

1 1 1

using the above equation

2/78 = 0.0256 moles $SiO_2.H_2O$ = 0.0256 moles H_2O

Thus, mass of water = 0.0256 x 18 = 0.461g (Theoretical)

But, from calcination we got 0.420g H_2O at 600°C and 0.437g of H_2O at 900°C.

Thus the number of moles of water in the silicic acid is 1.

A-2.1. Amorphous silica-alumina (ASA)

Using 500ml H_2O for the preparation of the support, implies 500g H_2O.

Thus moles = 500/18 = 27.78 moles

Our requirement is $H_2O/SiO_2.H_2O$ = 50

Thus moles of $SiO_2.H_2O$ = 27.78/50 = 0.555moles and

mass of $SiO_2.H_2O$ = 0.555 x 78 = 43.33g

% Si = 28/78 = 35.9%

mass of Si = 35.9% x 43.33 = 15.555g

The required ratio of Si/Al is 36:

moles of Silicon (Si)= 15.555/28 = 0.555 moles

moles of Aluminium (Al)= 0.555/36 = 0.0154 moles

mass of Al = 0.0154 x 27 = 0.4158g

From the preparation of TPA Aluminate we ended up with 200g of solution after dissolving 1g of Aluminium powder.

Then to get 0.4158g; 200 x 0.4158/1 = 83.16g TPA Aluminate.

The amount of TPA OH obtained from the 20g TPA Br used is;

ROH + TPA Br —> RBr + TPA OH

1 1

20g/266.67 = 0.075 moles

Thus, TPA OH = 0.075 x (186.67 + 17) = 15.275g

i.e. 15.275g TPA OH in 200g solution of TPA Aluminate.

Thus 83.16g contain: 15.275 x 83.16/200 = 6.35g TPA OH.

The procedure mentioned in section 3-1 is then followed. Ammonium hydroxide was added to increase the solution pH from 10.1 to 12.0. Still after stirring there was no gellation. HNO_3 (1:1) was added drop by drop till the pH changes from 12.0 to 8.0. Sample was filtered, then dried at 90°C for 4 hours. Finally it was calcined at 500°C for 36 hours.

A-2.2. Sodium Silica-Alumina (SSA)

4g of NaOH was used and 250ml of H_2O. The above form of calculation was then followed. The following moles were obtained (61);

	Al_2 :	Si:	TPA OH :	H_2O :	Na_2O
moles	0.00386	0.2778	0.01559	13.89	0.05
or	1	72	4.03	4152.17	12.95

The moles of water from TPA OH are added to that of water; (i.e. 41.688-3.184 = 38.504g implying 2.1391 moles and dividing by the moles of alumina (Al_2) we got 554.1739g and adding that to that of water alone (3598g) gave the total 4152.17g)

The same procedure of preparation as above was followed for the sodium silica-alumina except no ammonium hydroxide or HNO_3 was added. The pH was initally 12.3 and it drops to 11.3 after stirring at room temperature for 1 day.

TABLE A-2.1: Amount of chemicals used for the preparation of the supports.

CHEMICAL	Amorphous Silica-Alumina	Sodium Silica-Alumina
Water	500g	250g
Silicic Acid	43.33g	21.5g
Aluminium Metal powder	0.4158g	0.2076g
TPA aluminte solution	83.16g	41.5g
TPA OH	6.35g	3.175g
pH	8.0g	11.3
NaOH	0.0	4g

A-3: Supporting Nickel Catalyst

A-3.1. Nickel Ion Exchange

1M Ni precursor solution was prepared from $Ni(NO_3)_2.6H_2O$ using the following equation (16,63,68);

Concentration = Mass/(Molar Mass x Volume in dm^3)

The Nickel solution (250ml) and 5g of the support are then refluxed as described in section 3-1. The above procedure was repeated three times so as to ensure maximum exchange. For the support with sodium (SSA), ammonium (NH_4NO_3) exchange was first carried out using the above procedure three times so as to reduce the amount of sodiun (Na) incorporated in the support (63). Then Nickel exchange was carried out as described in section 3-1.

A-3.2. Nickel Impregnation

To calculate the amount of Nickel (Ni) to be impregnated the following was adopted;

% of Ni in $Ni(NO_3)_2.6H_2O$ = 58.71/290.71 = 20.2%

i.e. 1g of $Ni(NO_3)_2.6H_2O$ contain 0.202g of Ni

Suppose we need 4% Ni

Then, using 5g of the support, we get

0.04 x 5 = 0.2g

We thus, roughly need 1g of $Ni(NO_3)_2.6H_2O$ in order to get 0.2g of Ni

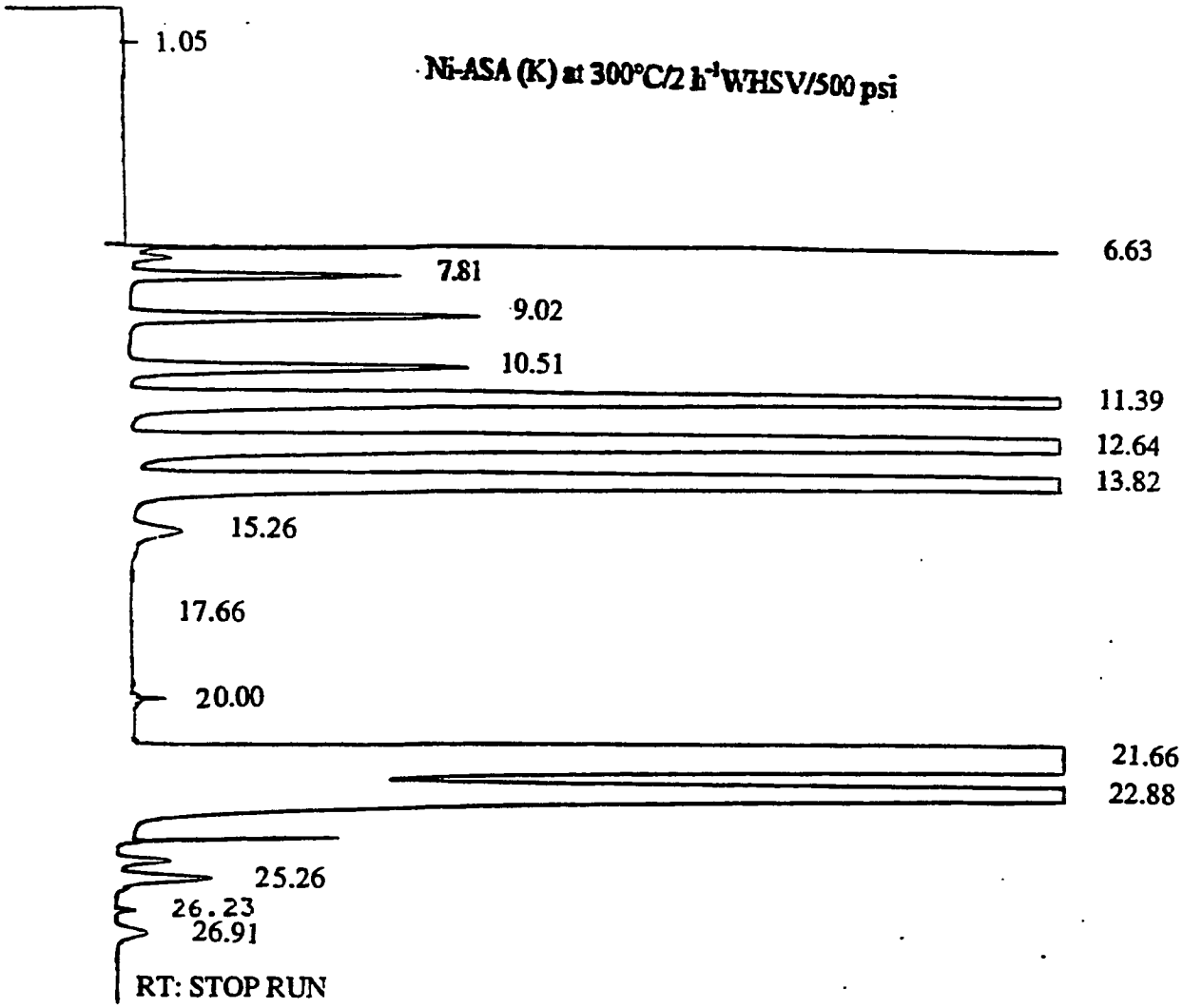
and the amount loaded will be 0.2/5.2 = 3.84%

The same approach was followed for the impregnation of cobalt. The procedure described in section 3-2 is then followed (16,63).

TABLE A-4: List of Elements Screened in Chemical Analysis [ICP].

Ag	Al	Ni	Co
Ca	Cd	As	Cu
Hg	In	Ir	K
Na	Nb	Sb	P
Rh	S	Te	Si
Th	Tl	Au	Ti
B	Ba	Be	Bi
Cr	Fe	Ge	Hf
Li	Mg	Mn	Mo
Re	Pb	Pt	Pd
Sc	Se	Sr	Sn
V	W	Zn	Zr

A-5: GC of one of the Gas Products



[hp] 5880 MANUAL INJECTION @ 01:07 MAR 26, 1995
********** PN 11105
ESTD

RT	AREA	TYPE	CAL	AMOUNT	NAME
7.81	46317.30	VV	2	0.468	C3+
9.02	70505.60	BB	3	0.698	IC4
10.51	78393.60	BV	4	0.666	N C4
11.39	625921.00	VV	5	6.635	C4=1
12.64	1389730.00	VV	6	14.314	TC4=2
13.82	846967.00	VV	8	10.079	C C4=2
15.26	2309.60	VB	9	0.278	I C5
17.66	368.46	BB	10	5.417E-03	N C5
21.66	4294130.00	VV	12	51.100	C2=
22.88	850703.00	VV	13	9.273	C2
26.91	9060.81 +	PH	15	0.161	C1

MULTIPLIER = 1

A-6: GC of some of the Liquid Products

For the Liquid chromatograms the following tag signs were used;

C.150.D refers to Ni-ASA (C) at 150°C/2 h^{-1}WHSV/500 psi

C.300.D refers to Ni-ASA (C) at 300°C/2 h^{-1}WHSV/500 psi

K.250.D refers to Ni-ASA (K) at 250°C/2 h^{-1}WHSV/500 psi

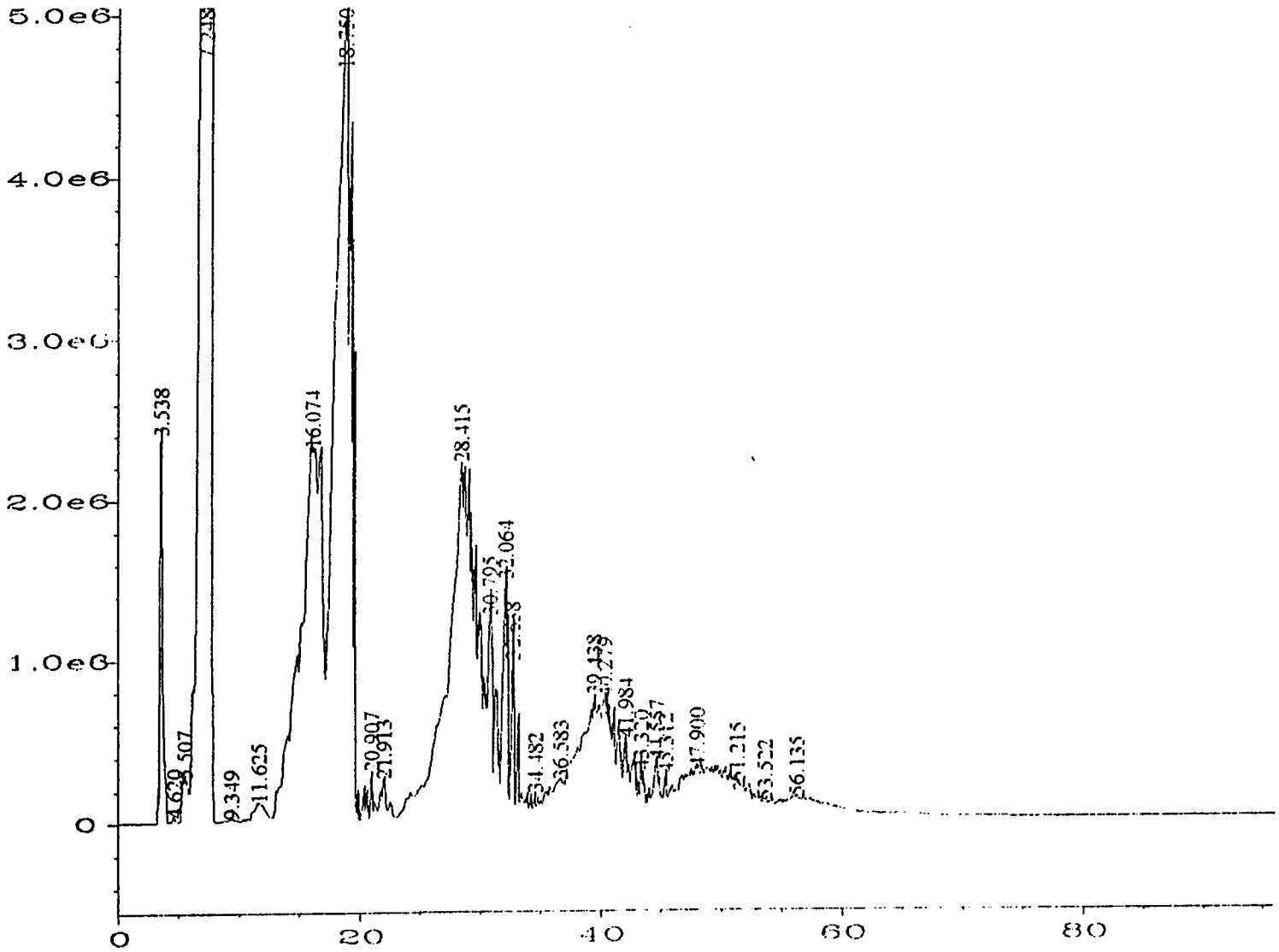
J.250.D refers to Ni/ASA (J) at 250°C/2 h^{-1}WHSV/500 psi

D.300.D refers to Ni-SSA (D) at 300°C/2 h^{-1}WHSV/500 psi

G.300.D refers to Ni-SSA (G) at 300°C/2 h^{-1}WHSV/500 psi

L.200.D refers to Co/Ni-ASA (L) at 200°C/2 h^{-1}WHSV/500 psi

The compounds in the liquid products were determined by comparing the ranges of retention time with that obtained from the GC-MS scanning and that of standard alpha olefins.



Sig. 1 in C:\HPCHEM\1\DATA\SANI\C150.D

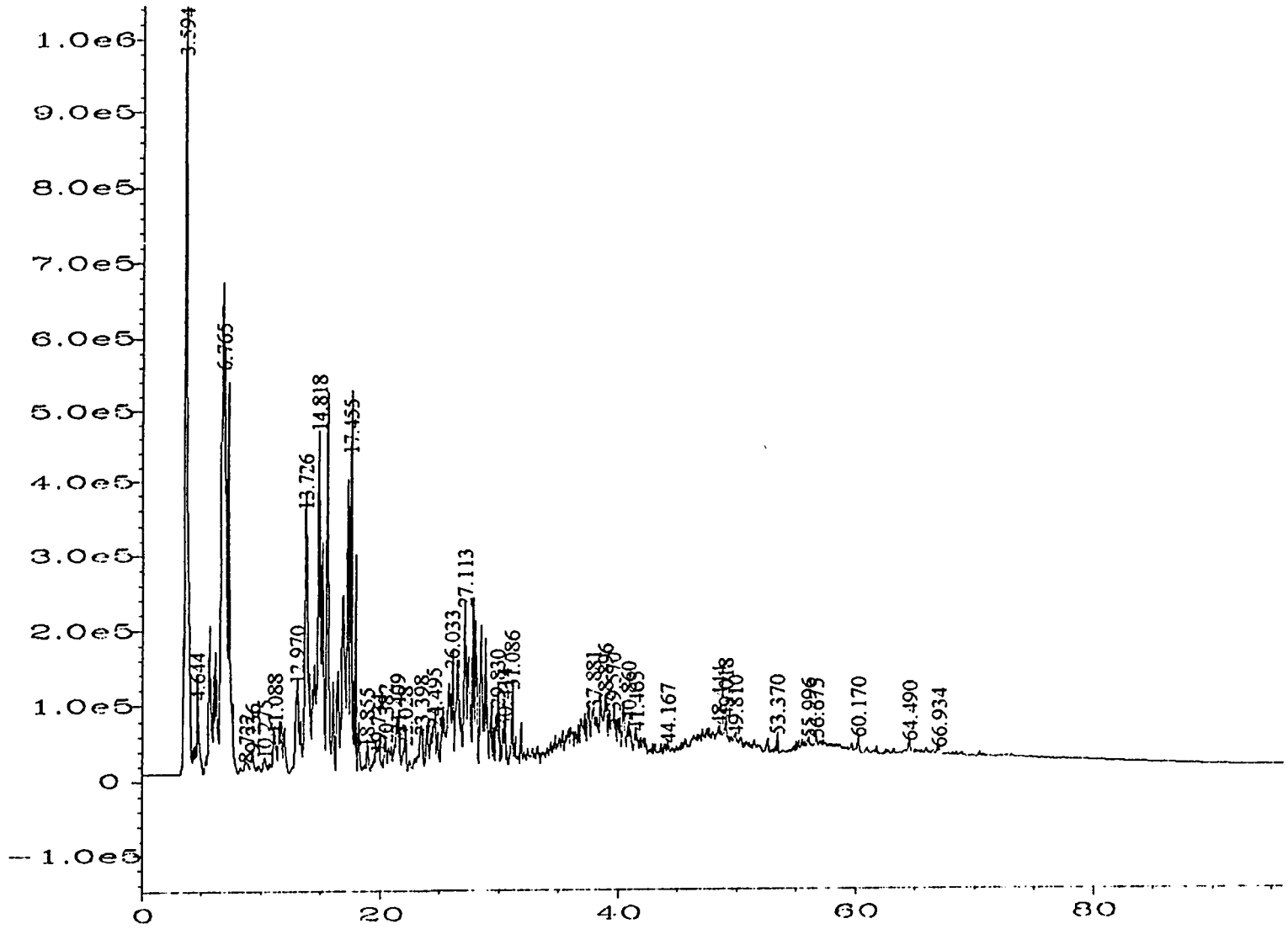
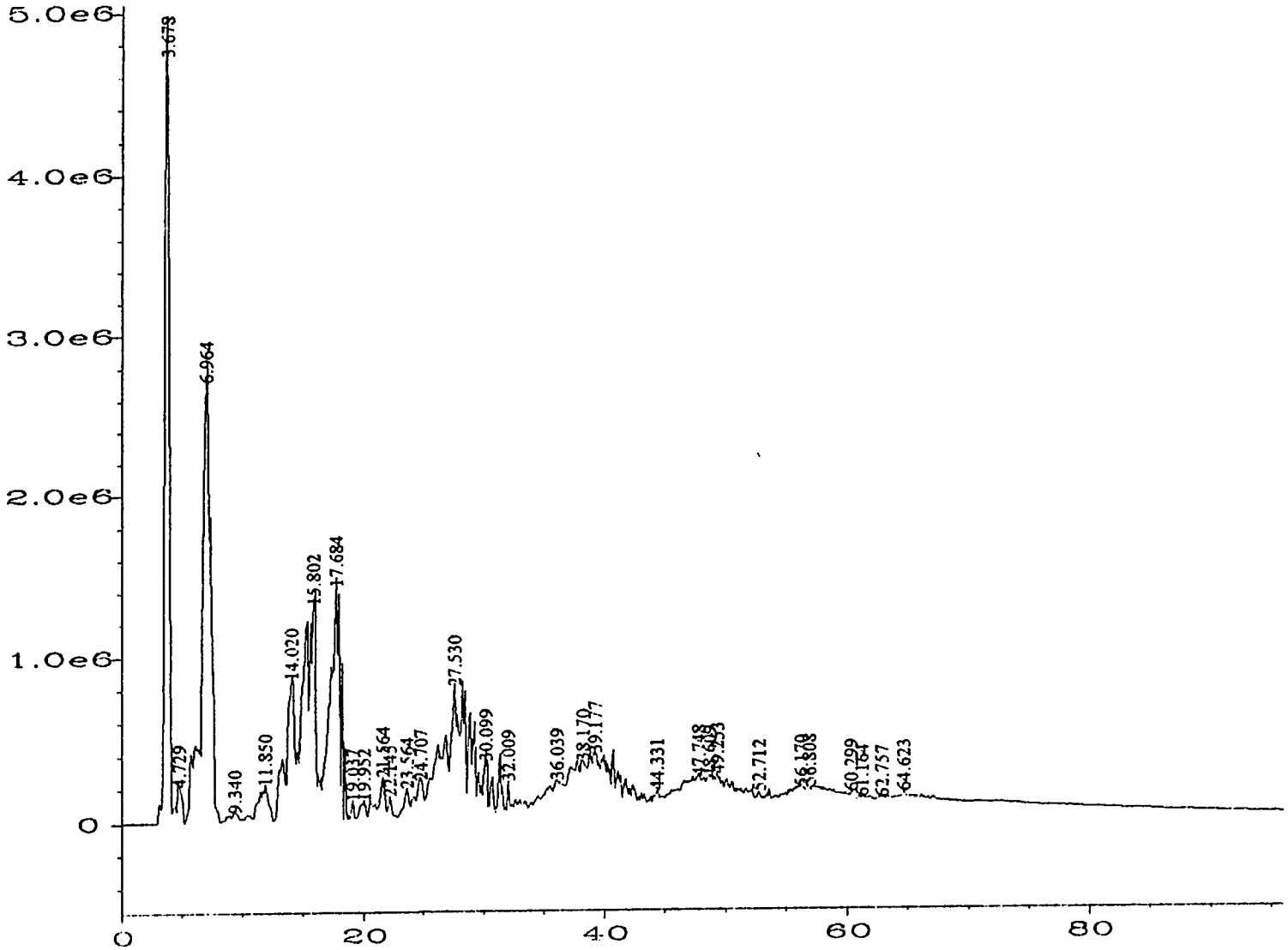
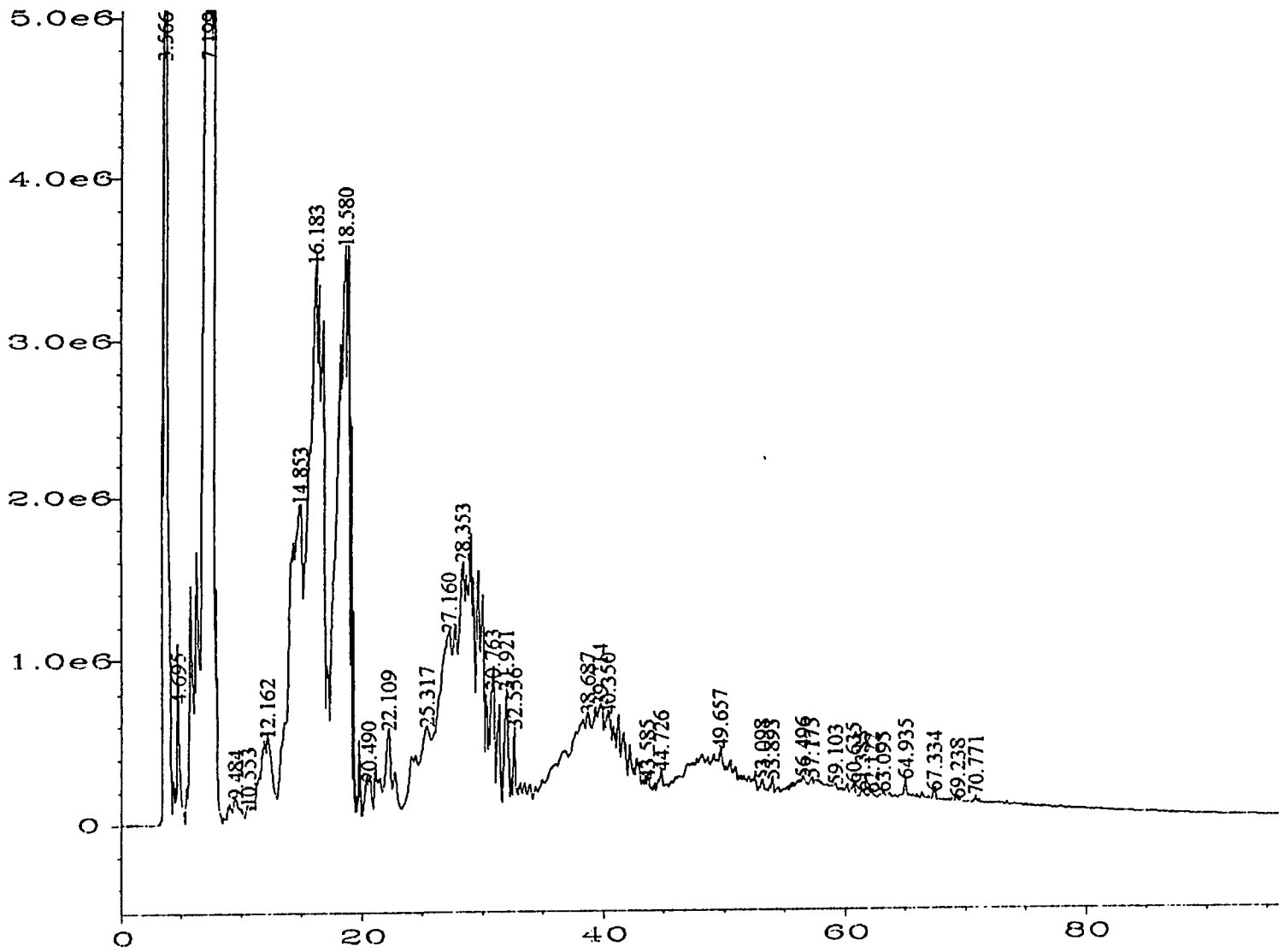


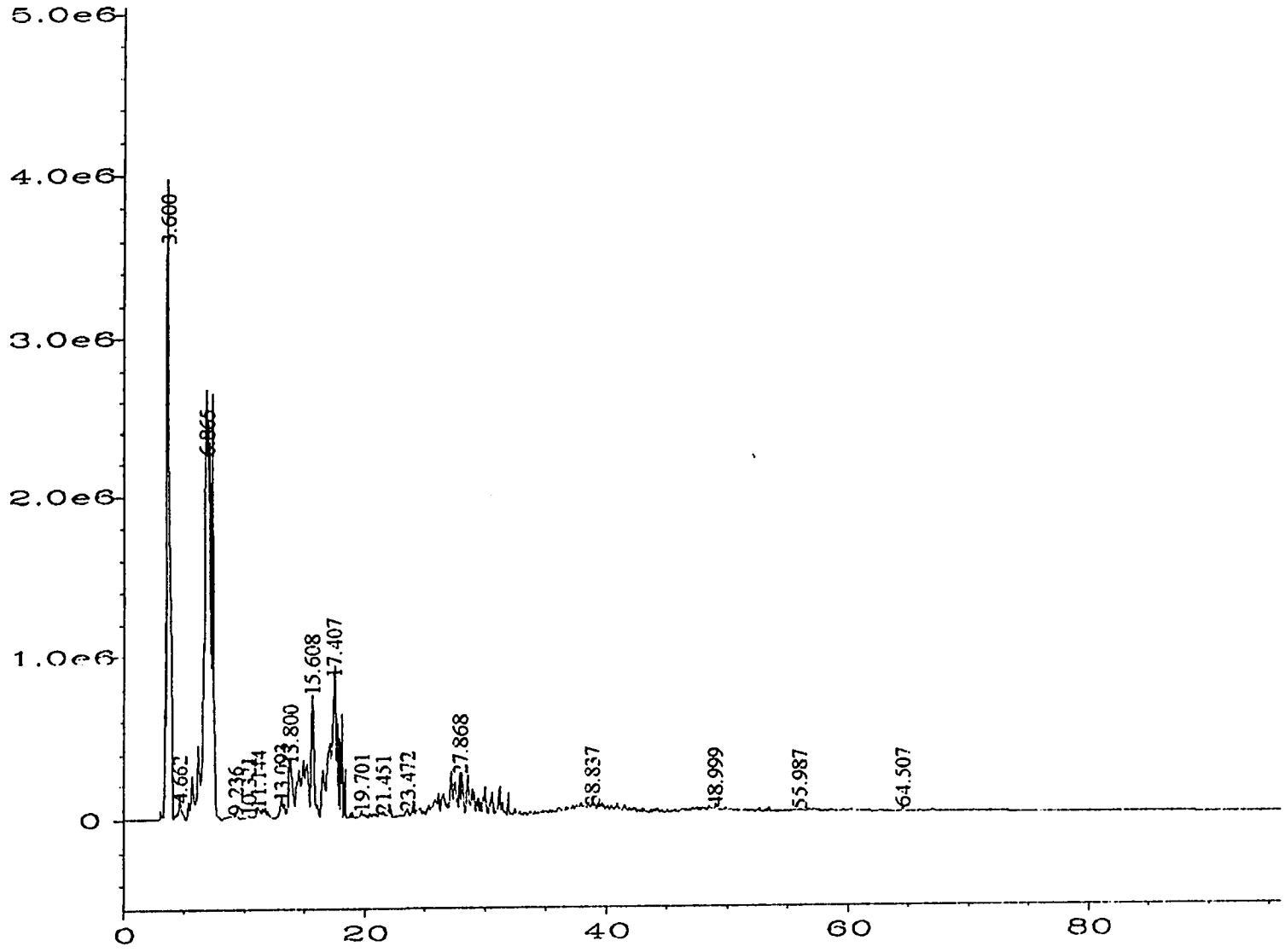
Fig. 1 In C:\HPCHEM\1\DATA\SANI-C300.D



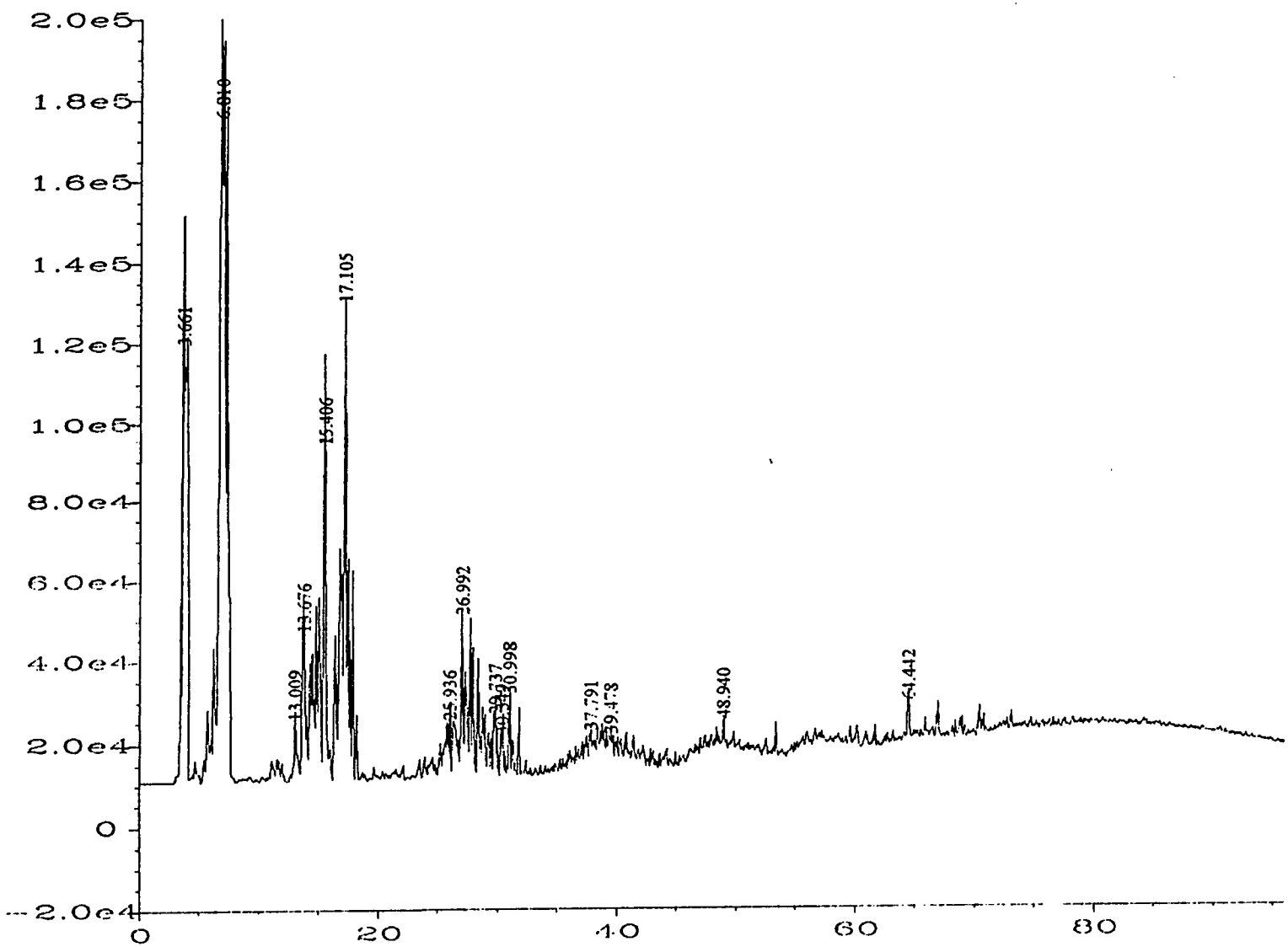
Sig. 1 in C:\HPCHEM\1\DATA\SANDK250.D



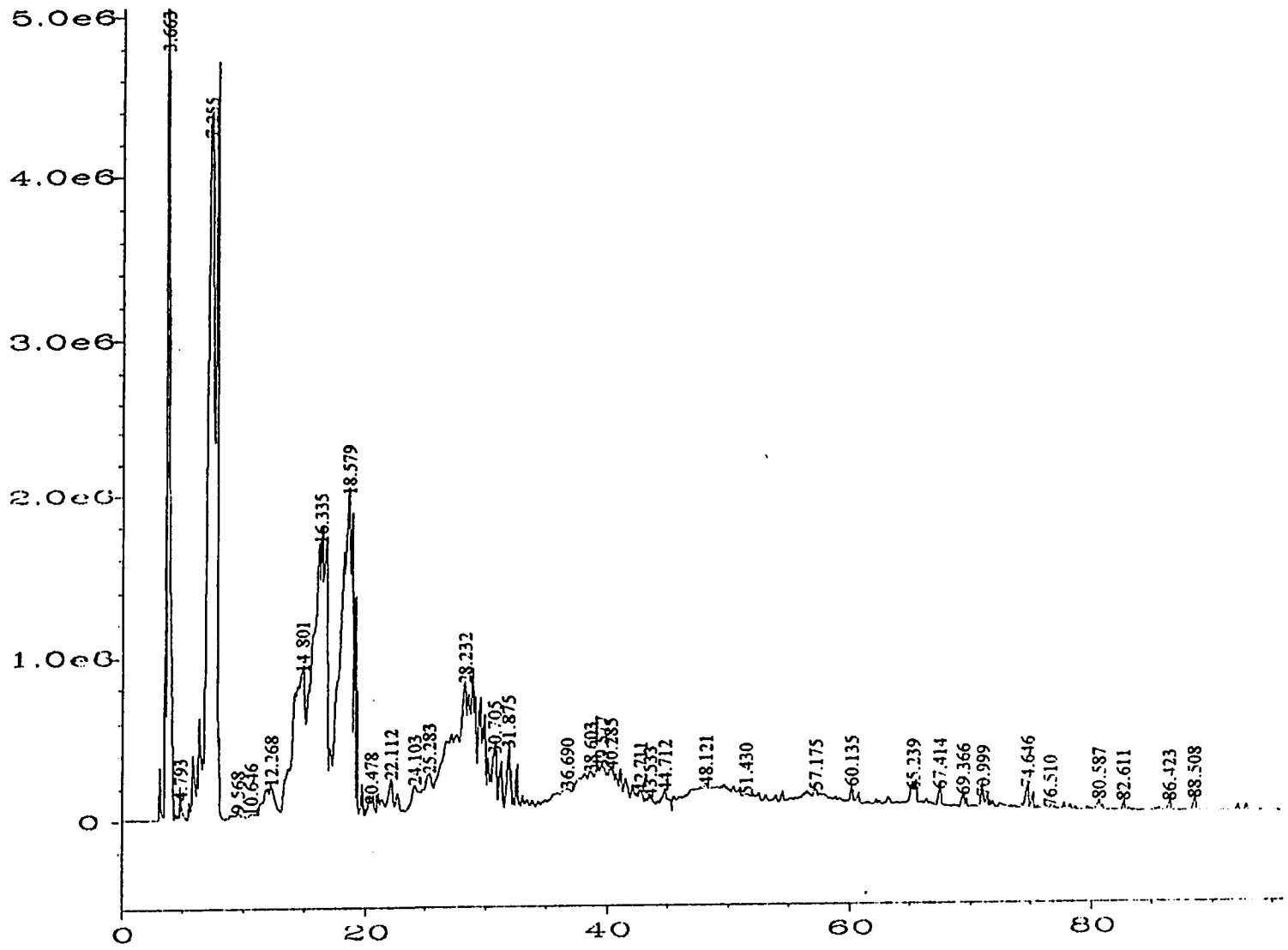
Sig. 1 in C:\HPCHEM\1\DATA\SANI\J250.D



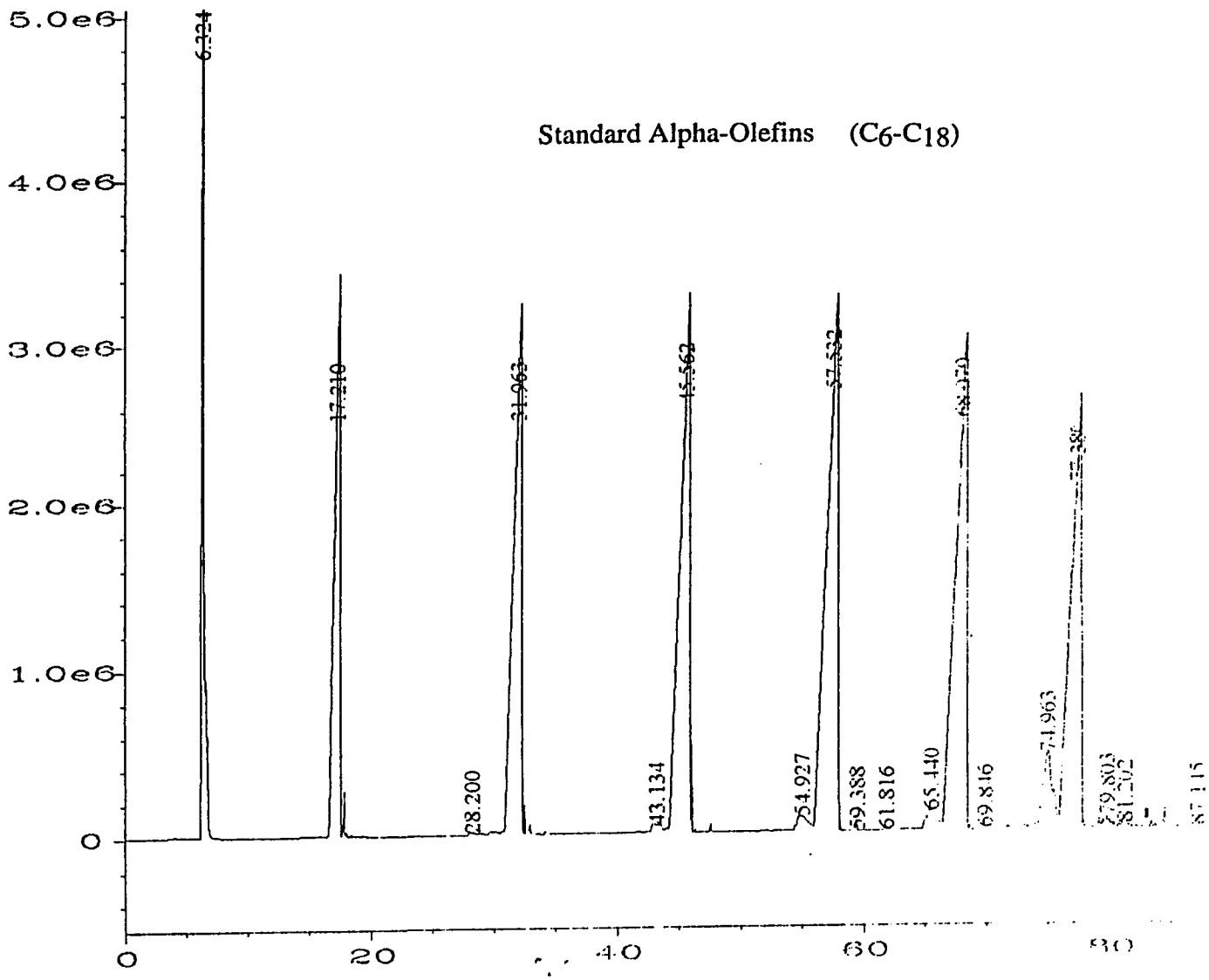
Sig. 1 in C:\HPCHEM\1\DATA\SANIND300.D



Sig. 1 in C:\HPCHEM\1\DATA\SANI\G300.D



Sig. 1 in C:\HPCHEM\1\DATA\SANI\L1--200.D

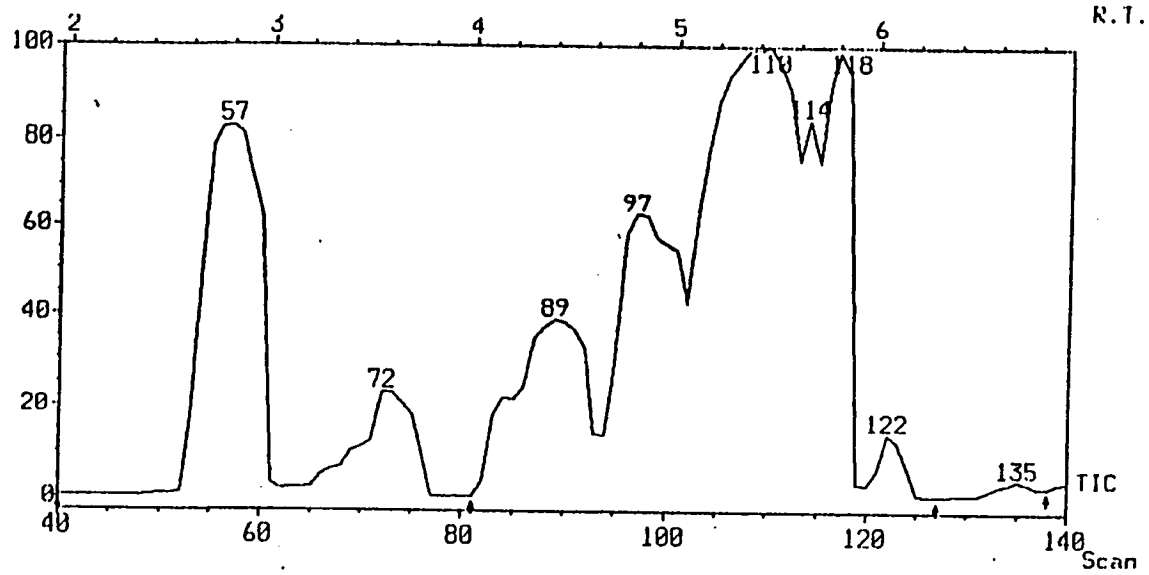


Sig. 1 in C:\HPCHEM 1\DATA\SANI-DSTD.D

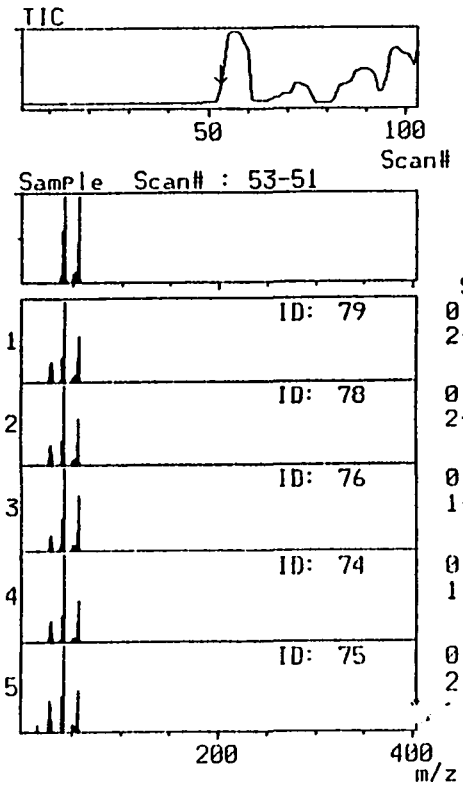
A-7: GC-MS of one of the Liquid Products

Ni-SSA (D) at 300°C/2 h^{-1}WHSV/500 psi

TIC Data File: OLD1 19-FEB-95 14:03
Sample: CAL-985, DJ OLEFINS C4-C14 INJ 0.5uL IM=1.1, 100uA
Scan# 40 to 140(802) RT 1'57" to 6'57"(40'02") EI(Pos.) Lv 0.00
Operator: Analytical



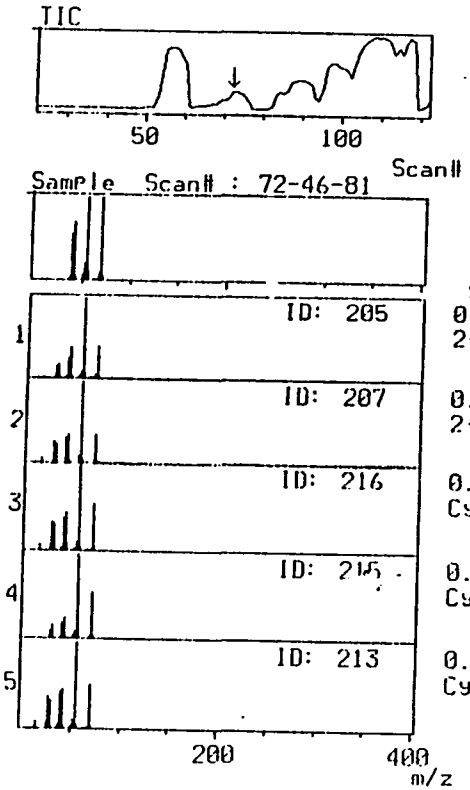
MSD>



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.933	56	C4H8	2-Butene, (E)- (8CI9CI) , (E)-2-Butene , trans-
0.927	56	C4H8	2-Butene, (Z)- (8CI9CI) , (Z)-2-Butene , cis-Bu
0.917	56	C4H8	1-Propene, 2-methyl- (9CI) , Propene, 2-methyl
0.880	56	C4H8	1-Butene (8CI9CI) , .alpha.-Butene , .alpha
0.856	56	C4H8	2-Butene (8CI9CI) , .beta.-Butene , .beta.

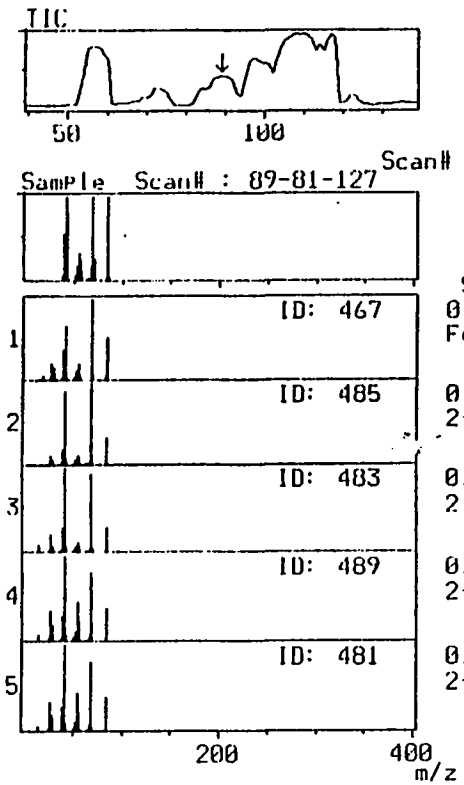
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.797	70	C5H10	2-Pentene (8CI9CI) , .beta.-n-Amylene , sym-Me
0.790	70	C5H10	2-Butene, 2-methyl- (8CI9CI) , .beta.-Isoamylene
0.775	70	C5H10	Cyclopropane, 1,2-dimethyl-, trans- (8CI9CI) , t
0.758	70	C5H10	Cyclopropane, 1,1-dimethyl- (8CI9CI) , gem-Dimet
0.743	70	C5H10	Cyclopropane, 1,2-dimethyl-, cis- (8CI9CI) , c

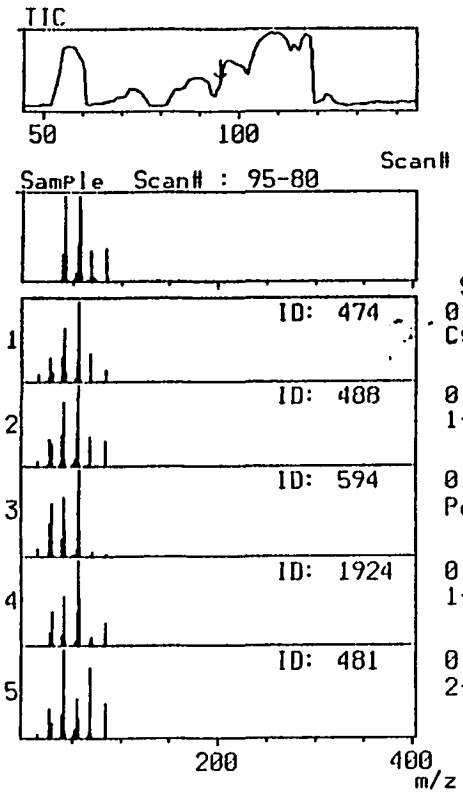
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.730	84	C5H8O	Furan, 2,3-dihydro-3-methyl- (8CI9CI)
0.652	84	C6H12	2-Pentene, 4-methyl-, (Z)- (8CI9CI) , (Z)-4-Met
0.612	84	C6H12	2-Pentene, 4-methyl-, (E)- (8CI9CI) , (E)-4-Met
0.602	84	C6H12	2-Pentene, 3-methyl-, (Z)- (8CI9CI) , (Z)-3-Met
0.601	84	C6H12	2-Pentene, 3-methyl-, (E)- (8CI9CI) , (E)-3-Met

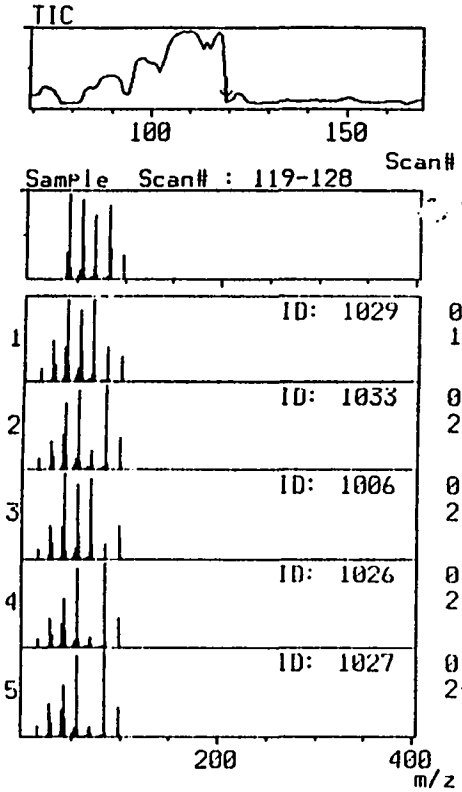
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, DI OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.782	84	C6H12	Cyclopentane, methyl- (8CI9CI) , Methylcyclope
0.777	84	C6H12	1-Pentene, 2-methyl- (8CI9CI) , 2-Methyl-1-pe
0.743	86	C6H14	Pentane, 3-methyl- (8CI9CI) , 3-Methylpentane
0.611	112	C8H16	1-Hexene, 3,4-dimethyl- (8CI9CI) , 3,4-Dimethyl-
0.610	84	C6H12	2-Pentene, 3-methyl-, (E)- (8CI9CI) , (E)-3-Met

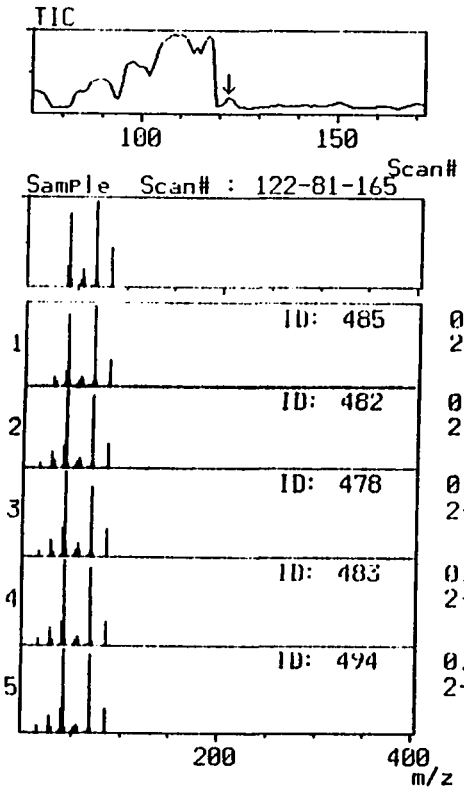
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.656	98	C7H14	1-Butene, 2-ethyl-3-methyl- (8CI9CI) , 2-Ethyl-3
0.633	98	C7H14	2-Pentene, 2,3-dimethyl- (8CI9CI) , 2,3-Dimet
0.564	98	C7H14	2-Pentene, 3-ethyl- (8CI9CI) , 3-Ethyl-2-Pentene
0.564	98	C7H14	2-Pentene, 3,4-dimethyl-, (Z)- (8CI9CI) , (Z)-3
0.563	98	C7H14	2-Pentene, 3,4-dimethyl-, (E)- (8CI9CI) , (E)-3

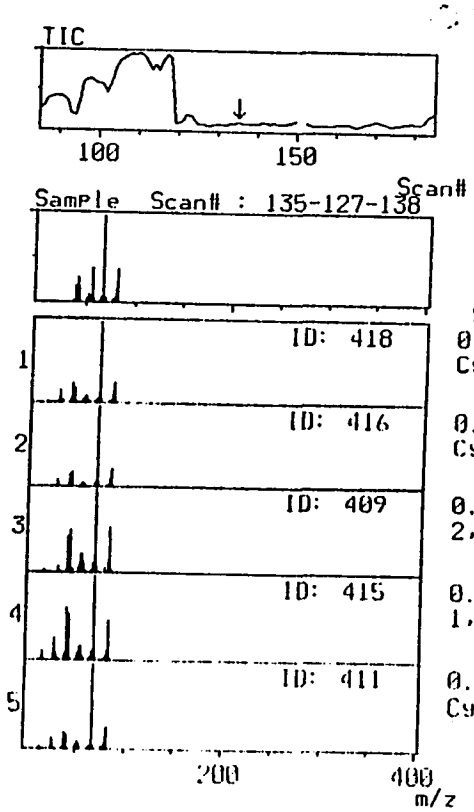
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.816	84	C6H12	2-Pentene, 4-methyl-, (Z)- (8CI9CI) , (Z)-4-Met
0.784	84	C6H12	2-Pentene, 2-methyl- (8CI9CI) , 2-Methyl-2-Pe
0.775	84	C6H12	2-Butene, 2,3-dimethyl- (8CI9CI) , Tetramethylet
0.764	84	C6H12	2-Pentene, 4-methyl-, (E)- (8CI9CI) , (E)-4-Met
0.748	84	C6H12	2-Pentene, 4-methyl- (8CI9CI) , 1,1-Dimethyl-

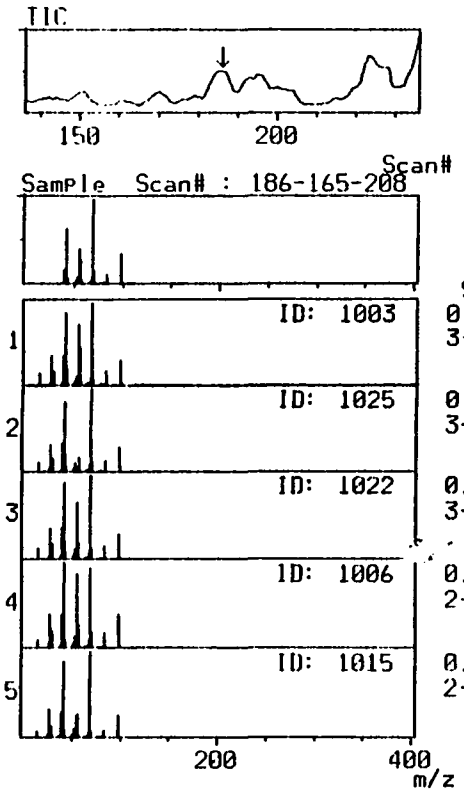
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.714	82	C6H10	Cyclopentene, 4-methyl- (8CI9CI) , 4-Methylcyclo
0.711	82	C6H10	Cyclopentene, 3-methyl- (8CI9CI) , 3-Methylcyclo
0.676	82	C6H10	2,4-Hexadiene (8CI9CI) , Bipropenyl , Diprop
0.656	82	C6H10	1,3-Pentadiene, 2-methyl- (8CI9CI) , 1,3-Dimet
0.632	82	C6H10	Cyclopentene, 1-methyl- (8CI9CI) , 1-Methyl-1-cy

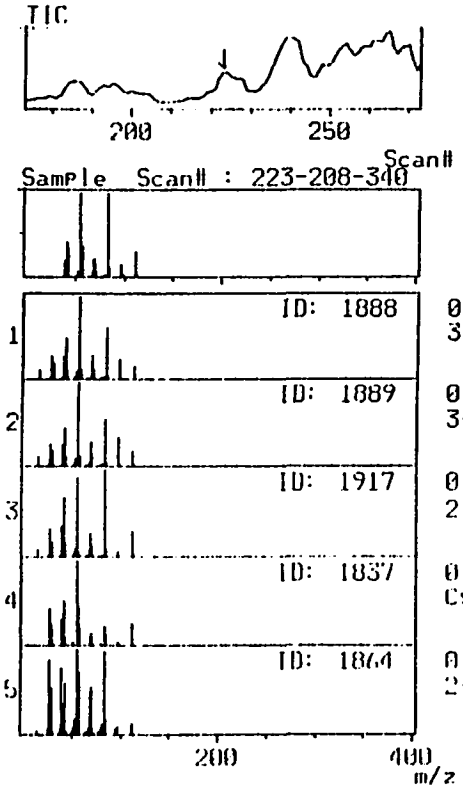
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.784	98	C7H14	3-Hexene, 2-methyl-, (E)- (8CI9CI) , (E)-2-Met
0.754	98	C7H14	3-Hexene, 3-methyl-, (Z)- (8CI9CI) , cis-3-Met
0.745	98	C7H14	3-Hexene, 3-methyl-, (E)- (8CI9CI) , (E)-3-Met
0.740	98	C7H14	2-Pentene, 3-ethyl- (8CI9CI) , 3-Ethyl-2-Pentene
0.739	98	C7H14	2-Hexene, 2-methyl- (8CI9CI) , 2-Methyl-2-hexene

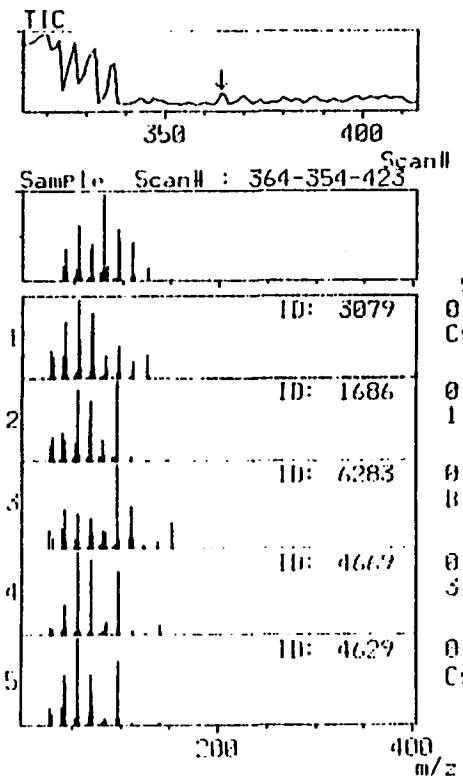
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: ISA:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-905, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.622	112	C8H16	3-Hexene, 2,2-dimethyl-, (Z)- (8CI9CI) , (Z)-2
0.614	112	C8H16	3-Hexene, 2,2-dimethyl-, (E)- (8CI9CI) , (E)-2
0.588	112	C8H16	2-Hexene, 2,3-dimethyl- (8CI9CI) , 2,3-Dimethyl-
0.573	112	C7H12O	Cyclohexanone, 4-methyl- (8CI9CI) , 4-Methylc
0.563	112	C7H12O	2-Heptenal, (E)- (8CI9CI) , (E)-2-Heptenal

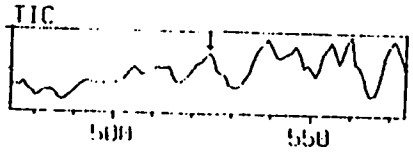
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



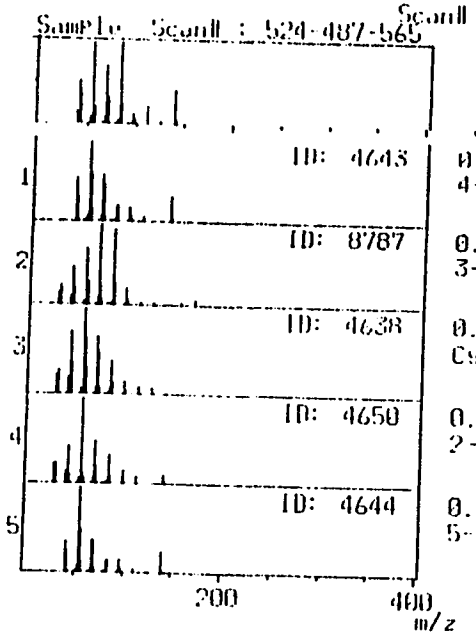
Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.526	126	C9H18	Cyclohexane, 1,2,3-trimethyl- (8CI9CI) , 1,2,3
0.478	110	C8H14	1,5-Hexadiene, 2,5-dimethyl- (8CI9CI) , Bimet
0.472	152	C10H16O	Bicyclo 2.2.1 heptan-2 one, 5,5,6 trimethyl-, ex
0.467	140	C10H20	3-Hexene, 3-ethyl-2,5-dimethyl- (9CI)
0.465	140	C10H20	Cyclopentane, (1-methylbutyl)- (9CI) , Pentane,

*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19 FEB-95 14:3



SIM. MW Formula
0.653 140 C10H20
4-Decene (8C19C1)

0.592 168 C12H24
3-Decene, 2,2-dimethyl-, (E)- (9C1) , trans-2,2

0.590 140 C10H20
Cyclooctane, 1,4-dimethyl-, cis- (9C1) , Cyclo

0.590 140 C10H20
2-Octene, 4-ethyl- (9C1)

0.587 140 C10H20
5-Decene (8C19C1)

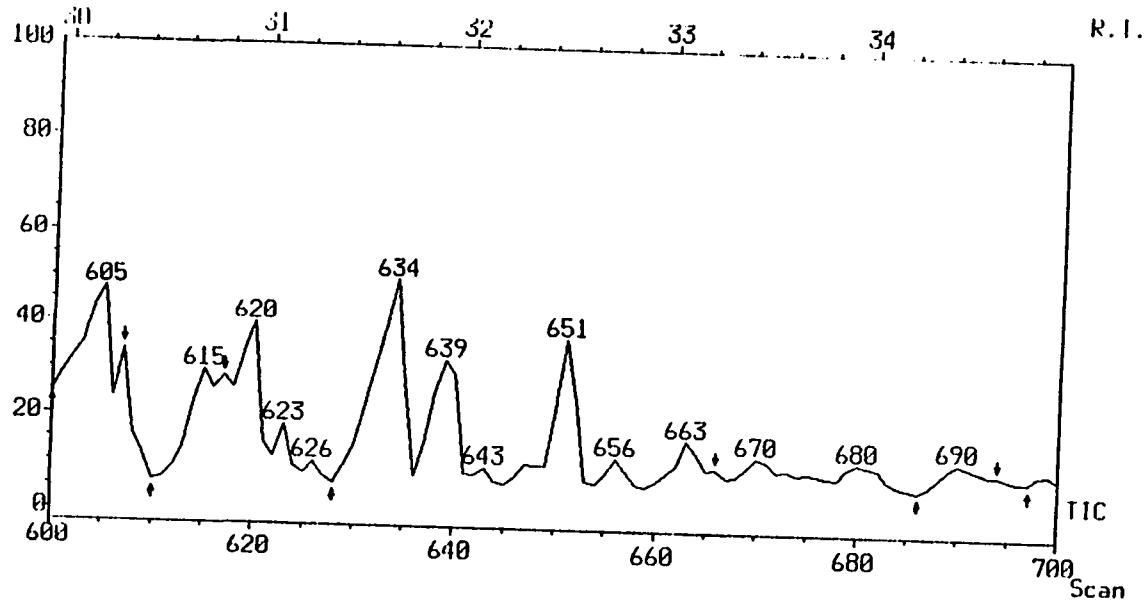
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):

TIC Data File: 01D1

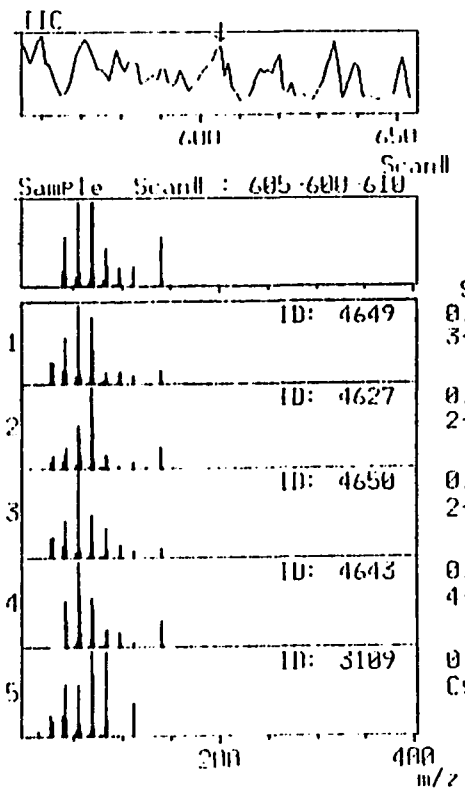
Sample: CHL 985, D1 OLEFINS C4-C14 INJ 0.5ul IM-1.1, 100uM 19-FEB-95 14:03

Scan# 600 to 700(80%) RT 27'57" to 34'56"(40'02") EI(Pos.) Lv 0.00

Operator: Analytical



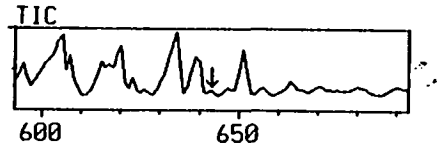
MSD>



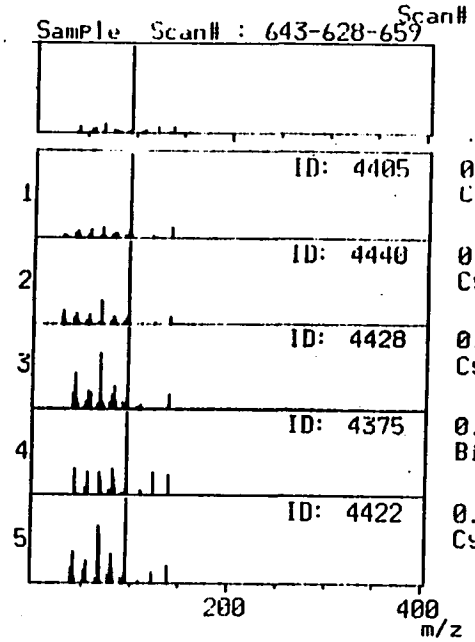
Library: LS0:[2,6]FULLIB.LIB
Data : SYA:01 D1.DAT
Sample : CHL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IN 1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.615	140	C10H20	3-Octene, 4-ethyl- (9CI)
0.572	140	C10H20	2-Octene, 2,6-dimethyl- (8CI9CI) , 2,6-Dimethyl-
0.571	140	C10H20	2-Octene, 4-ethyl- (9CI)
0.565	140	C10H20	4-Decene (8CI9CI)
0.551	126	C9H18	Cyclopentane, 1,1,3,4-tetramethyl-, cis- (9CI)

*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):

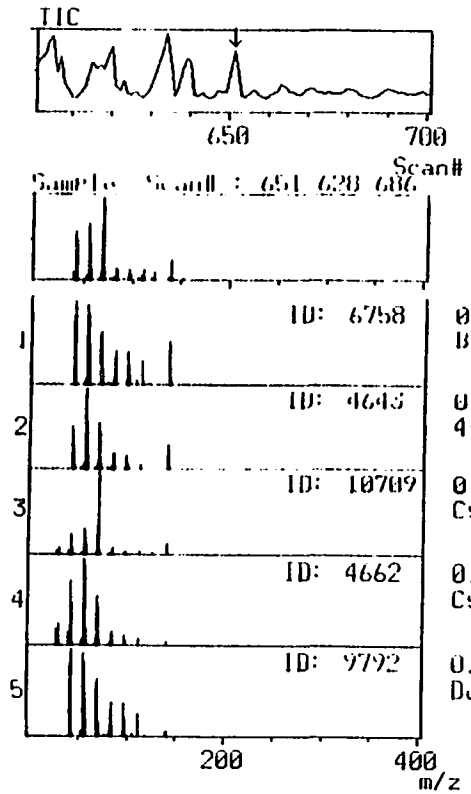


Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3



SIM.	MW	FORMULA	
0.463	138	C10H18	Cyclohexene, 1-methyl-3-(1-methylethyl)- (9CI)
0.362	138	C10H18	Cyclopentene, 1,4-dimethyl-5-(1-methylethyl)- (9
0.348	138	C10H18	Cyclopentane, (3-methylbutylidene)- (9CI)
0.324	138	C10H18	Bicyclo 2.2.1 heptane, 1,7,7-trimethyl- (9CI)
0.319	138	C10H18	Cyclohexane, 1-methyl-4-(1-methylethyl)-, didehy

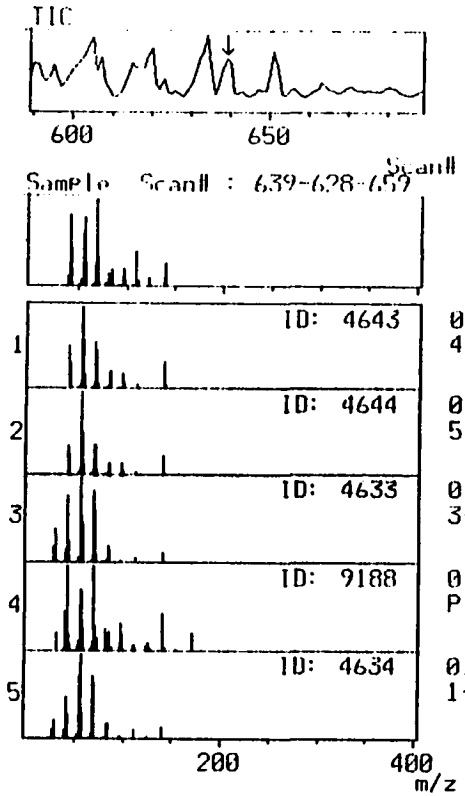
*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):



Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.668	154	C7H6O2S	Benzenecarbothioic acid, 2-hydroxy- (9CI) , S
0.652	140	C10H20	4-Decene (8CI9CI)
0.633	182	C13H26	Cyclobutane, 2-hexyl-1,1,4-trimethyl- (9CI)
0.621	140	C10H20	Cyclopropane, 1-ethyl-2-pentyl- (9CI)
0.616	176	C10H21Cl	Decane, 3-chloro- (8CI9CI) , 3-Chlorodecane

*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):

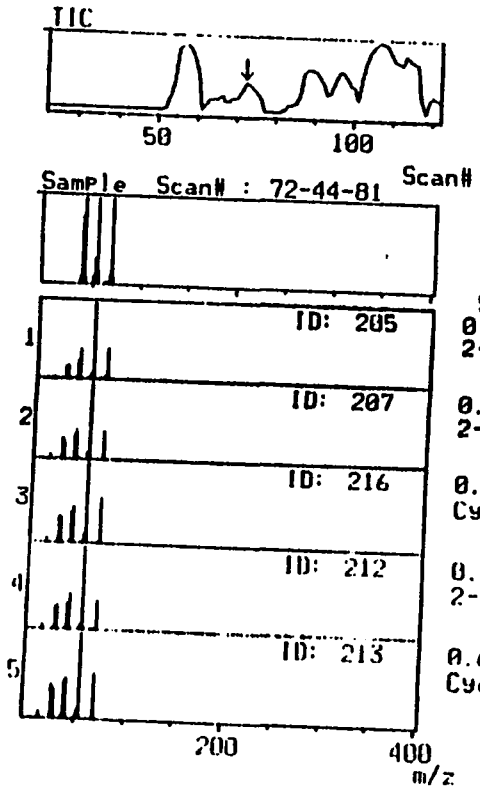


Library: LS0:[2,6]FULLIB.LIB
Data : SY0:OLD1.DAT
Sample : CAL-985, D1 OLEFINS C4-C14 INJ 0.5u
L IM=1.1, 100uA
Date : 19-FEB-95 14:3

SIM.	MW	FORMULA	
0.547	140	C10H20	4-Decene (8CI9CI)
0.530	140	C10H20	5-Decene (8CI9CI)
0.528	140	C10H20	3-Octene, 2,6-dimethyl- (8CI9CI) , 2,6-Dimethyl-
0.522	170	C9H18N2O	Piperidine, 2,2,6,6-tetramethyl-1-nitroso- (8CI9
0.515	140	C10H20	1-Octene, 2,6-dimethyl- (8CI9CI) , 2,6-Dimethyl-

*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):

Ni-ASA (C) at 300°C/2 h^{-1}WHSV/500 psi




```
Library:  LS0:[2,6]FULLIB.LIB
Data    :  SY0:OLC1.DAT
Sample  :  CAL-985, OLEFINS C4-C14 INJ 0.5uL I
           M=1.1, 100uA
Date    :  19-FEB-95  13:11

 SIM.    MW FORMULA
0.713    70 C5H10
2-Pentene (8C19C1)    , .beta.-n-Amylene , sym-Me

0.711    70 C5H10
2-Butene, 2-methyl- (8C19C1) , .beta.-Isoamylene

0.684    70 C5H10
Cyclopropane, 1,2-dimethyl-, trans- (8C19C1) , t

0.677    70 C5H10
2-Pentene, (E)- (8C19C1) , (E)-2-Pentene    , tr

0.674    70 C5H10
Cyclopropane, 1,2-dimethyl-, cis- (8C19C1)    , c

*(R:Param, N:Next data, O:Printer, C/R:Page, X:Exit):
```

TABLE A-8: Chemical Analysis of Ni-ASA (0.40wt % Ni) [ICP].

ANALYTE	CONCENTRATION (% wt/wt)
Al_2O_3	2.5
BaO	<0.1
CaO	0.1
K_2O	<0.1
MgO	0.1
Na_2O	<0.1
NiO	0.7
SiO_2	92.7
ZnO	<0.1
SiO_2/Al_2O_3	75.50

A-9: Thermal Analysis

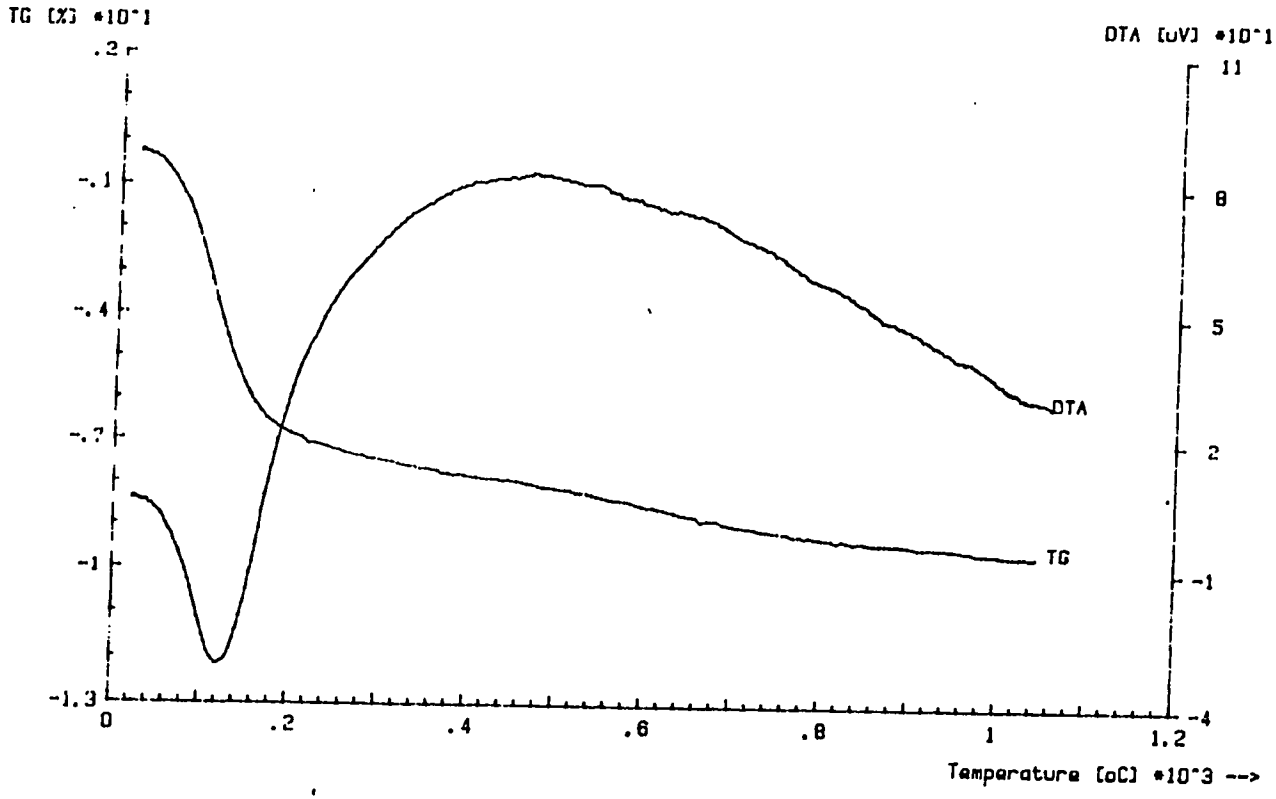


Figure A-9.1: Thermograms of Ni-ASA (C)

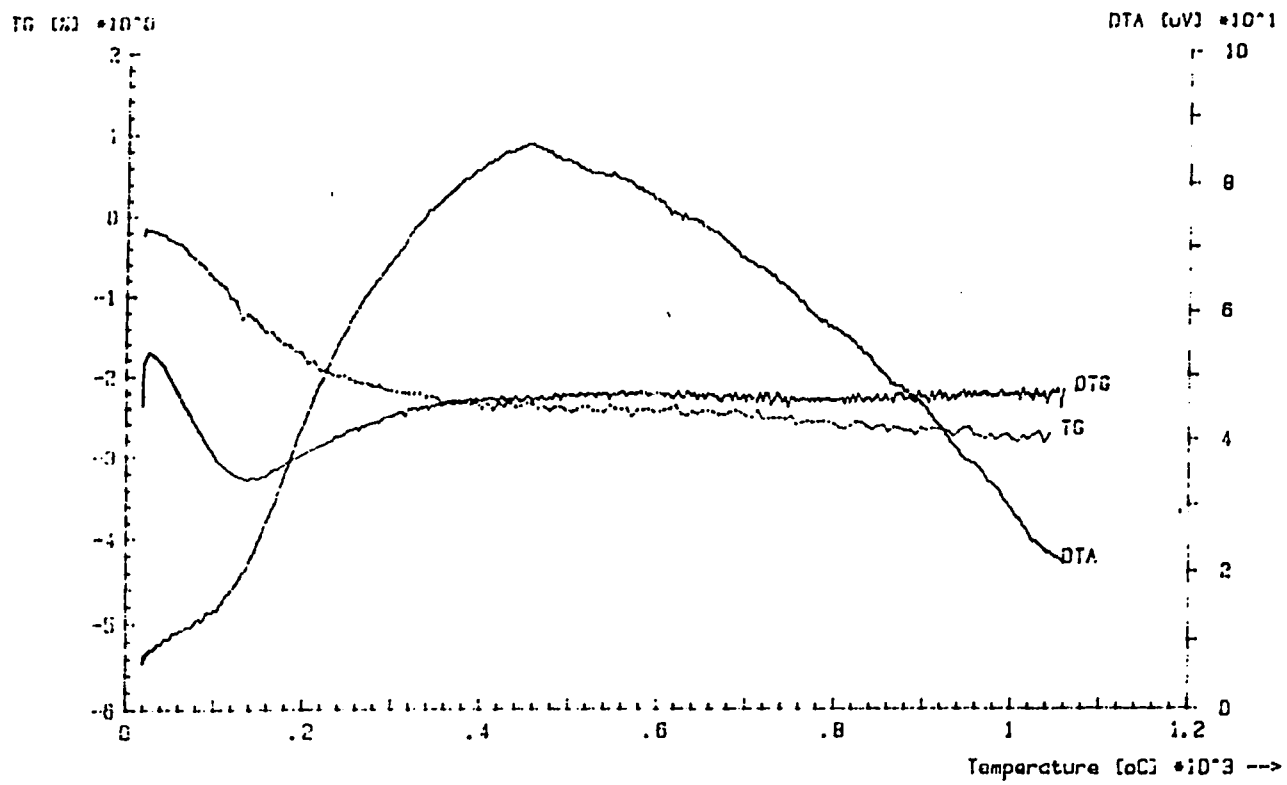


Figure A-9.2: Thermograms of Ni-SSA (D)

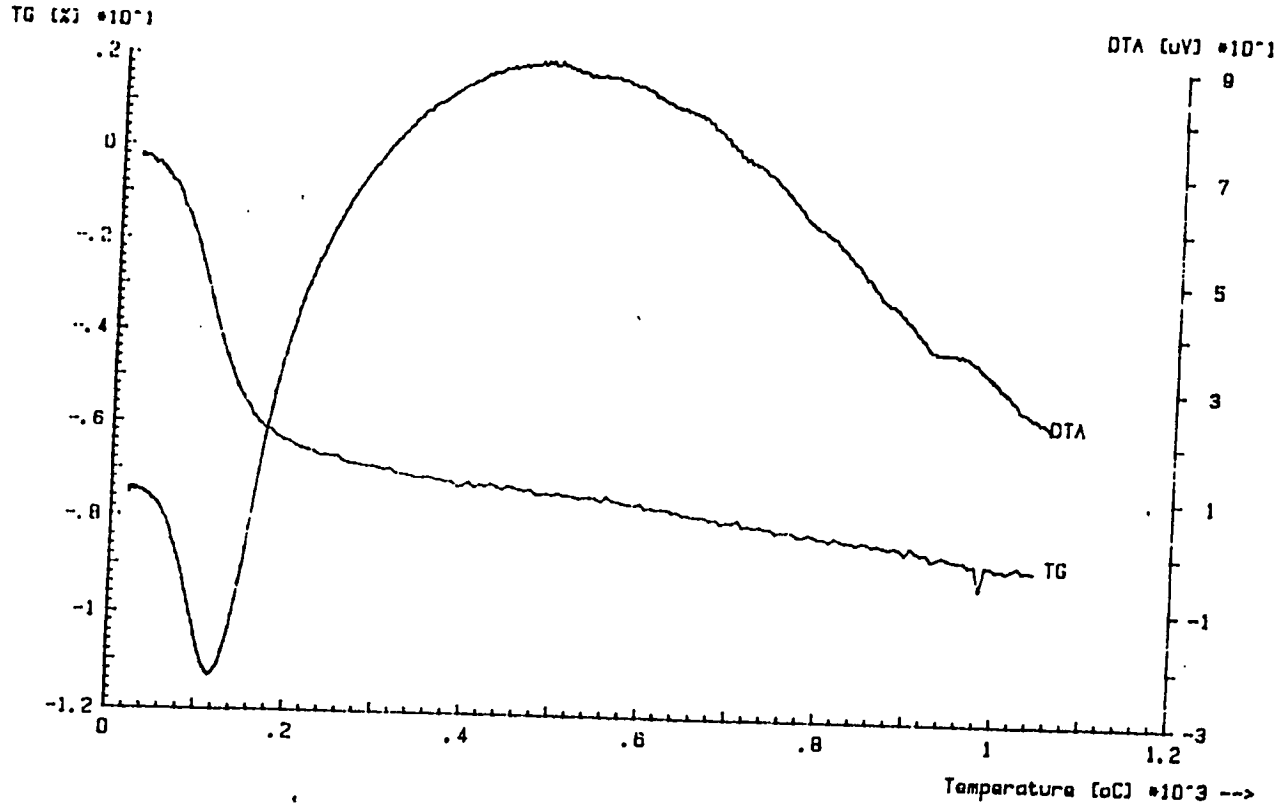


Figure A-9.3: Thermograms of Co/Ni-ASA (L)

TABLE A-10: Pore Size Distribution of the Supports.

SUPPORT	PORE SIZE DISTRIBUTION (A)			
	37-1000	1000-10000	10000-50000	>50000
Amorphous Silica-Alumina (ASA)	0	0	68.4	31.6
Sodium Silica-Alumina (SSA)	8.4	10.4	69.7	11.5

A-11: Calculation of Conversion, Products Yield and Butenes Distribution

Starting from mass balance

In = Out

Feed (ethylene) = Gas products + Liquid Products

The amount of feed is calculated from Gas law (68);

$$\mathbf{mass = n_1.P_2.V_2.T_1.Molarmass/(T_2.P_1.V_1)}$$

where,

P_1,V_1 and T_1 are at STP.

(n = mass/molar mass)

n_1=1

P_2 = Atmospheric pressure (where the measurement of flow rate was carried out)

T_2 = Temperature of the outlet gas (measured using thermometer)

V_2 = Volume of the gas (measured using a buble meter)

<u>Basis of Calculation: 1 hour</u>

Mass of Ethylene = 1x760x(0.029x60)x273x28/(298x760x22.4)

= 2.0g

Ethylene Flow (Space Velocity) is calculated using the relation (13);

$$\mathbf{WHSV = g_{ethylene}/(g_{catalyst}.\ hour)}$$

Ethylene flow = 2.0g of Ethylene/(1.0g of Catalyst loaded x 1 hour)

= 2 h^{-1} WHSV

Lets now carryout the calculations of conversions, products yield and mass balances by making use of the data from Ni-ASA(K) at 300°C, 2 h^{-1} WHSV and 500 psi after 4 hours time on stream. Using external standard method in the Gas Chromatogram the amount % of the gas products were determined. For $C4^{=}$ the amount % from $C4^{=}1$, $TC4^{=}2$ and $CC4^{=}2$ were added. For C4, IC4 and NC4 were added and for C5, IC5 and NC5 were added. Example, amount % of $C4^{=}$ = 33.1222% (The data is presented on page 145).

Gas flowrate was measured using bubble meter and an intelligent flow meter and it was found to be 2cc/min. Thus, the amount (mass) of say $C4^{=}$ in the gas product is calculated using the gas law as follows;

Mass of $C4^{=}$ = 1x760x(0.002x60x0.331222)x273x56/(296x760x22.4)

= 0.0916g

Similarly amounts for the other products were calculated.

For the liquid products the amount collected was first weighed it was found to be 1.5604g/hr. It was then injected into GC and the amount % of each product was determined. To get for example total $C6^{=}$, all the isomers of $C6^{=}$ as obtained from the GC-MS scanning and by comparison with the alpha-olefins standard ranges were added. The total amount % of $C6^{=}$ (sum-of for all the $C6^{=}$ isomers amount %) is multiplied by the liquid weight to get the actual mass of $C6^{=}$ product in the liquid product. $C4^{=}$ was also obtained in the liquid products (0.3507g/hr) and so total $C4^{=}$ is now 0.0916+0.3507 = 0.4423g/hr

Yield was then calculated as follows;

Yield = Mass of Gas Produced x 100/Feed Mass

Yield of $C4^{=}$ = 0.4423x100/2.0 = 22.1%

Calculated yields were then normalized by first summing of all the yields then using the following relation;

Normalized Yield = Yield/Total Yield

Normalized yield of $C4^{=}$ = 22.1/87.4 = 25.3%

Conversion was calculated as follows;

Conversion = 100 - Yield of Ethylene

Conversion = 100-4.3 = 95.7%

and **Product yield** was then calculated as follows;

Product Yield = Normalized Yield x 100 / Conversion

Product yield of $C4^{=}$ = 25.3x100/95.7

= 26.4%

For the mass balance;

Mass Balance = Products Total Mass x 100/Feed Mass

Mass Balance = (mass of gas products+mass of liquid products)x100/Feed mass

= (0.1882+1.5604)x100/2.0

= 87.4%

A computer program (**Fortran**) was written to carry out this task of calculating yield, mass balance, conversion and products yield. A sample result from the program is attached here.

Butenes Distribution

The three isomers of butenes in the gas products (butene-1, trans-2-butene and cis-2-butene) amounts are added to get the total amount of butene. From which each individual amount divided by the total gave its distribution.

```
*************************************************************
* SAMPLE RESULT: NI-ASA (K) AT 300'C, 2 WHSV AND 500 PSI    *
*************************************************************
```

GAS DISTRIBUTION

CARBON #	AMOUNT %	NORM-AMNT
C1	0.1610	0.1719
C2=	51.1000	54.5489
C2	9.2730	9.8989
C3=	0.4680	0.4996
C3	0.0000	0.0000
C4=	31.0280	33.1222
C4	1.3640	1.4561
C5	0.2834	0.3025
TOTAL	93.6774	100.0000

LIQUID DISTRIBUTION

CARBON #	AMOUNT %	NORM-AMNT
C4=	22.4695	22.4695
C5=	5.8886	5.8886
C6=	14.1624	14.1624
C7=	1.7373	1.7373
C8=	23.1322	23.1322
C9=	2.6958	2.6958
C10=	12.8125	12.8125
C11=	2.1104	2.1104
C12=	9.0933	9.0933
C13=	2.2754	2.2754
C14=	2.5108	2.5108
C15=	0.1918	0.1918
C16=	0.9199	0.9199
TOTAL	99.9998	100.0000

CARBON #	MASS	YIELD %	YLD-NORM	PRDCT YEILD %
C1	0.0001	0.0068	0.0078	0.0081
C2=	0.0755	3.7733	4.3158	0.0000
C2	0.0147	0.7336	0.8391	0.8770
C3=	0.0010	0.0518	0.0593	0.0620
C3	0.0000	0.0000	0.0000	0.0000
C4=	0.4423	22.1130	25.2922	26.4330
C4	0.0042	0.2086	0.2386	0.2494
C5=	0.0919	4.5943	5.2548	5.4918
C5	0.0011	0.0538	0.0615	0.0643
C6=	0.2210	11.0495	12.6381	13.2081
C7=	0.0271	1.3554	1.5503	1.6202
C8=	0.3610	18.0478	20.6425	21.5735
C9=	0.0421	2.1033	2.4057	2.5142
C10=	0.1999	9.9963	11.4335	11.9492
C11=	0.0329	1.6465	1.8833	1.9682
C12=	0.1419	7.0946	8.1146	8.4806
C13=	0.0355	1.7753	2.0305	2.1221
C14=	0.0392	1.9589	2.2406	2.3416
C15=	0.0030	0.1496	0.1712	0.1789
C16=	0.0144	0.7177	0.8209	0.8579
TOTAL	1.7486	87.4301	100.0000	100.0000

CONVERSION=95.68423
MASS BALANCE=87.43008

VITA

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Born: February 27, 1969.

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(iv) Interim Joint Matric. Board Cert. ***(IJMB)*** 'A' Levels, 1987, S.B.S, Zaria.