EXPERIMENTAL ANALYSIS OF 1-BUTENE ISOMERIZATION OVER NAFION^{TM} RESIN/SILICA NANOCOMPOSITE CATALYST

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Graduate College of the
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in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 2000

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ACKNOWLEDGMENTS

First of all, I am very thankful for the generous support from Conoco, Inc., the OSU Chemical Engineering Department, the OSU Graduate program, and the American Indian Science and Engineering Society to provide much needed resources to complete this work. I also wish to express my sincere appreciation to Dr. Martin S. High for his courtesy and patience while aiding and directing my graduate course work and research endeavors. Much thanks go also to Dr. D. Alan Tree, Dr. Karen High, Dr. Arland (AJ) Johannes, Dr. Jan Wagner, Charles Baker and the rest of the Chemical Engineering faculty and staff for their forbearance and tutelage. I also wish to thank Prakash Karpe and Doug Jack of Conoco, Inc. for providing much needed direction.

I am also grateful to my siblings Frank, James, Marla, Eric, and my children Wilma Kaye and Tahlee Karl for their support, love and encouragement. I also want to thank Prashanth Navuduri, David Echo Hawk and Rev. Ted Freeman for their helpfulness and companionship. Much praise also goes to Aunt Kat, Aunt Carole, Uncle Ray and Aunt Tinie, Aunt Ruth, Shelley, Jana, Robert, and Anita for their support in those early and latter years.

Finally I am most indebted to my mother and father for their fortitude, strength, endurance, and undying love for life. Being blessed with such parents encourages me to reach toward many formidable goals.

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NOMENCLATURE

Roman Letters

a, b, r	Reaction Coefficient
A_i	Area of analyte in a GC chromatogram
BTRS	Bench Top Reactor System
C_A	Concentration
C_{AO}	Initial Concentration
cc	Cubic centimeters
D_{AB}	Molecular Diffusion coefficient
D_L	Diffusion coefficient
D_p	Diameter of catalyst pellet
f/P	Fugacity coefficient
E	Energy of activation for a reaction
ECN	Effective carbon number
F_{AO}	Molar feed rate
G	Mass velocity per unit area
GC	Gas Chromatography
k	Reaction rate constant
K_a	Equilibrium concentration constant
$K_{f/P}$	Fugacity coefficient equilibrium constant
K_y	Gas composition equilibrium constant

L	Characteristic length
M	Mass of analyte in GC chromatography
M_A, M_B	Molecular weight of specie
MHSV	Mean Hour Space Velocity
n	Order of reaction
n_i	Number of moles
n_{io}	Initial number of moles
P	Pressure
p_{atm}	Absolute pressure
P_c	Critical pressure
P_c'	Combined critical pressure of a mixture
Pe	Peclet number
PID	Proportional, integral, differential controll
PLC	Programmable Logic Controller
r	Rate of reaction
r'	Rate of reaction per unit mass
r_a'	Rate of reaction per unit mass for plug flow model equation
R	Gas Constant
Re	Reynolds number
RF_i	Response factor for an analyte in a GC chromatogram
RTD	Resistance Temperature Detectors

Sc	Schmidt number
t_r	Retention time of an analyte in GC analysis
t'_r	Adjusted retention time in GC analysis
T	Temperature
T_c	Critical temperature
T_c'	Combined critical temperature of a mixture
u	superficial fluid velocity
U	Interstitial gas velocity
V	Volume of Reactor (Total)
W	Mass of Catalyst
Wt%	Weight percent
X_A	Conversion of reactant
y	Mass fraction of a component in a mixture
Z	Active catalyst surface site

Greek Letters

ΔG^o	Change of Gibb's free energy for reaction
ΔH^o	Change of Enthalpy for reaction
Ω_D	Emperical Lennard-Jones collision integral constant
ε	Porosity of catalyst pellet
$\in_{AB}$	Combined energy of molecular interaction of a binary system
η	Reaction effectiveness factor
κ	Boltzmann constant
ρ	Density of fluid
ρ_b	Bulk density of catalyst
ρ^*_{mol}	Molar density
μ	Viscosity of fluid
μ_c	Critical viscosity of fluid (at the fluid critical point)
μ_c'	Combined critical viscosity of fluid for a mixture
ν	Stoichiometric coefficient
σ_{AB}	"Collision integral" for molecular diffusion
τ	Weight time of catalyst pellet
ξ_k	Extent of reaction

CHAPTER 1 - INTRODUCTION

This thesis reports on an investigation of heterogeneous catalytic isomerization of 1-butene over Nafion™ supported on silica using a small-scale, continuous flow, tubular reactor. Since the reaction under study, 1-butene isomerization, is currently widely used in the petrochemical industry, and since increased operational and safety concerns are apparent with current practice, this system was identified by Conoco and Oklahoma State University as an important system to review [Sun 1995].

In general, refiners consider gasoline as the major product from crude oil. After crude distillation, liquid petroleum gas and isobutane are fed to a fixed-bed reactor where an alkylation reaction occurs combining the olefin and isoparaffin into a constituent with a higher octane number. Preceding this alkylation step, 1-butene is converted to 2-butene [Scherzer and Gruia, 1996]. This secondary olefin and isoparaffin combination gives a product with a higher octane number than its primary olefin and isoparaffin counterpart [UOP 1997].

Currently, homogeneous H_2SO_4 or HF mineral acids have been used to catalyze 1-butene to 2-butene isomerization. Although this type of reaction system is efficient in converting 1-butene to *cis*- and *trans*-2-butene, effluent products are usually chemically reactive and highly corrosive [Harmer *et al.*, 2000]. Using a solid substance such as Nafion™ resin/silica nanocomposite as a catalyst to convert 1-butene to 2-butene is beneficial since the solid substance is easier to handle, purification is simpler and cheaper, and the general operation of a large chemical process is safer [Harmer *et al.*, 2000].

The use of unsupported Nafion™ as a catalyst for various reactions produced low conversions since the reaction occurred on the resin outer surface only [Sun *et al.*, 1996; Waller and Van Scoyoc, 1987]. The supported composite catalyst, Nafion™ resin/silica nanocomposite, provides additional intraparticle surface area (by many orders of magnitude over the homogeneous Nafion™ resin homologue) by increasing pore radius [Harmer *et al.*, 2000].

This effort determined the conversion of 1-butene isomerization over Nafion™ SAC 25 catalyst (a silica composite catalyst with a 25 weight percent Nafion™ acidic resin concentration) and compared the conversion to results previously reported [Sun *et al.*, 1996]. Sun *et al.* (1996) reported a conversion of 1-butene over Nafion™ SAC 13 (a silica composite with a 13 weight percent Nafion™ acidic resin concentration) to near equilibrium concentration at low temperature and ambient pressure.

This work differs from these other efforts [Harmer *et al.*, 1998; Sun *et al.*, 1996] by investigating this system at different temperatures and the degree of catalyst loading. Also different system conditions were explored and operating conditions were identified (e.g. temperature, pressure, and catalyst loading) where an effective rate constant could be determined. Selected dimensionless groups were calculated for various system conditions; findings and general comments were compared and reviewed.

The test apparatus consisted of a gas and liquid feed preparation system, a continuous tubular flow reactor (Autoclave Engineers, Inc. Bench Top Reactor System), and a gas chromatographic system for analysis (Hewlett-Packard HP-6890 Gas Chromatograph). The GC system was equipped with a capillary column; detection of products was accomplished with a flame ionization detector. A capillary column with methylsiloxane as the stationary phase, ideal for analyzing petroleum fractions, was used.

System temperature, pressure, flow rate, and catalyst loading for this effort were similar to another study [Sun *et al.*, 1996]. This effort differed, however, with the amount of catalyst loaded into the reactor and the technique used to pre-treat the catalyst. The catalyst was pretreated *in situ* at 230°C and ambient pressure with approximately 150 sccm of standard grade helium charged over it overnight to dry it.

A discussion of the history, production and use of the supported composite, reaction conditions, parameters and mechanisms proposed by various researchers for 1-butene isomerization reactions over different catalysts are included in Chapter 2. A detailed discussion of the apparatus and the operating procedure is included in Chapter 3. A discussion of the results developed in this work is included in chapter 4. Finally a discussion of the conclusions and recommendations for the use of this system is included in Chapter 5.

CHAPTER 2 - PREVIOUS STUDIES

This chapter reviews the fundamental concepts of olefin isomerization, particularly as it applies to the initial steps of alkylation, or joining a β olefin with an isoalkane, to produce an alkylate with a higher octane number. The historical use of homogeneous catalysts for conversion will be reviewed. The use of a solid superacidic catalyst will be reviewed emphasizing its use as an alternative to current practice. Kinetic parameters, reactor apparatus considerations, and reactor performance equations will be reviewed. Finally, open tubular gas chromatography as it applies to this effort will be reviewed.

2.1 DEVELOPING THE 1-BUTENE ISOMERIZATION PROCESS

In the latter nineteenth century petroleum crude products were introduced into the common marketplace by the demand for kerosene for lamp oil [UOP 1997]. Crude oil products were batch distilled to obtain the kerosene [UOP 1997]. After the emergence of the automobile, gasoline became the primary product of crude [UOP 1997]. Continuous distilling operations were essentially developed to remove the gasoline fraction from the crude [UOP 1997]. Currently gasoline is still the major component of crude refining operations, consisting of approximately 50% of the crude oil processed [Satterfield 1980].

Product gasoline has three principle requirements as outlined previously [Satterfield 1980]. These are:

1. Gasoline must have a suitable volatility range. Some portion of the gasoline mixture must be volatile enough to flame ignite in the combustion chamber of an automobile engine. Yet the major portion must not be volatile to reduce the likelihood of pre-ignition or cause vapor lock in major component parts such as the fuel pump or the carburetor of an automobile.
2. Gasoline should have low viscosity. Mixtures with lower viscosity can reduce flow drag and pressure buildup in the transfer lines and the carburetor of an automobile.
3. Gasoline with a higher octane number is preferred. Fuels with a higher-octane number increase the performance of an internal combustion engine.

Essentially the octane number is a quantified parameter that compares the knocking characteristics of given mixture with the mixture containing 2,2,4-trimethylpentane and *n*-heptane [Satterfield 1980]. Knocking is the excessive rate of pressure increase caused by an unburned mixture compressing and self igniting before being ignited by a flame [Satterfield 1980]. 2,2,4-Trimethylpentane is assigned an octane number of 100; *n*-heptane is assigned octane number of 0 [Olah and Molnár, 1995]. A mixture with an octane number of 90 is commensurate with a mixture containing ninety parts 2,2,4-trimethylpentane with ten parts *n*-heptane [Olah and Molnár, 1995]. Methods used to determine the octane number of a mixture are the research method (F-1) and the motor method (F-2) and are outlined elsewhere [Satterfield 1980].

The gasoline fraction separated from the distillation process has an octane number of approximately 50 [Olah and Molnár, 1995]. Reforming reactions increases the octane number of gasoline by increasing the composition of branched alkanes, olefins, and aromatics [UOP 1997]. Crude oil contains no olefins and acetylenes [Scherzer and Gruia, 1996]. Olefins are primarily developed by thermal and catalytic cracking operations [Olah and Molnár, 1995]. Light ends, or liquid petroleum gas, which are separated in the distillation process consist mainly of propane and butanes [Olah and Molnár, 1995],

To boost the gasoline fraction in the crude product, researchers developed the alkylation process in the early 1930's when it was found that light olefins could combine with certain isoparaffins using boron trifluoride promoted with water or hydrogen fluoride [UOP 1997]. Moreover, some alkyl products also increased the octane number of gasoline mixtures. This alkylation process utilizes olefins from cracking effluent streams and isoparaffins (derived from skeletal isomerization of lower boiling normal alkanes from distillation) to develop an isoparaffin with a higher octane number [Olah and Molnár, 1995]. Alkylation using both 1- and 2- butene gives high yields of octanes with differing compositions [Olah and Molnár, 1995]. Hydrogen fluoride catalyzes 1-butene with isobutane to give dimethylhexane with an octane number ranging from 55-75; 2-butene combined with isobutane with the same catalyst produces 2,2,4-trimethylpentane (isooctane) which has an octane number of 100 [Olah and Molnár, 1995].

The butene concentration sent to the alkylation process usually contains 66% 2-butene with 34% 1-butene [Sun 1995]. It is advantageous to convert 1-butene to 2-butene to increase the concentration of higher octane 2,2,4-trimethylpentane. Hence refiners can realize a $0.25 per barrel per octane number increase in product gasoline [Sun 1995].

The aromatic concentration can also increase the octane number of refined gasoline [Satterfield 1980]. Benzene, toluene, and xylene are major aromatic compounds that increase the octane number in a gasoline mixture since these alone have an octane number over 100 [Satterfield 1980]. Recently, however, these aromatic compounds have proven to be carcinogenic [Satterfield 1980]. The maximum concentration of toluene in a gasoline mixture is 2%; the maximum concentration of all aromatics is 35% [Satterfield 1980]. With current environmental regulations, the aromatic concentration in gasoline is likely to decrease prompting refiners to increase the octane number of gasoline by increasing the composition of isoparaffins.

2.2 REACTOR ENGINEERING CONSIDERATIONS

For general reactor studies and designs, practitioners need to understand the physical condition of the reactor including the kinetics, the contacting pattern, and the performance equation of the system [Levenspiel 1996]. If sufficient mixing and isothermal conditions exist, intrinsic kinetics can be measured from experimental data [Hill 1977; Levenspiel 1996]. With positive reaction orders tubular reactors can treat larger volumes of reactant compared to the continuous stirred-tank counterpart [Levenspiel 1972]. Continuous flow reactors are ideal if the reaction rate constant is not too large [Levenspiel 1996].

For an ideal plug flow reactor, plugs of fluid traverse axially through the reactor eventually leaving at a set time [Hill 1977]. These plugs have ideal concentration profiles (i.e. all elements within in the plug have the same radial and axial concentration). These plugs are also considered isothermal [Hill 1977]. Consequently the concentration changes with distance from the entrance of the reactor. The fluid exhibits minimal longitudinal mixing as it traverses axially through the reactor [Hill 1977]. Hence all fluid elements within each plug traverse the reactor at the same time [Hill 1977].

Variations or gradients within these plugs can occur if the reactant fluid experiences diffusion and turbulent mixing [Hill 1977]. These gradients are increased by the degree of molecular and eddy diffusion and by radial temperature gradients caused by conductive and convective heat transfer [Hill 1977]. Intraparticle temperature and concentration gradients can affect the conversion in a tubular reactor [Hill 1977; Levenspiel 1972].

Studies in catalytic deactivation have been conducted by many researchers involving olefin isomerization [Clark and Subramaniam, 1999; Garcia-Ochoa and Santos, 1995]. Some researchers have found that impurities within the feed may contribute to the deactivation of the catalyst by coking [Clark and Subramaniam, 1999]. Efforts proposed previously to remove these impurities have a substantial effect on catalytic stability and longevity [Clark and Subramaniam, 1999].

An effort to model the deactivation process of heterogeneously catalyzed butene isomerization has been reported [García-Ocha and Santos, 1995]. The model assumes that a concentration of products developed by olefin polymerization is later cracked and is responsible for coking [García-Ocha and Santos, 1995]. This polymeric reaction promotes catalyst deactivation for reactions involving olefins [García-Ocha and Santos, 1995].

2.3 HETEROGENEOUS BUTENE ISOMERIZATION

The Nafion™ resin/silica nanocomposite for 1-butene isomerization to *cis*- and *trans*-2-butene is an important system under current review [Harmer *et at.*, 1996; Sun *et al.*, 1996]. This system has indicated excellent conversion, discussed below, and may support its use in industrial heterogeneous reaction applications. Current efforts to use the Nafion™ resin/silica nanocomposite for other reactions including alkylation, acylation, and benzylation reactions have been reported [Harmer *et al.*, 1996; Harmer *et al.*, 2000].

Currently, refiners carryout *n*-butene isomerization reactions with sulfuric or hydrofluoric acid in a homogeneous phase. Researchers have also surveyed butene isomerization catalyzed with a variety of homogeneous and heterogeneous catalysts. These include homogenous H_2SO_4 and HF acids, and heterogeneous catalysts including zeolites, supported metal catalysts, and more recently acid complexes on silica support composites [García-Ocha and Santos, 1995]. 1-Butene isomerization is also catalyzed using oxidized metal catalysts, metal supported catalysts, solid acids, bases, and transition metal hydrides, coordinated complexes such as halides, radical molecular salts, a number of semiconductors, and insulator solid oxides [Béres *et al.*, 1995; Hightower and Hall, 1967; Kalló and Preszler, 1968; Kondo *et al.*, 1998; Sun *et al.*, 1996].

Environmental concerns associated with increased costs in separation and disposal of homogeneously catalyzed products have relegated the petroleum industry to consider alternatives that ultimately lean toward heterogeneously catalyzed reactions [Sun *et al.*, 1996; Waller and Van Scoyoc, 1987]. The Nafion™ resin/silica nanocomposite, in the acid form, is easy to handle and doesn't require an excessive amount of protective equipment or handling operations [Sun *et al.*, 1996]. This fact makes the composite less cumbersome for operators to load or clean and dispose of catalytic residue [Sun *et al.*, 1996].

2.3.1 Proposed Butene Isomerization Mechanisms

Homogeneously catalyzed 1-butene isomerization to *cis*- and *trans*-2-butene has been proposed to proceed through a carbocationic intermediate step (Figure 2.1) initiated by a proton furnished by a catalyst [Olah and Molnár, 1995]. In its elemental form, 1-butene converts to a secondary olefin primarily by hyperconjugation, a resonance form of the intermediate alkene structure [Reid 1968]. The overall energy of the molecule is relaxed which ultimately leads toward conversion to a secondary olefin if the transition energy is reached [Reid 1968]. This secondary olefin is more stable energetically than its primary counterpart which ultimately leads to a mixture with a higher ratio of secondary to primary olefins [Kalló and Preszler, 1968].

For heterogeneously catalyzed olefin isomerization, the selectivity can be affected by the choice of catalyst used since numerous mechanisms exist depending on the nature of the catalyst and the geometry of the olefin [Hightower and Hall, 1968]. Several mechanisms focusing on a surface intermediate structure have been proposed by various researchers [Béres *et al.*, 1995; Boronat *et al.*, 1996; Kondo *et al.*, 1998; Santos and García-Ocha, 1994; Uematsu 1972]. The intermediate structure ultimately leans toward an established secondary carbonium ion structure attached to the catalyst active site.

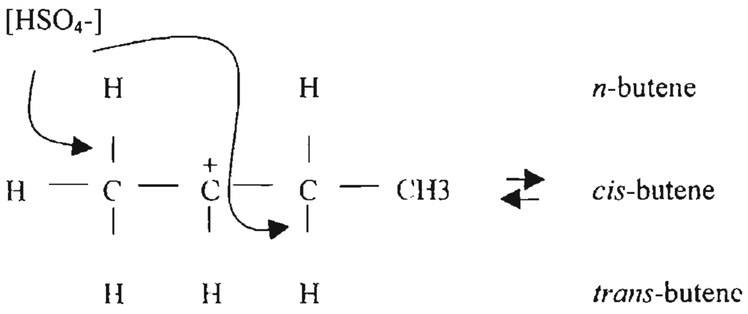


Figure 2.1 The Removal of a Secondary Hydrogen by H_2SO_4 to Produce Secondary Butenes Via Homogeneous Reaction with H_2SO_4 [Reid 1968].

Since heterogeneous catalytic reactions tend to form ionic and metallic bonds and not covalent bonds [Satterfield 1980], the system produces a carbocationic structure that is inherently stable. Similar studies using Amberlyst catalyst (an SO_3H activated acid, ion-exchange resin made from divinylbenzene and polystyrene) to catalyze 1-butene to secondary butenes, where the main acidic functional group is a sulfonyl acid, have claimed a similar mechanism [Kalló and Preszler, 1968; Uematsu 1972]. 1-butene isomerization to 2-butene using Amberlyst 15 as a catalyst has an activation energy of 16 kcal/mol [Kalló and Preszler, 1968].

With increased acidity, however, the carbocationic structure tends toward skeletal rearrangement [Satterfield 1980]. Rearrangement occurs namely with a radical intermediate and a methyl and hydride transfer which is characteristic of a dual function catalyst (i.e. both metal and acidic sites present on the catalyst surface) such as zeolites and hydrated metals on alumina [Scherzer and Gruia, 1996; Olah and Molnár, 1995].

The energy of formation of the intermediate structure indicates which step in the reactant-to-product sequence will be rate limiting [Satterfield 1980; Levenspiel 1972]. The rate will be limited by the development of the intermediate structure if the energy of formation of the intermediate is low where the affinity between the surface site and the reactant is weak [Satterfield 1980]. The rate will be limited by the breakup of the intermediate structure if the energy of formation is high where the affinity between the intermediate and the surface site is stable [Satterfield 1980]. The rate-limiting step is the reaction pathway that consumes essentially all of the driving force, or the chemical potential, available in a specific system [Satterfield 1980].

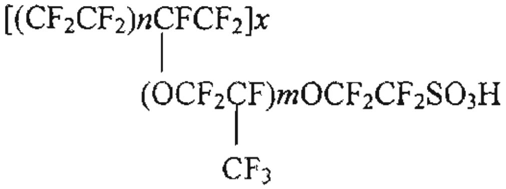
2.3.2 Nafion™ Resin/Silica Composite Catalyst

Nafion™ in its pure form can convert primary olefins to secondary olefins [Waller and Van Scoyoc, 1987]. Requisite conversions, however, proved to be restricted do to limited surface area available for adsorption and subsequent reaction [Sun *et al.*, 1996]. Researchers have proposed that only the outer surface provided acid sites for 1-butene adsorption and reaction and intraparticle diffusion proved to be low; the reactant did not swell the Nafion™ resin [Sun *et al.,* 1996].

The attractive feature for using the Nafion™ resin/silica nanocomposite is the polyperfluoroethene structure which attributes electron withdrawing ability to the attached sulfonyl group and to the increased surface area for reaction, compared to the unsupported Nafion™ resin homologue [Harmer *et al.*, 1996; Harmer *et al.*, 2000]. This feature, together with its dramatic increase in reaction surface area, attributes increased activity for olefin isomerization.

This Nafion™ nanocomposite material supported on silica is developed using sol-gel chemistry. Developers have claimed that the general makeup of this superacid composite can be altered to suit the need of the user. Thus the composite can be altered by varying the micelle concentration, varying the active surface area, altering the pore radius, establishing a concentration gradient within the particle, and varying the homogeneity of the composite [Harmer *et al.*, 1996].

The functional group of the Nafion™ resin/silica nanocomposite is a superacidic micelle (sulfonyl acidic groups) which have a terminal $-CF_2CF_2SO_3H$ group [Harmer *et al.*, 1996]. This polyperfluoroethyl group gives this acid micelle additional ordered structure and durability [Waller and Van Scoyoc, 1987; Harmer *et al.*, 1996; Harmer *et al.*, 2000]. The general structure is:



$$[(CF_2CF_2)_n\underset{\substack{|\\ (OCF_2\underset{\substack{|\\ CF_3}}{C}F)_mOCF_2CF_2SO_3H}}{C}FCF_2]_x$$

Figure 2.2 General Structure of a Pure Nafion™ Micelle.

Here m=1, 2 or 3; n is typically 6-7, and x is about 1000 [Waller and Van Scoyoc, 1987]. This resin has a Hammett acidity of about 12, which is similar to strong acids such as sulfuric acid [Waller and Van Scoyoc, 1987].

The Hammett acidity expresses the acid strength of a solid by determining its ability to change a neutral organic base into its conjugate acid form [Satterfield 1980]. This process may occur by the transfer of a proton from a Brönsted acid site to the adsorbed base, or by transfer of an electron pair from the adsorbed molecule to a Lewis acid site, thus forming an acidic addition product [Satterfield 1980].

The nanocomposite is developed as a copolymer from tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether. The "superacidity" of the terminal $CF_2CF_2SO_3H$ group can be attributed to the electron withdrawing ability of the attached fluoride ions, thereby rendering the terminal sulfonyl acid a greater ability to hydrogen bond with many constituents including Brönsted bases [Waller and Van Scoyoc, 1987].

The development of Nafion™ composite is described by Harmer *et al.*, 1996. It is developed from a basic Nafion™ solution, utilizing a sol-gel process where tetramethyl orthosilicate [$Si(MeO)_4$] or tetraethyl orthosilicate [$Si(EtO)_4$] are combined in a two-step acid/base hydrolysis and condensation process. The Nafion™ resin is combined with NaOH to form a basic solution. This alkoxy saline solution is combined with the Nafion™ basic solution until gelation occurs. This gel is then dried and processed to obtain a composite bead. The composite is then re-acidified and re-dried to yield a hard glass-like substance.

Dual porosity can be achieved by the addition of $CaCO_3$ in the Nafion™ basic solution as described above [Harmer *et al.*, 1996]. Following gelation, the $CaCO_3$ becomes entrapped within the composite structure [Harmer *et al.*, 1996]. After acidification, $CaCl_2$ and CO_2 are then removed, producing void layers of about 500 nm in the microstructure [Harmer *et al.*, 1996].

Varying the concentration of the Nafion™ basic solution also increases the pore diameter of the final composite [Harmer *et al.*, 1996]. At a higher pH, the Nafion™ solution (e.g. using 0.8 M NaOH solution instead of 0.4 M NaOH) tends to increase the pore diameter [Harmer *et al.*,1996]. In essence, readily altering and adjusting the pH of the gelation solution and adding $CaCO_3$ to the mixture increases the dual porosity of the composite and increases its accessible surface area [Harmer *et al.*, 1996].

The polyperfluoroethene group, affixed to the sulfonyl group, constitutes the substrates hydrophobic region [Harmer *et al.*, 1996]. The chemically resistant polymeric backbone [Waller and Van Scoyoc, 1987] can be attributed to the polyperfluoroethene structure, which is similar to Teflon™ and has a $F(CF_2)_nF$ chemical structure [Alliger 1976, Olah *et al.*, 1979]. The sulfonyl group tends to form interfacial zone exchange sites that have not been incorporated into the polymeric clusters [Sondheimer 1986].

2.3.3 Butene Isomerization with Nafion™ Resin/Silica Nanocomposite

Past efforts have shown that 1-butene isomerization approaches equilibrium concentration when catalyzed with Nafion™ resin/silica nanocomposite under mild operating conditions [Harmer *et al.*, 1996; Sun *et al.*, 1996]. If the reaction is said to follow the carbocationic intermediate, the reaction is considered to be a first-order, with parallel. competing, reversible reactions [Kalló and Preszler, 1968]. However, similar studies have shown that primary olefin isomerization over acidic alumina can be modeled using first-order irreversible kinetics [Clark and Subramaniam, 1999].

For reactions carried-out at elevated temperatures, the equilibrium concentration may increase the reactant concentration [Levenspiel 1972]. This shift in equilibrium is a thermodynamic phenomenon as opposed to a kinetic one since equilibrium is a function of temperature [Hill 1977]. For an exothermic reaction, the equilibrium constant reduces with increasing temperature [Hill 1977].

2.4 KINETIC VARIABLES

In the study of heterogeneously catalyzed 1-butene isomerization, several tools are available to model or mathematically show the approximate composition of products and the thermodynamic state for the system of a reactor. Thermodynamics gives two important pieces of information need to design reactors, the heat liberated or absorbed during reaction and the maximum possible extent of reaction [Levenspiel 1972]. Chemical kinetics is primarily interested in the factors that influence the rate of reaction where a rate is measured and explanations are proposed for the values found [Levenspiel 1972]. For design purposes, these kinetic values are measured to ensure that reacting equipment are designed properly on a technical scale [Levenspiel 1972].

This section outlines the methods to determine the volumetric flow rate for a given continuous tubular flow arrangement, methods to determine the extent of the reaction, the equilibrium concentration, and kinetic parameters for a continuous flow tubular reactor with heterogeneously catalyzed 1-butene isomerization.

2.4.1 Volumetric Flow Calculations

The volumetric flow rate of 1-butene and helium charged over a solid catalyst can be calculated by the following equation:

$$MHSV = \frac{\rho V}{W} \tag{2. 1}$$

Here ρ is the mass density of the feed, V is a characteristic volumetric flow rate of the fluid, and W is the dried weight of catalyst in the tubular reactor chamber [Hill 1977]. The liquid reactant can be mixed with an equivalent molar flow of helium for dilution. Helium carrier gas can be used to provide kinetic energy for desorption and diffusion [Hill 1977].

The ideal gas equation of state can be utilized to determine the diluent density as shown:

$$\rho = MW\left(\frac{P}{RT}\right) \tag{2. 2}$$

Here *MW* is the molecular weight of the diluent, *P* is the pressure of the reactor system in the reactor chamber in atmospheres, *R* is the universal gas constant, and *T* is the system temperature in Kelvin.

The following ideal gas relation can be used to improve the prediction at the temperature and pressure of the reacting vessel:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \tag{2.3}$$

The Benedict-Webb-Rubin (BWR) equation of state can be used to determine the vapor density of 1-butene since the reactor system temperature and pressure are close the 1-butene saturation zone (i.e. vapor zone) [Miller 1996]:

$$p_{atm} = A\rho^{\bullet}_{mol} + B{\rho^{\bullet}_{mol}}^{2} + C{\rho^{\bullet}_{mol}}^{3} + D{\rho^{\bullet}_{mol}}^{6} + E{\rho^{\bullet}_{mol}}^{3} + F{\rho^{\bullet}_{mol}}^{5} e^{-\gamma {\rho^{\bullet}_{mol}}^{2}} \tag{2.4}$$

Here p_{atm} is the pressure in atmospheres and ρ^{*}_{mol} is the molar density (mol/dm^3). The parameters for the BWR equation are given for a number of hydrocarbons [Miller 1996]. The BWR equation is ideal for predicting state variables for hydrocarbon mixtures in the vapor zone [Balzhiser *et al.*, 1972; Gasem 1999; Miller 1996]. With the predicted vapor density, the volumetric flow rate for 1-butene vapor can be estimated in the reaction chamber.

The mass hourly space velocity of 1-butene can thus be calculated using the liquid density and the liquid volumetric flow rate of 1-butene entering the reaction chamber (Equation 2.1).

2.4.2 Fractional Conversion

The molar fractional conversion of the reactant, as established by many kineticists and researchers in reactor design industry [Froment and Bischoff, 1979; Levenspiel 1972] is a measure of the progress of a reaction. Fractional conversion, for a constant volume first-order irreversible reaction system, is calculated in the following manner [Levenspiel 1996]:

$$X_A = 1 - \frac{C_A}{C_{A_o}} \qquad \textbf{(2.5)}$$

Since no change in moles is realized in butene isomerization, the fractional conversion of the system can be calculated by the above equation. Also changes in the system product species relative to other constituents in the system are calculated as follows:

$$X_A = 1 - \frac{n_i}{n_{io}} \qquad \textbf{(2.6)}$$

A side reaction of 1-butene is butene oligomerization [Garcia-Ochoa and Santos, 1995]. The volume of the system will change; here the fractional conversion is calculated in the following fashion [Hill 1977]:

$$X_A = \frac{n_{i_0} - n_i}{n_{i_0}} \tag{2.7}$$

Considering a specific reaction taking place, the extent of reaction of a particular constituent A_i is given by ξ, or for a combination of reactions, ξ_k (for the k^{th} reaction), and is shown below [Hill 1977]:

$$\xi_k = \frac{n_i - n_{i0}}{v_i} \tag{2.8}$$

This is the extent of reaction for a single reaction. If several reactions are occurring, the appropriate equation is [Hill 1977]:

$$n_i - n_{iO} = \sum_{k-1}^{k=R} v_{ki} \xi_k \tag{2.9}$$

Here the stoichiometric coefficient, v_i, is positive for products and negative for reactants.

2.4.3 Equilibrium Concentration

The equilibrium concentration of 1-butene isomerization has been calculated previously with results listed; at 50°C the product concentration is 4.1% 1-butene, 70.5% trans-2-butene, and 25.4% cis-2-butene [Sun *et al.*,1996]. However, the equilibrium concentration varies with temperature [Balzhizer *et al.*,1972] since, for a standard temperature, the standard Gibb's free energy is related to the equilibrium constant K_a:

$$-\Delta G^o = RT\ln K_a \tag{2.10}$$

A correction is introduced into the equilibrium constant as shown below [Balzhizer *et al.*, 1972]:

$$\frac{d}{dT}\left(\ln K_a\right) = \frac{\Delta H^o}{RT^2} \tag{2.11}$$

The equilibrium constant at the system temperature can be calculated as follows:

$$\ln\frac{(K_a)_{T_2}}{(K_a)_{T_1}} = \int_{T_1}^{T_2}\frac{\Delta H^o}{RT^2}dT \tag{2.12}$$

The change in ΔH^o can be approximated by a linear function of C_P with temperature [Balzhiser *et al.*, 1972]. In some systems one can assume the heat of formation to be constant [Hill 1977].

To correct variations for K_a in temperature, the following equation is warranted [Hill 1977]:

$$K_a = K_{f/p} K_y P^{\Sigma v} \tag{2.13}$$

This equation can be reduced to the following if pressure and concentration are combined:

$$K_a = K_{f/p} K_p \tag{2.14}$$

With a reaction bB + cC → sS + tT, the preceding equation for K_a can be better represent below:

$$K_a = \left(\frac{y_S^s y_T^t}{y_B^b y_C^c} \right) \left[\frac{\left(\frac{f}{P}\right)_S^s \left(\frac{f}{P}\right)_T^t}{\left(\frac{f}{P}\right)_B^b \left(\frac{f}{P}\right)_C^c} \right] P^{s+t-b-c} \tag{2.15}$$

Here K_p is the equilibrium constant considering mixture component partial pressures.

(f/P) is the fugacity coefficient for a pure component at the temperature and total pressure of the system [Hill 1977].

2.4.4 Determining Kinetic Parameters

Any reaction can be modeled in a pseudo-homogeneous fashion if certain conditions are met [Hill 1977, Levenspiel 1972]. The pseudo-homogenous model can be applied if the fluid within the differential volume element associated with a single catalyst pellet, or a group of pellets, can be characterized by bulk temperature, pressure, and composition, and that these quantities vary continuously with position in the reactor [Hill 1977]. The resultant equation measures these quantities as they differ in position throughout the reactor. An overall or global reaction rate equation must be given for a pseudo-homogeneous model [Hill 1977].

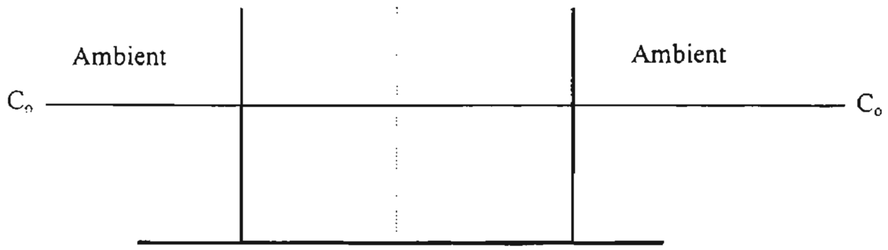
The global reaction rate must take into account both external heat and mass transfer effects on the reaction rate and the efficiency to which the internal surface area of a porous catalyst is used [Hill 1977]. The global reaction rate can be influenced by concentration and temperature differences between the bulk fluid and the external surface of the catalyst and by intraparticle temperature and composition gradients [Hill 1977]. In the absence of these gradients, these rate parameters, generated from experiment, can be considered intrinsic values [Levenspiel 1972]. As a general rule, the global rate reduces to an intrinsic expression evaluated utilizing bulk fluid properties when one of the chemical steps at the catalyst surface is slow [Hill 1977]. These influences can be visualized (Figure 2.3) by concentration versus characteristic length plots of a spherical catalyst pellet [Satterfield 1980].

For an axial dispersion model, a continuously feed, tubular reactor (ideal plug-flow analysis) can be applied to an experimental reactor if the temperature and concentration gradients are minimized. Conducting tubular reactor experiments on micro scale (bed volume = 2.5 – 25 mL) or bench-scale (bed volume = 60 – 700 mL) reactors, the apparent axial diffusion parameter, $\mathcal{D}_L$, can be superimposed on the plug-flow velocity to represent the extent of dispersion the reactant fluid deviates from plug flow [Hill 1977].

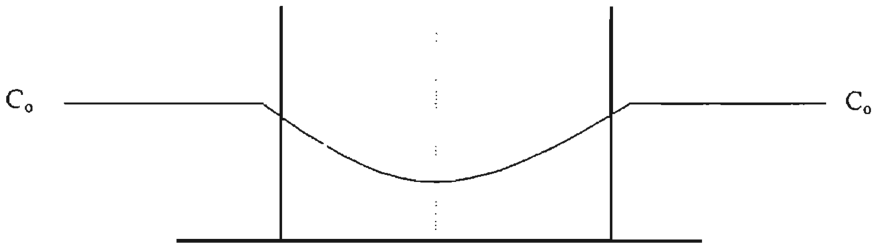
Ideally, the dimensionless parameter, $\mathcal{D}_L/uL$, can indicate whether the dispersion is close to perfect plug-flow ($\mathcal{D}_L/uL = 0$) or perfectly mixed flow ($\mathcal{D}_L/uL = \infty$) [Hill 1977; Levenspiel 1972]. The apparent axial dispersion parameter, $\mathcal{D}_L$, accounts for mixing both by molecular diffusion processes and by turbulence affected by eddies and vortices [Hill 1977; Levenspiel 1972]. These two flow characteristics have been incorporated into a single parameter; here we force the model to fit the form of Fick's law of diffusion. The resultant apparent axial dispersion parameter, $\mathcal{D}_L$, should then be regarded as an effective dispersion coefficient having the units of ordinary molecular diffusivity (length^2/time) [Hill 1977].

In another effort, researchers were able to fit this axial dispersion term into a dimensionless parameter for measuring the deviation from plug flow [Sie 1996]:

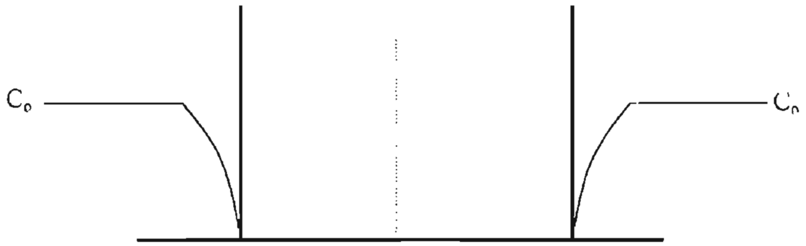
$$\text{Pé} = L * u / \mathcal{D}_L > 8 * n * \ln \{1 / (1-X_A)\} \qquad \textbf{(2.16)}$$



Low Temperature. Very slow reaction



Potential available to cause reaction in porous catalyst is less than C_o



Very Active catalyst. Reaction occurs at or near outside surface. Rate limited by mass transfer from ambient fluid to surface.

Figure 2.3 The Concentration Profile of a Spherical Catalyst Particle for Various Mass Transfer Limiting Situations (*from Satterfield 1980*).

Here L is the reactor length, u is the superficial fluid velocity, $\mathcal{D}_L$ is the apparent axial diffusivity, n is the reaction order and X_A is the fraction of reactant converted. The Péclet number, $P\acute{e}$, is a dimensionless parameter that indicates the ratio of bulk mass transport to diffusive mass transport within a fluid medium [Satterfield 1980]. In essence, the more a reacting fluid depends on bulk mass transport, the more a fluid will behave as a piston or plug flow through a tubular conduit. A Péclet number of at least 100 is optimal for plug flow analysis [Sie 1996].

The rate for a homogeneous first order reaction is equivalent to the heterogeneous counterpart by the following relation [Levenspiel 1996]:

$$rV = r'W \tag{2.17}$$

Here r' is the rate constant for a heterogeneously catalyzed reaction characteristic of packed-bed reactors and has dimensions of moles reacted per weight of catalyst per unit time (moles reacted/kg$_{(cat)}$ s) [Levenspiel 1996].

The following relation gives the performance equation for a plug-flow, tubular reactor [Levenspiel 1996]:

$$\frac{C_{Ao}W}{F_{A_0}} = C_{Ao} \int_0^{X_{Af}} \frac{dX_A}{-r'_a} \tag{2.18}$$

For the above performance equation, the weight-time for the reaction is given below [Levenspiel 1996]:

$$\tau' = \frac{\left(C_{A_0}\right)\left(W_{Catalyst}\right)}{\left(F_{0,reactant}\right)} \tag{2.19}$$

This olefin isomerization reaction proceeds in a first-order reversible fashion for all three butene isomers:

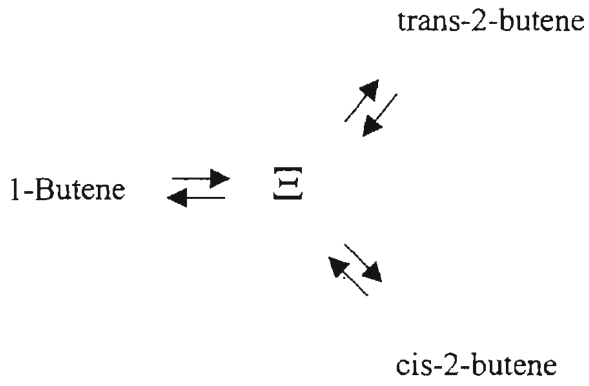


Figure 2.4 Reaction pathway for three butene isomers

Here Ξ signifies a surface intermediate structure. Both forward and reverse reactions are first-order. Hence the overall reaction consists of six (6) individual steps.

One study to characterize 1-butene isomerization over a $CoO\text{-}MoO_3/Al_2O_3$ proposes the following reactions taking place listed in Table 2.1 [Eliyas *et al.*, 1987]. For this system, steps 1, 2, and 3 are very fast reactions; steps 4 and 5 are rate limiting [Eliyas *et al.*, 1987]. The overall rate constant for the *cis-* isomer is based on the kinetic control product while the *trans-* isomer step (Step I) is the thermodynamic control step (Step II);

1. $1\text{-}C_4H_8 + Z \leftrightarrow Z1\text{-}C_4H_8$ Z, Z1 = active surface site

2. $cis\text{-}2\text{-}C_4H_8 + Z \leftrightarrow Zcis\text{-}2\text{-}C_4H_8$

3. $trans\text{-}2\text{-}C_4H_8 + Z \leftrightarrow Ztrans\text{-}2\text{-}C_4H_8$

4. $Z1\text{-}C_4H_8 \leftrightarrow Zcis\text{-}2\text{-}C_4H_8$

5. $Z1\text{-}C_4H_8 \leftrightarrow Ztrans\text{-}2\text{-}C_4H_8$

I. $1\text{-}C_4H_8 \leftrightarrow cis\text{-}2\text{-}C_4H_8$

II. $1\text{-}C_4H_8 \leftrightarrow trans\text{-}2\text{-}C_4H_8$

Table 2.1 Fast Elementary Reaction Steps (1, 2, and 3) and Slow Intermediate Steps (4 and 5) for the Overall Reaction of 1-Butene Isomerization (*from Eliyas et al., 1987*).

equilibrium concentration of the three isomers is assumed to be adsorbed to active sites on the surface of the catalyst [Eliyas *et al.*, 1987]. Other efforts have concluded similarly complex mechanisms [Hightower and Hall, 1967; Santos and García-Ocha, 1995].

Determining kinetic data for these single, separate reaction steps prove difficult. Usually, these data are extracted using a batch-type reactor. Various methods, including first-order reaction networks with special linear combinations or eigenvector transformations of rate parameters using matrix algebra, are used to determine these kinetic parameters [Froment and Bischoff, 1979].

A similar study, using an effective first-order reaction for 1-hexene isomerization, has been completed [Clark and Subramaniam, 1999]. In this study, where the system was operated at near critical temperature and pressure, product oligomer concentration was less than 0.1% by weight. Here the intrinsic kinetics involve only the isomerization step [Clark and Subramaniam, 1999].

The proposed equation, for estimating the effective reaction rate constant, ηk, using the plug-flow reactor equation, is as follows [Clark and Subramaniam, 1999]:

$$\eta k = -\left\{ \ln\left(\frac{X_e}{X_o}\right) \right\} \left(\frac{v}{W}\right) \rho_b \tag{2.20}$$

Here X_e represents the gas chromatograph (GC) area fraction of the cis- and trans-hexene isomers in the reactor effluent, X_o represents the GC area fraction of 1-hexene in the feed stream, v is the volumetric sweep rate in the catalyst bed, and W is the weight of the catalyst. In essence, Clark and Subramaniam (1999) assumed an equivalent response factor for each isomer detected by the flame ionization detector. Hence, the response factor for all isomers, either on a mass or molar basis, were identical and the above mass-to-area ratio in the logarithmic term can be assumed [Clark and Subramaniam, 1999].

The energy of activation can be calculated using the following analysis [Hill 1977]:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \tag{2.21}$$

Here E is the activation energy for the reaction, R is the gas constant, and T is the absolute temperature. If E is temperature invariant, a plot of *ln k* versus $1/T$ will give a slope equivalent to $-(E/R)$ [Hill 1977].

2.5 REACTOR PERFORMANCE EVALUATION

Several empirical relations exist that can aid reactor designers to evaluate the reactor performance. Several of these have been outlined previously [Sie 1996] which utilize the dimensionless Péclet number, *Pe*, to compare convective to molecular transport effects in a traversing fluid. The Péclet number is the ratio of the bulk mass transport to the diffusive mass transport and is given by the following relation [Satterfield 1980]:

$$Pe = \frac{LU}{D} \tag{2.22}$$

Here L is the characteristic length, U is the superficial velocity and D is the diffusive parameter. This Péclet number can depict various fluid characteristics that depend on the chosen characteristic length and the magnitude of the diffusive parameter [Bird *et al.*, 1960].

This diffusive parameter, D, is ideally computed from residence time distribution (RTD) tracer curves using second order partial differential equations and thermodynamically predicted physical constants [Gunn 1987]. The RTD approach is widely used in non-ideal reactor modeling and can be easily found in advanced modeling or reactor design books.

In the absence of experimental data, these effective axial and radial diffusive parameters can be estimated using reactor, catalyst, fluid, and other properties [Gunn 1987]. To determine the axial dispersion parameter, the parameters and coefficients of a dispersion model depend on physical properties of the fluid and solid in a manner that is consistent with the established laws of fluid mechanics [Gunn 1987]. An equation proposed previously utilizes the Reynolds and Schmidt numbers to determine the axial dispersion coefficient, D_L [Gunn 1987]:

$$D_L = UD_p\left[\frac{\mathrm{Re}\,Sc}{4(1-\varepsilon)}(1-p)^2 + \frac{\mathrm{Re}^2\,Sc^2}{16(1-\varepsilon)^2}p(1-p)^3 \times \left[\exp\left(\frac{-4(1-\varepsilon)}{p(1-p)\,\mathrm{Re}\,Sc}\right) - 1\right] + \frac{\varepsilon}{\tau\,\mathrm{Re}\,Sc}\right] \tag{2.23}$$

Here, U is the interstitial velocity within the bed, D_p is the particle diameter, Re is the Reynolds number, Sc is the Schmidt number, ε is the bulk porosity, and τ, for spherical pellets, is equivalent to 1.4. The Reynolds number, Re, is defined by the following relation:

$$\mathrm{Re} = \frac{D_p G}{\mu} \tag{2.24}$$

Here, D_p is the equivalent diameter of the catalyst particle, G is the mass velocity based on the total (superficial) cross sectional area of the reactor, and μ is the fluid viscosity.

The Schmidt number, Sc, is given by the following:

$$Sc = \frac{\mu}{\rho D_{AB}} \tag{2.25}$$

For the Schmidt number, ρ is the density of the fluid and D_{AB} is the molecular diffusivity of the species of interest being transferred in the system [Welty *et al.*, 1984].

The molecular diffusivity, D_{AB}, is presented by an equation for the diffusion coefficient for gas pairs of non-polar, non-reacting molecules [Welty *et al.*, 1984]:

$$D_{AB} = \frac{0.001858 T^{3/2}\left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2}}{P \sigma_{AB}{}^{2} \Omega_D} \tag{2.26}$$

Here, D_{AB} is the mass diffusivity of A through B, in cm^2/s; T is the absolute temperature, in K; M_A, M_B are the molecular weights of A and B, respectively; P is the absolute pressure, in atmospheres; σ_{AB} is the "collision integral" for molecular diffusion, a dimensionless function of the temperature and of the intermolecular potential-field for one molecule of A and one molecule of B [Welty *et al.*, 1984].

The collision parameter is given below:

$$\sigma = 2.44\left(\frac{T_c}{P_c}\right)^{1/3} \tag{2.27}$$

Here, T_c is the critical temperature of the fluid in K; P_c is the critical pressure of the fluid in atmospheres. For a combined (mixture) diffusion integral, the following relation is warranted [Welty *et al.*, 1984]:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{2.28}$$

Empirical Lennard-Jones collision integral constants, Ω_D, are given, in tabular format, for various $(\kappa T/\epsilon_{AB})$ values [Welty *et al.*, 1984]. Here, T is the absolute temperature, in K; κ is the Boltzmann constant. The combined energy of molecular interaction of a binary system, ϵ_{AB}, is given by the following relation [Welty *et al.*, 1984]:

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} \tag{2.29}$$

Here, the individual energies of molecular interaction, ϵ_A, is given by the following relation [Welty *et al.*, 1984]:

$$\epsilon_A / \kappa = 0.77 T_c \qquad \textbf{(2.30)}$$

To determine the Reynolds and Schmidt numbers of the traversing fluid, a method to determine the combined (mixture) absolute viscosity of the fluid is needed. If experimental data is lacking, an estimation of the viscosity using reduced temperature and pressure can be used to estimate this parameter [Bird *et al.*, 1960].

The reduced temperature and pressure, together with the determination of the critical viscosity of pure components, are given as follows [Bird *et al.*, 1960]:

$$T_r = T / T_c \qquad \textbf{(2.31)}$$

$$P_r = P / P_c \qquad \textbf{(2.32)}$$

$$\mu_c = 7.7 M^{1/2} p_c^{\,2/3} T_c^{\,-1/6} \qquad \textbf{(2.33)}$$

Here, T is the absolute temperature in K, P is the system pressure in atmospheres, and μ_c is the critical viscosity is in micropoises. Once the pure component reduced variables are obtained, the following relations are given to determine reduced-variables of the mixture:

$$p_c' = \sum_{i=1}^{n} x_i p_{ci} \qquad \textbf{(2.34)}$$

$$T_c' = \sum_{i=1}^{n} x_i T_{ci} \qquad \textbf{(2.35)}$$

$$\mu_c' = \sum_{i=1}^{n} x_i \mu_{ci} \qquad \textbf{(2.36)}$$

Here, p_c', T_c', and μ_c' are the reduced mixture critical pressure, temperature, and viscosity, respectively. A Watson-Uyehara graphical method is required to determine the reduced viscosity which is subsequently multiplied with the mixture critical viscosity to obtain the mixture viscosity, μ' [Bird *et al.*, 1960].

Empirical methods to determine the deviation from the plug flow model are outlined in a related study [Sie 1996]. For this effort, a plug flow model is assumed in all kinetic examinations using the ideal, integral plug flow equation (see Equation 2.18 and Equation 2.20). A qualitative assessment to determine the suitability of a plug flow model will be reviewed in Chapter 4.

2.6 OPEN TUBULAR COLUMN GAS CHROMATOGRAPHY

The main component of the GC system is the column [McNair and Miller, 1998]. The column is responsible for separating different fractions in a mixture [McNair and Miller, 1998]. The column is made of a stationary phase that serves as an adsorbate [McNair and Miller, 1998]. A carrier gas, usually helium, is passed over the stationary phase with the mixture. Stationary phases include components like polysiloxanes, polyethylene glycol, and fused silica [McNair and Miller, 1998]. Various salts, ion-exchanged onto the stationary phase, are also available [McNair and Miller, 1998].

Historically, gas chromatographic separations were conducted using packed columns made of stainless steel or glass [McNair and Miller, 1998]. With an insurgence in polymer engineering, capillary columns are generally the industry standard. Capillary columns makeup about 80% of the column market today [McNair and Miller, 1998].

Each component injected into a column has a relative volatility, which is a function of temperature [Grob 1995]. This relative volatility is a measure of each organic component in a mixture as it adsorbs and desorbs while traversing down the column [McNair and Miller, 1998]. Hence each component in a mixture has different adsorption and desorption properties that are influenced by temperature, diffusion and other thermodynamic properties of the mixture [McNair and Miller, 1998]. Underlying theory of gas chromatography has been detailed previously, with procedures to determine specific characteristics of a column and the analyte such as the partition coefficient, molecular diffusion, the number of theoretical plates, and column height [Grob 1995, McNair and Miller, 1998]. These, however, will not be reviewed in this work.

Injectors for capillary columns include cool on-column injectors, split-splitless injectors, and purged-packed injectors. The type of injector utilized for a particular elution method depends on the analysis of interest [McNair and Miller, 1998]. For pesticides, cool on-column injection is paramount since analytes are diluted in a solvent medium [Grob 1995]. GC methods for pesticide analysis require all the analyte to be measured instead of purging away most of the sample which is characteristic of split-

splitless injectors. For hydrocarbon fractions, either the split-splitless or purged-packed injector is preferred since the need to purge portions of a vaporous sample is required to ensure a homogeneous mixture going to the column and deter carbonaceous buildup inside the injector [McNair and Miller, 1998].

Several detectors are available for GC analysis. The flame ionization detector is a proven detector for analyzing hydrocarbon fractions [Grob 1995]. Flame ionization detectors are designed to incorporate a small hydrogen-air diffusion flame burning at the end of a jet, where introduced organic compounds are directed to the flame from the column [Grob 1995]. An electrically charged species is formed and amplified by an electrometer and sent to an analyzer [Grob 1995].

Gas chromatography has been used to analyze products of butene isomerization [Eliyas *et at.*, 1987; García-Ocha *et al.*, 1995; Guisnet *et al.*, 1999; Hightower and Hall, 1986; Kalló and Preszler, 1968; Santos and García-Ocha, 1995]. Researchers have used a plethora of column types and methods for analysis; all with varying results based on the type of analysis administered.

Open tubular gas chromatography offers a wide range of options for use in characterizing kinetic parameters for reaction conditions [Paryjczak 1986]. Usually these processes consider the column as the reaction vessel and mixture separator. The GC techniques used in adsorption and reaction studies are the elution technique, frontal analysis, elution-on-a-plateau technique, displacement technique, and the thermo-desorption technique [Paryjczak 1986]. More directly, GC analysis can be used to identify and quantify mixture components.

The retention time, t_R, is the time needed for a particular analyte to traverse the column and the detector [Grob 1995]. The retention volume (absolute), V_R, is the product of the retention time of the sample component and the volumetric flowrate of the carrier gas [Grob 1995]. The adjusted retention time, t_R', is the difference between the retention time, t_R, and the retention time needed for a non-adsorbing medium to traverse the column, $t_{R,non\ ads}$[Grob 1995]. Methane, CH_4, is used to determine $t_{R,non\ ads}$ for a flame ionization detector [Grob 1995; McNair and Miller, 1998].

An equation for the response factor of the measured current generated by the flame ionization detector is listed below [Grob 1995]:

$$A_i = RF * M_i \qquad \textbf{(2.37)}$$

The area of integration, generated by an integrating algorithm, of a particular analyte is proportional to the mass fraction of the analyte in the mixture, which is the response factor, RF_i [Grob 1995].

The response factor, RF_i, is sensitive to the amount of organic carbons contained in a particular analyte [Grob 1995]. Response factors previously determined by various researchers are available [Grob 1995; McNair and Miller, 1998].

The effective carbon number, ECN, of a particular analyte is the number of aliphatic carbons contained in the analyte. Hence propane has an effective carbon number of 3.0, but n-propanol has an ECN of 2.4, having three aliphatic carbons and one primary alcohol oxygen (-0.6) [Grob 1995].

Flame ionization detector does not respond to substances such as CO_2, He, O_2 and N_2 [McNair and Miller, 1998]. The flame ionization detector is very sensitive to organic carbon containing compounds but can be adversely affected by the presence of heteroatoms such as oxygen, sulfur, and halogens [Grob 1995].

The Kovats Retention Index (KRI) method uses a series of normal alkanes as a reference base to confirm the structure of the organic molecules generated in a chromatogram [Grob 1995]. To identify peaks, both the area of response and the relative retention time are used to determine KRI values [Grob 1995]:

$$I = 100n + \frac{100[\log t'_R(A)] - [\log t'_R(n)]}{[(\log t'_R(n) - (\log t'_R N)]} \tag{2.38}$$

Here the adjusted retention time of compound of interest, A, can be weighed between the adjusted retention time of the normal paraffin eluting previously, n, and subsequent, N, to the analyte of interest. The KRI method uses a series of normal alkanes as a reference base. The retention indices for normal alkanes are defined as 100 times the number of carbon atoms in the molecule [Grob 1995].

For our analysis, 1-butene will elute after propane but previous to *n*-butane, which has a Kovats Retention Index, I, of 300 and 400, respectively [Grob 1995]. Several other methods, including external and internal standardization techniques, are available to identify peaks.

CHAPTER 3 – APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used for this study was an AE Micro-Scale Bench Top Reactor System manufactured by Autoclave Engineers, Inc. (now a division of Snap-Tite, Inc.) which was a complete gas and liquid phase reaction system, designed to facilitate catalytic reaction studies. The apparatus was ideal for investigating 1-butene isomerization since reaction parameters such as temperature, pressure, and flow rates can be controlled easily. The reactor apparatus was housed within a temperature-controlled oven. The reactor and tubing was set up to provide a well-defined flow path for process fluids to prevent feed and product stream condensation.

The BTRS system was located in the Advanced Technology Research Center (ATRC) at the Oklahoma State University Stillwater, Oklahoma campus. The building was located adjacent to the Engineering North building, the locale of the School of Chemical Engineering. The ATRC was an ideal location for the BTRS system, since the building was designed to provide technical accommodations and resources for research operations.

The apparatus consisted of three main modules: the feed system, the reactor system, and the analytical system (Figure 3.1). This modular concept ensured an increased degree of flexibility and provided enhanced control for feed concentration, reaction temperatures and pressures, and sampling time intervals.

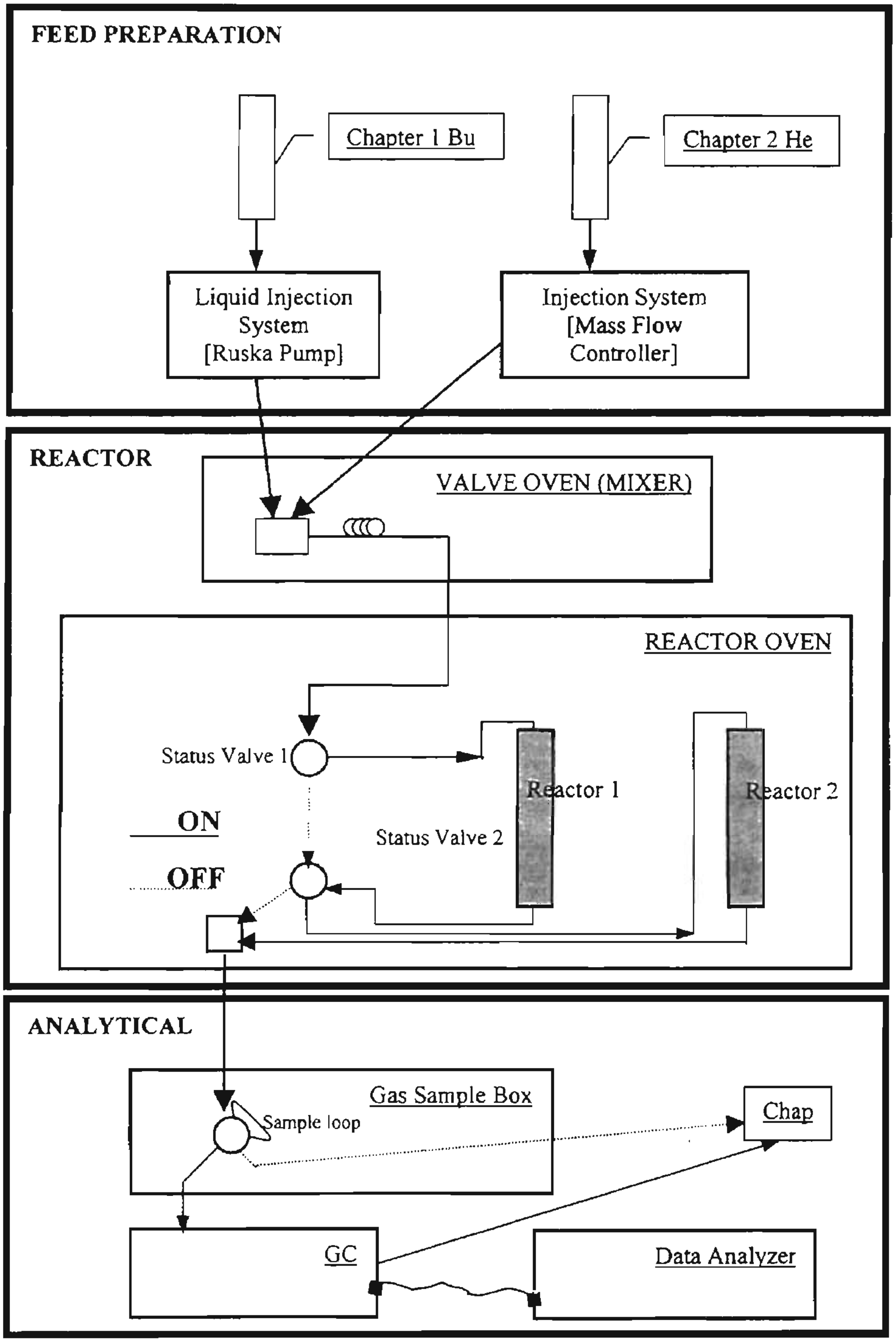


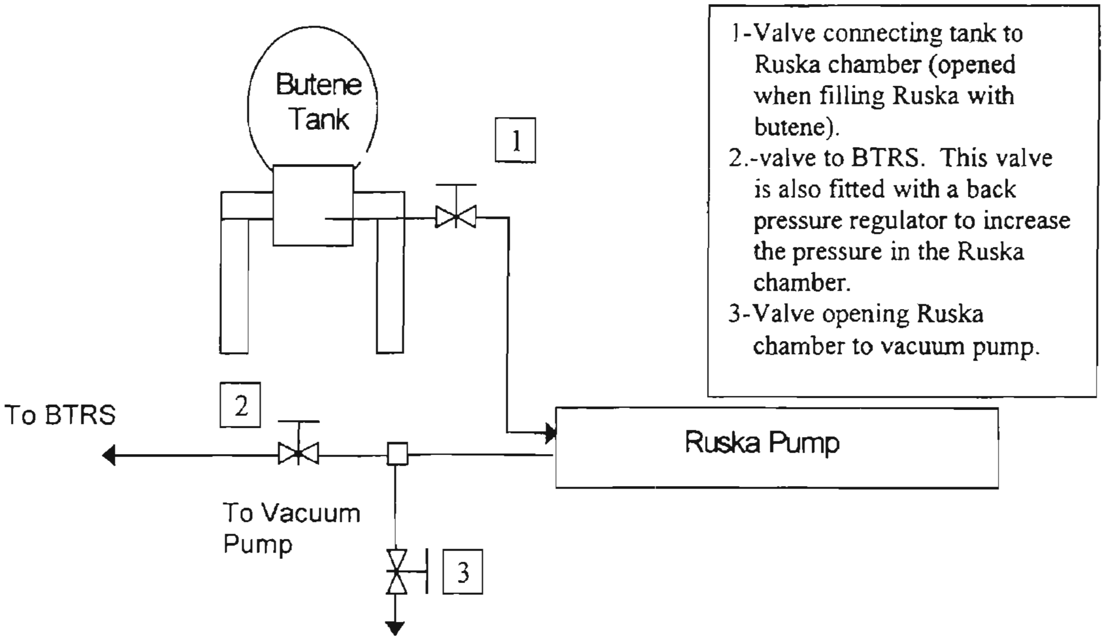
Figure 3.1 Three Main Modules (Feed Preparation, Reactor System, and Analytical System) of the BTRS.

3.1 OVERALL DESCRIPTION OF THE EXPERIMENT/APPARATUS

For the 1-butene injection system, a 1-butene tank was connected to a liquid positive displacement pump (Ruska Pump). To fill the liquid pump, the cylinder was cooled with ice to near 0°C. After filling with 1-butene, the liquid pump was allowed to warm to room temperature before each experiment. A pressure slightly above 1-butene saturation was maintained in the liquid pump cylinder, at runtime, by manipulating a manual back-pressure regulator (Figure 3.2). 1-butene was injected into the reactor oven (BTRS) as a liquid. The hydrocarbon was mixed with helium in the vaporizer where it entered the reactor chamber as a vapor mixture.

Inlet 1-butene was diluted with standard grade helium (Appendix D) to an approximately equivalent molar ratio. The feed helium was calibrated using a bubble flow meter. A mass flow controller (Brooks Model 5850TR) controlled the flow rate of the helium feed and was programmed and maintained by a programmable logic controller (PLC).

Three types of composite catalyst (sol-gel prepared, Nafion™ resin/silica composite) were investigated in this effort. Nafion™ SAC 25, was purchased by Du Pont, Inc., and existed as granular solids with a diameter of 0.5 to 3.0 mm. Nafion™ SAC 13 and SAC 13-531, both extruded rods, were purchased from Engelhard Corporation. The Nafion™ micelle concentration in the SAC 25 composite was 25 weight percent (wt%) while the Nafion™ micelle concentration for the SAC 13 composite was 13 wt% (see Appendix D).



1-Valve connecting tank to Ruska chamber (opened when filling Ruska with butene).
2.-valve to BTRS. This valve is also fitted with a back pressure regulator to increase the pressure in the Ruska chamber.
3-Valve opening Ruska chamber to vacuum pump.

Figure 3.2 Schematic of the Ruska Pump/Liquid System Used for Loading 1-Butene into the BTRS

The catalyst was loaded either into 5 cc or a 20 cc reactor (ranging between 0.3 to 20.9 grams) (see Figure 3.3). The inlet and outlet openings to the adapter couplings were fitted with glass wool. The catalyst was dried online with approximately 150 sccm helium flowrate at 230°C for approximately 12 hours (overnight). One sample of the spent catalyst had a BET surface area of 69-73 m^2/g surface area, a pore volume of 0.42 cm^3/g, and an average pore radius of 136 Å (Appendix C).

The experiments were performed while varying catalyst loads, temperature, pressure, and reactant space velocities. At each separate run, the reaction was allowed to come to steady-state as determined by visual inspection of the area ratio of butene isomers on the gas chromatogram. Steady state was usually maintained in 3-10 hours, depending on the reaction conditions.

For each experiment, it was assumed the reactor reached steady state when the reactor bed and zone temperatures did not vary with time. This analysis was accomplished visually. The reaction bed temperature, shell temperatures (3 different zones), system pressure, oven temperature, and gas and liquid flow rates were controlled using a PLC (GE Fanuc Programmable Logic Controller). The control program was monitored and maintained with PLC programming software (LM-90 Logicmaster) run on a desktop (Gateway 2000). System pressure and various temperatures were annotated in a notebook immediately before the reactant mixture was fed to the reactor and during each gas chromatographic analysis (every one-half hour to one hour).

The reactant effluent stream was sent to a manually operated valve-box that contained a 20 μL sample loop. The valve box was heated to 150°C (equivalent temperature of the GC purged-packed injector) (Figure 3.4).

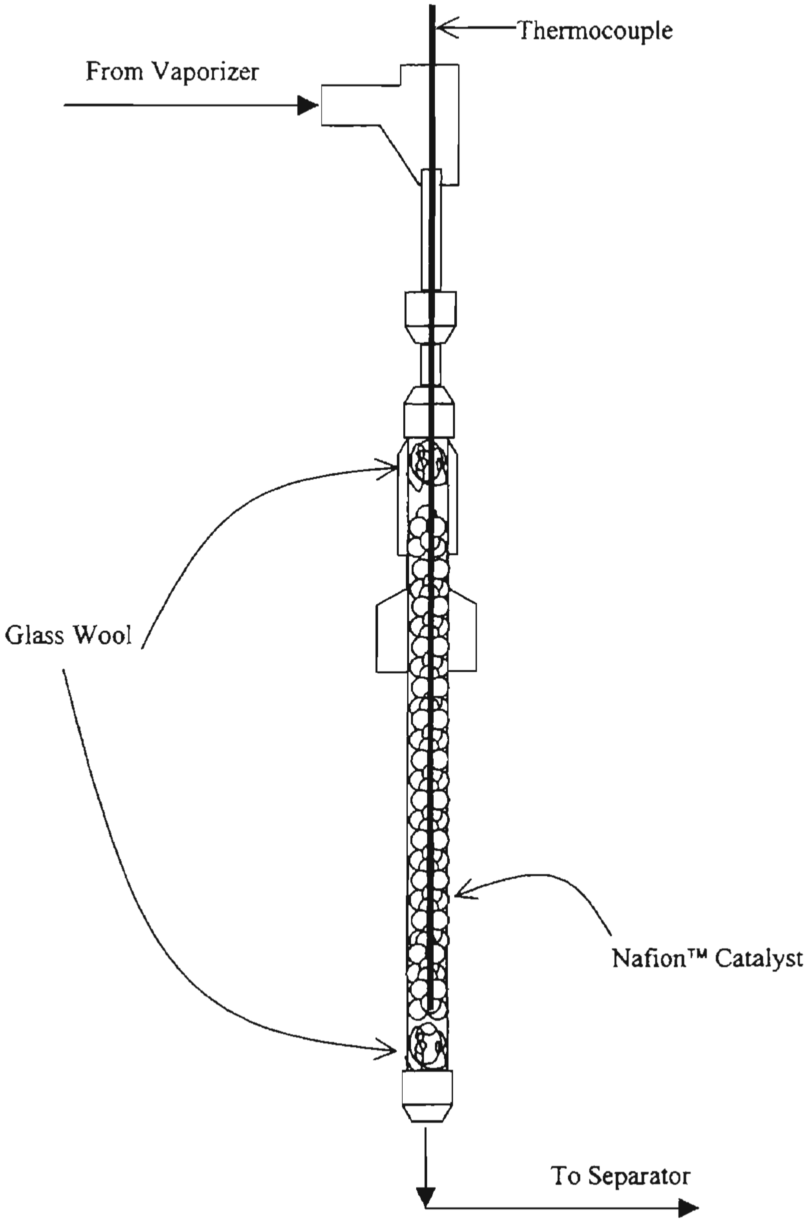


Figure 3.3 Reactor System Showing Catalyst, Glass Wool, and Thermocouple.

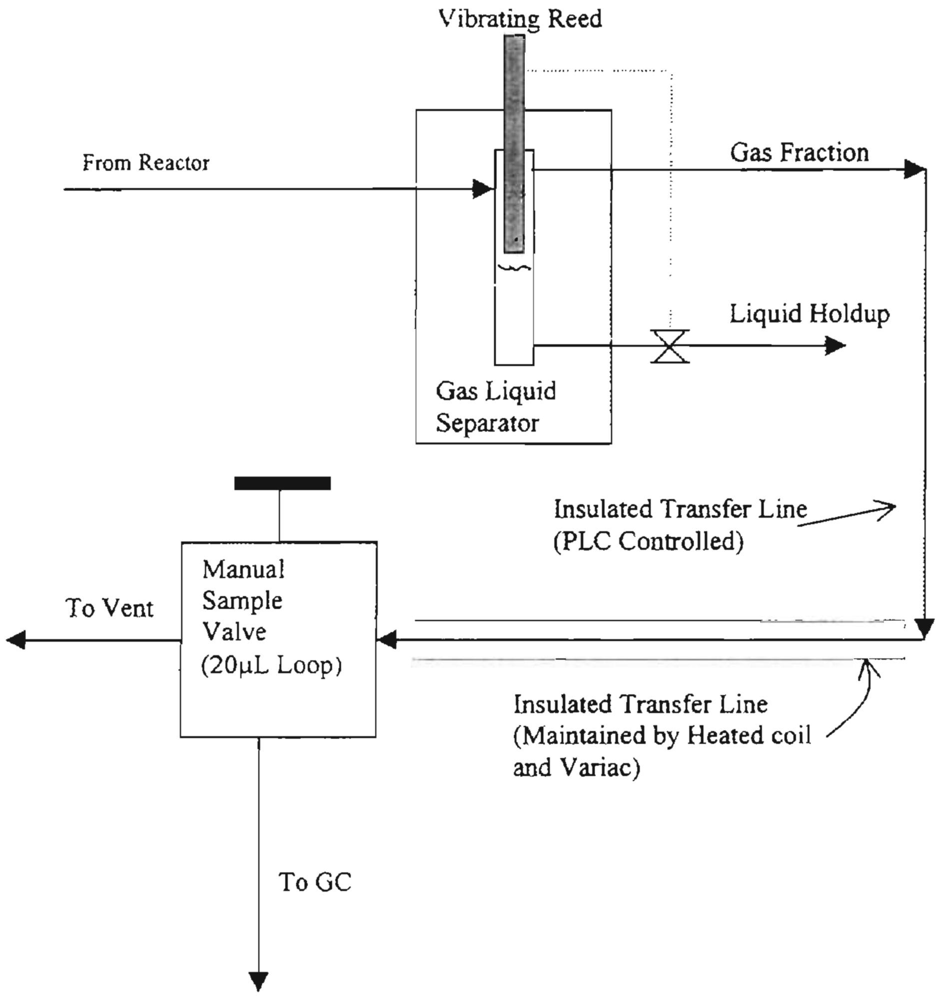


Figure 3.4 Schematic of Flow After Products Leave the Reactor.

A gas-liquid separator was located directly downstream from the reactor. The separator temperature was set at 50°C for each run. The gas-liquid separator (designed by Autoclave Engineers) operated automatically and was controlled by the PLC. The gas-liquid separator maintained a small aliquot of liquid in a holdup, separator chamber. A vibrating reed, located in the center of the holdup chamber, was positioned directly above the liquid level in the holdup chamber. When this liquid level reached the vibrating reed, a 1/10 to 1/20 cc aliquot of liquid was injected into a holding cell (see Figure 3.4).

The gas chromatograph was operated with a temperature-ramp programmed method (Table 3.1). Data analysis was accomplished using HP Chemstation software. Identification of peaks was accomplished using Kovats Retention Indexes (see Chapter 4.5). Area integration was accomplished using a HP 6890 integrating algorithm. Other characteristics of the gas chromatographic method are detailed in Table 3.2.

3.2 FEED PREPARATION

A positive displacement pump (Series 2250 Ruska – see Appendix A for details) was used to introduce 1-butene in liquid phase into the reactor. The liquid pump was a bench-scale, motorized pump that was mounted on a pan shaped, cast iron base. The liquid pump, rated to 8,000 psi, had a piston that traveled into a stainless steel cylinder, displacing a known amount of fluid. By turning the spindle, the cylinder was rapidly advanced into, or withdrawn from, the cylinder. The spindle was rotated by a worm and worm gear drive. The worm shaft was rotated by a motor, which was connected to the

Table 3.1 Major Components to the Gas Chromatograph Utilized in the Nafion Catalyst Research Study.

GAS CHROMATOGRAPHIC SETTINGS	
Injector Type	Purged-Packed
Inlet Injector Temperature	150°C
Carrier Gas	Helium, Ultra-High Purity (App. D)
Column Type	Supelco DH Petrocol Column
Column Polarity	Low
Column Size	100m x 0.25 mm ID, 0.5 μm film
Initial Oven Temperature	35°C (hold 10 minutes)
Ramp Rate	10°C/min
Final Temperature	220°C (hold 10 minutes)
Detector	Flame Ionization
Make-up Gas	Helium, Ultra-High Purity (App. D)
Air Flow Rate	450 ml/min
Make-up Flow Rate	45 ml/min
FID Compartment Temperature	250°C
Flow control	Constant Pressure Mode

Table 3.2 Major Components and Their Functions for the HP 6890 Gas Chromatographic System.

SYSTEM	TYPE	FUNCTION
Valves	Manual actuator assembly	Inject 20μL aliquot vapor into GC inlet
Inlet	Purged Packed	Ensure homogenous mixture enters column
Column	Capillary, low polarity, bonded methoxy siloxane	Separate (elute) analytes in mixture
Detector	Flame Ionization Detector	Detect Separated Analytes leaving column
Data Analysis	HP Chemstation	Perform integration methods of generated peaks from GC; perform other data analysis

gearbox. The electric motor, reductor, chain, and sprocket were mounted on one side of the pump. The worm gear can be disengaged from the spindle using a pin assembly on the hand-wheel drive, allowing manual adjustments by rotating the hand-wheel. This mode also allowed for the rapid withdrawal or insertion of the plunger under no-load conditions.

The liquid pump was equipped with an electric drive and a positive gear transmission, so the contents can be discharged at a constant rate. A pressure gage, located upstream from a three-way valve, was used to monitor pressure in the stream from the liquid pump. 1-Butene was maintained in the liquid state by throttling the 1-butene through a manually adjustable valve. The valve was adjusted to maintain a pressure above the saturation. A pump controller (SCR Ruska controller) adjusted the liquid ejected from the pump.

3.2.1 Calculating Liquid Flow Rate

The molar flow rate was determined by timing the rate of rotation of the spindle, noting the vernier scale affixed next to the spindle. The scale was divided into 0.10 ml units. One revolution of the spindle was equivalent to 3 ml by volume. The volume was determined by timing a predetermined volume, noting the displacement on the vernier scale, using a stopwatch. The molar flow rate ($F_{mol,Butene}$) was calculated by noting the volume displaced divided by the time for displacement, multiplied by the molar liquid density, and divided by the molecular weight:

$$F_{mol,butene} = \frac{V * \rho_{liq}}{t * MW} \tag{3.1}$$

Here the density of 1-butene, ρ_{liq}, was 0.588 g/ml and the molecular weight of 1-butene, MW, was 56.11 g/gmol [Lide 1995]. A two-way ball valve was fitted downstream from the valve and pressure gage.

3.2.2 Mass Flow Controller

A mass flow controller (Brooks model 5850TR) was located upstream from a filter and three-way ball valve, and was used to regulate the inlet flow of helium to the reactor. Housed in a separate compartment, the mass flow controller maintained a constant helium flow at ambient temperature. This highly accurate flow-measuring device guaranteed an accurate volume of helium was fed to the reactor.

3.2.3 Determination of Helium Volumetric Flow

A bubble flow meter was used to measure the volumetric flow of helium directed to the BTRS. A rubber hose was connected both to the bubble flow meter and the feed vent tube to measure the helium outflow from the reactor housing. A stopwatch was used to record the elapsed time.

The mass flow controller was calibrated by entering different input values into the Programmable Logic Controller (GE Fanuc Series 90-30) using the requisite programming software (Logicmaster™ LM-90). The change in volumetric flow of helium, as recorded by the bubble flow meter, was noted and recorded. Measurements were made at different inlet helium pressures (250, 500 and 750 psig) and at constant room temperature.

As the resultant graph (Figure 3.5) clearly indicates, the volumetric flow rate of helium was independent of the pressure of inlet helium feed to the mass flow controller. The graph also shows that a maximum flow rate was reached at 800 ml/min. A linear equation was generated using linear least squares; this equation was used to determine helium molar flow in subsequent calculations.

3.3 REACTOR SYSTEM

Inside the reactor oven housing, the apparatus received and mixed 1-butene and helium streams into a mixture that was then transferred to a tubular reactor. A pressure gauge and a pressure transducer both measured the upstream pressure of the tubular reactor. Reactor effluent was routed to the gas chromatograph; heated transfer lines were needed to ensure effluent products remain in the vapor phase.

The valve-oven subsection combined inlet 1-butene and helium; this mixed stream then entered the reactor. This reactant feed was fed through a filter, a check valve, an air-actuated valve, a ball valve, and a metering valve (Figure 3.6). A 7 μm

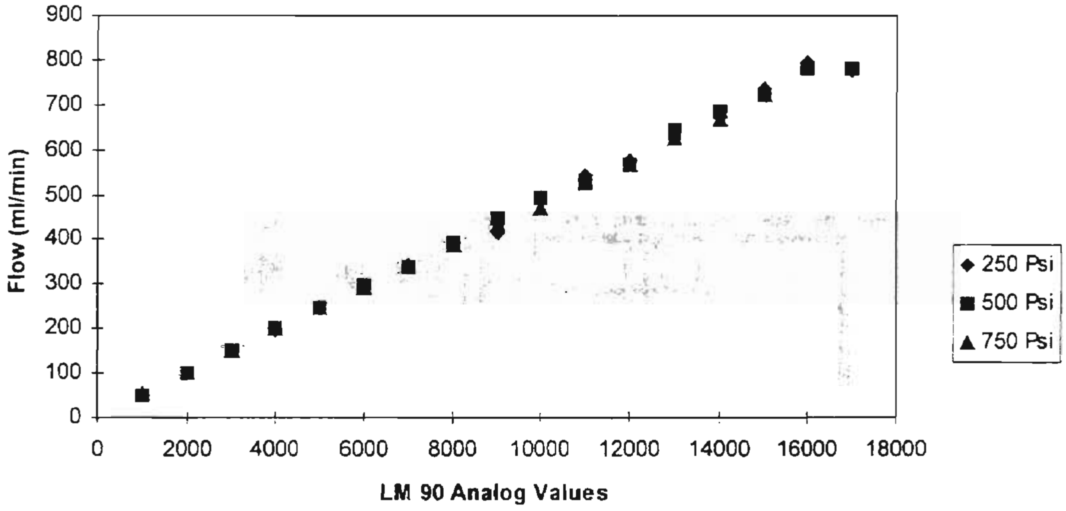


Figure 3.5 Graph of the Analog Versus Calculated Helium Flow Rate as Determined by a Bubble Flow Meter; Differing Inlet Pressures.

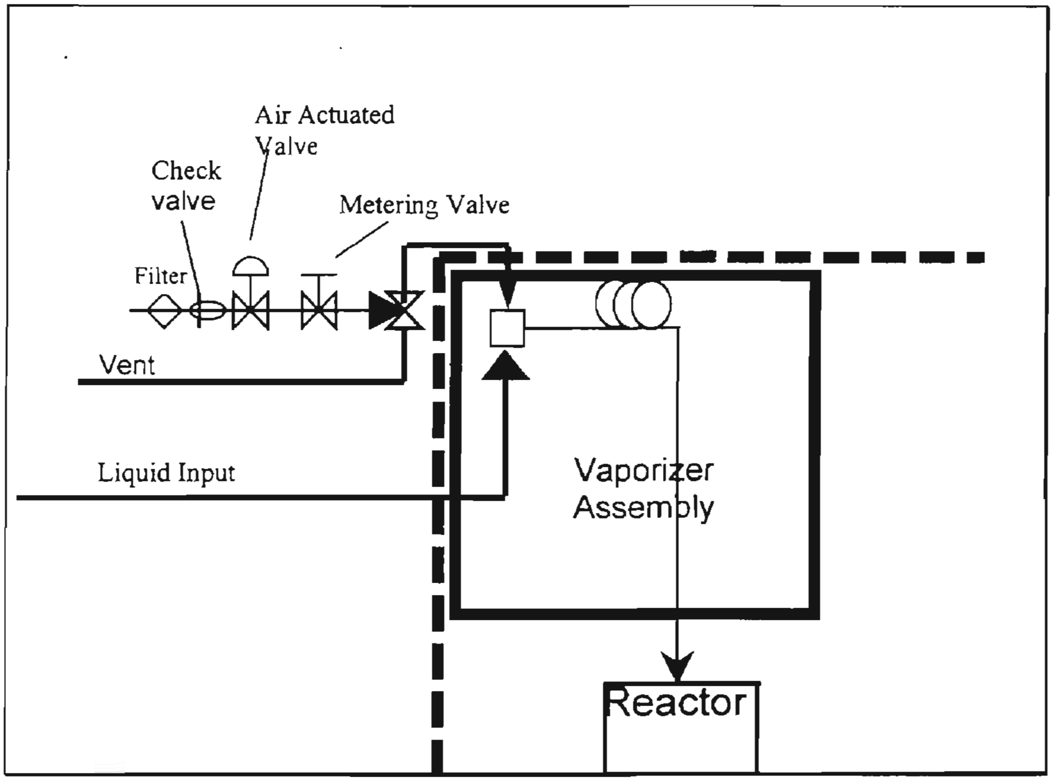


Figure 3.6 Schematic of the Vaporizer/Mixer Assembly Indicating the Mixture Point, and All Filters and Valves.

filter removed particles from the reactant feed. An air actuated valve turned flow on and off from the mixer inputs and was actuated by the control system.

For our analysis, the inlet gas helium was introduced into the vaporizer in the gas inlet port (located on the BTRS). The liquid 1-butene was introduced into the reactor housing (BTRS) by the liquid positive displacement pump (Ruska Pump), with a check valve online to eliminate back flow. A three-way ball valve was stationed between the flow streams to allow the reactant flow to be sent to vent in an emergency situation. This three-way valve also allowed the inlet mixture to be sent to an exit port where the flow stream could be measured with a bubble flow meter where the volumetric flow rate could be determined.

The valve oven assembly ensured a homogenous vapor stream was sent to the reactor. A separate liquid input was located next to the inlet gas/liquid feeds; this input was only fitted with a check valve. Liquid 1-butene was injected into this port.

The reactor system was supplied with two 20 ml, 0.52 inch (I.D.) Hastelloy C276 tubular reactors and two 5 ml, 0.31 inch (I.D.) Hastelloy C276, interchangeable reactors. The reactor furnaces, located inside the cryogenic cooling chamber within the reactor furnace assembly, have three-zone heaters (Figure 3.7). Each heater zone had resistance temperature detectors (RTD) connected to PLC; these were used to set and monitor reactor temperature.

The furnace assembly had a metal sleeve forming the inside of the stainless steel annular heater wall and also served as an annular space for cryogenic cooling. The electrical resistance heaters were wound on the exterior of the inner wall of the cryogenic annular jacket. The zone heaters were located just below the reactant entrance zone, in

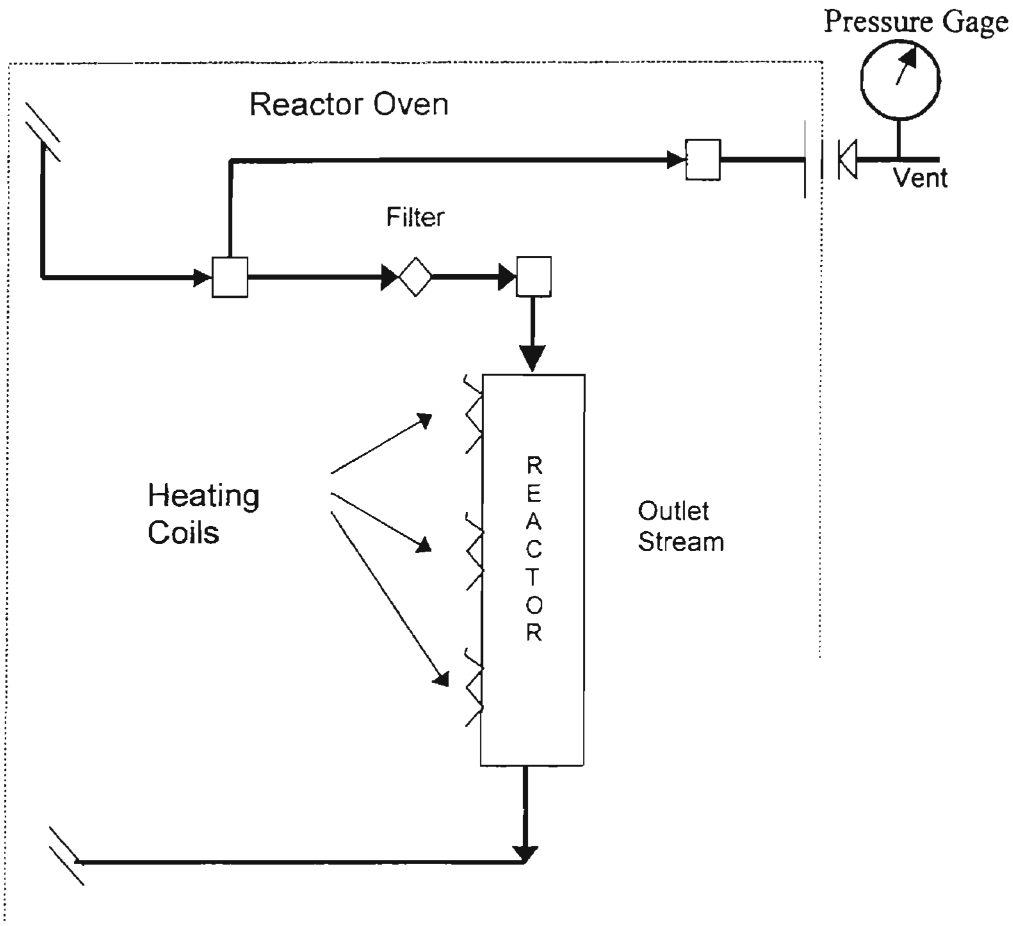


Figure 3.7 Reactor Assembly Showing the Reactor Zone Heaters, Thermocouples and Resistance Thermometer Devices.

the middle of the reactor, and at the exit end of the reactor (see Figure 3.7). Three RTDs were located inside 1/16th inch stainless steel tubing; these were attached axially to the outer side of the annular jacket. RTDs sensors were located in these tubes adjacent to the electrical heating elements. The shell chamber served as an insulator for the tubular reactor assembly from the bulk oven. A thermocouple was located within the reactor tube extending through the catalyst bed to measure the bed temperature.

In the valve oven, the homogeneous stream entered a reactor status valve. The reactor status valve was an air-actuated, two position, multiport valve. If the status valve was turned on, the reactant stream was diverted to the reactor. If the status valve was in the off position, the reactor was placed off-line or in the bypass position; here the reactant stream no longer entered the reactor (see Figure 3.1).

If the reactor status valve was not activated, the reactant stream passed through the back pressure regulator and to the analytical manually operated sampling valve located on top of the gas chromatograph.

An insulated, aluminum heating block surrounded the gas-liquid separator; this ensured a constant temperature throughout the apparatus. Energy for heating was maintained by an electric coil and controlled by the PLC. A preprogrammed temperature algorithm, controlled by the PLC, established a steady temperature profile in the headspace of the separator.

A pressure transducer (Sentra Type-205) was affixed to the reactor effluent stream and provided a means to determine the system pressure. Digital output from the pressure transducer was directed to the PLC. The PLC was programmed to receive this signal and compute the appropriate response factor for the back-pressure regulator. The pressure transducer was calibrated using ambient pressure as a standard.

Once the product gases exited the manual pressure regulator, this stream was sent through a series of heated transfer lines before it was sent to the GC system for analysis (see Figure 3.4). The first heated line consisted of an asbestos insulated transfer stainless steel tubing with a heating coil mounted inside the insulation jacket. This line was equipped with an RTD to determine the temperature of the transfer line; this heating element was controlled by the PLC. The next series of transfer line (approximately 4 feet) was heated with heating tape. A variac was used to control the output voltage need to heat the element.

3.4 SYSTEM CONTROL

A programmable logic controller (GE Fanuc) controlled the heater assemblies, flow rates, and fail-safes. The control sequence was programmed and stored in the PLC using programming software (Logicmaster LM-90). The PLC controller contained all the logic required to properly operate the reactor system. The controller consisted of a central processing unit (CPU), a power supply, a programmable coprocessor module (PCM), and RTD, thermocouple, and analog or digital input/output modules.

Various proportional integral and differential (PID) control loops were also programmed into the PLC to provide control and maintain preset conditions. For this study, set-point values were encoded directly into the PLC using controller programming software (LM90 Logicmaster).

The control system provided programming algorithms to monitor and maintain the reactor temperature, flow rate, pressure, valve actuation, external outputs, and output fail-safes. Temperature set-points for the reactor oven, the valve oven (vaporizer assembly), the inlet feed gas flow rate, the gas liquid separator, the GC transfer line, and the temperatures for the reactor heaters were preset before each run.

Helium flow was controlled by the PLC. The 1-butene liquid feed rate was controlled manually by manipulating liquid pump motor that varied the rate of liquid injection. The PLC controlled air actuated valves needed to establish flow rates and initiate failsafe procedures.

A portion of the PLC program monitored and checked for fail-safe conditions such as high pressure, temperature and flow conditions. These safety measures were inherent in the program to provided for fail-safe shutdown in case of sensor malfunction, power failure or exceeded limits. Rupture discs were located in various points throughout the system to ensure safe operation. Mechanical thermoswitches provided additional protection against high temperatures.

3.5 ANALYTICAL

The analytical system consisted of a Gas Chromatograph (Hewlett-Packard 6890) and a manually operated two-way gas sampling valve (Valco). A 100 m capillary column (Supelco DH Petrocol - 100m x 0.25mm x 0.5μm) was fitted to a purged-packed inlet; the effluent end of the column was fitted with a flame ionization detector (FID). The fuel for combustion in the FID was hydrogen with air as the oxidizer. Ultra-high purity helium (99.9% purity – Appendix D) served both as the carrier gas and the make-up gas for the flame ionization detector (Figure 3.8).

Product vapor exited the reactor system and entered a heated manual sampling valve assembly (Valco). The valve assembly was a two-position valve; normal operation passed the product stream to vent. When the valve was actuated, the helium carrier gas swept out a 20 μl aliquot of vapor product from the reactor effluent stream and directed it to the GC inlet.

An integrating algorithm inherent in the GC run software (HP Chemstation) located various peaks and calculated their relevant size. This algorithm also identified the start- and end-time for each peak and marked these points with vertical tick marks. The inherent software also had algorithms to determine the apex of each peak; these were designated as the retention/migration time. This algorithm also constructed a baseline and calculated the area, height and peak width for each peak.

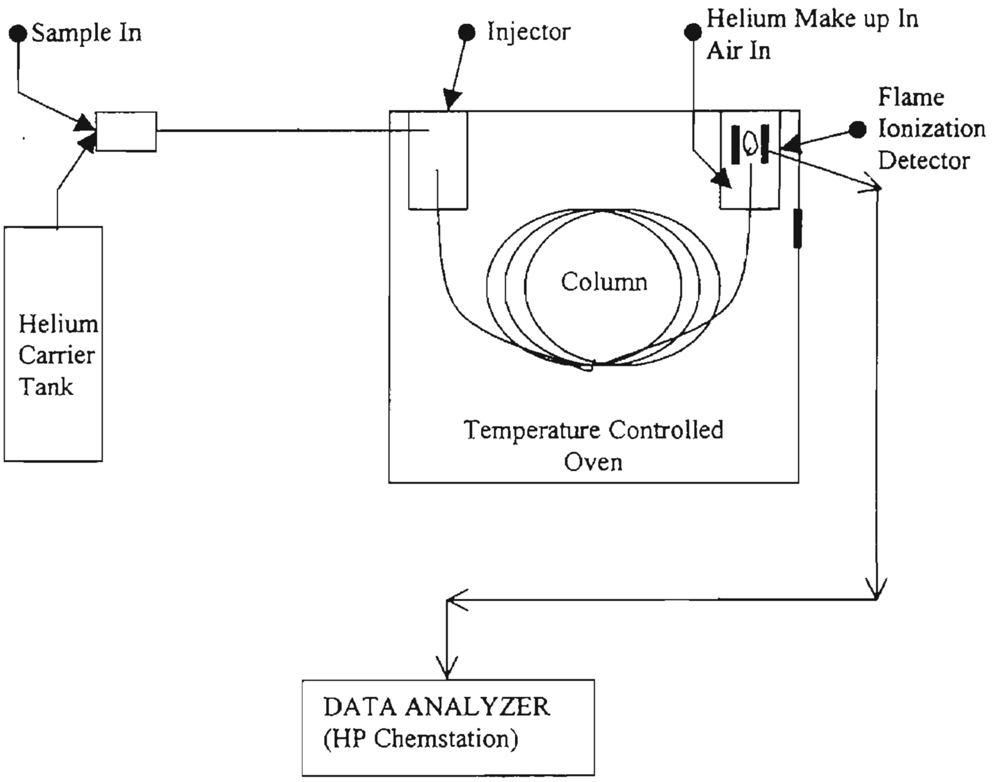


Figure 3.8 Schematic of the HP 6890 Gas Chromatograph.

CHAPTER 4 - RESULTS AND DISCUSSION

This chapter evaluates the performance and conversion of a 1-butene and helium mixture fed over two different types of Nafion resin/silica composite catalyst: Nafion SAC 25 and Nafion SAC 13. The analysis includes conversion comparisons for the two different reaction systems, conversion versus weight-time comparisons, and time variable analysis. A determination of the effective rate constant and the subsequent activation energy will be calculated and discussed.

The reactions were all carried out at steady pressure, temperature, and inlet mixture flow rate. Each run was allowed to reach steady state. The parameters that were varied were the temperature of the bed, system pressure, feed mixture and the weight of catalyst loaded into the reactor. The performance of the tubular reactor system will be discussed.

This chapter also outlines the procedure to calculate properties for the helium and 1-butene mixture, concentrations at thermodynamic equilibrium, and various dimensionless groups such as the Reynolds, Schmidt, and Péclet numbers. Also, axial and radial diffusion coefficients and the viscosity needed to determine dimensionless groups were calculated.

This chapter also outlines the methods to determine peak identification for the developed gas chromatograms. The use of the Kovats retention index, and other GC examination tools will be outlined and discussed.

4.1 BTRS SYSTEM BEHAVIOR

The core temperature of the reactor was monitored by a thermocouple, and was controlled by the PLC using heating jackets that surround the reactor and oven heaters. Oven heaters provided heat to maintain an isothermal catalyst bed, and also provided energy to preheat the reactant feed. This core temperature measured in the catalyst bed was considered the overall temperature of the bed (maximum gradient model) [Himmelblau and Bischoff, 1968] since a temperature profile along the centerline of the reactor was not available.

The PLC maintained and regulated the reactor system at near isothermal and isobaric conditions. The PLC was programmed to control and maintain the reactor-oven temperature, the valve-oven temperature, reactor zone (top, middle, and bottom) jacket temperatures, the gas inlet feed rate, the gas-liquid separator temperature, the GC transfer line temperature, and the overall system pressure. The PLC utilized single input, single output (SISO) proportional-integral-differential (PID) control algorithms to maintain the process variables of interest.

The GC transfer line and the gas-liquid separator assembly were maintained at 50°C throughout this study. Reaction products with saturation temperatures above 50°C (at ambient pressure) were removed from the effluent stream. Hence, condensation and liquid buildup were minimized in the product line to the gas chromatograph.

A constant temperature gradient was maintained between the shell of the reactor and the oven. The reactor jacket heaters were set to the experimental (target) temperature; oven heaters were set 10°C below this temperature. Preheating of the feed was accomplished in the valve oven where a large residence time allowed the mixture to reach a predetermined temperature.

For low temperature experiments (50°C) the reactor oven heater was used to provide all heating; the reactor jacket heaters were turned off. For these lower temperature experiments, the reactor oven heater was set and temperatures for all components inside the reactor oven were allowed to reach the set point temperature by the time the run was performed. With each experiment, the set point temperature for all heaters were set and allowed to arrive at steady state. Typical set point temperatures for a 150°C experiment are given in Table 4.1.

Figure 4.1 shows a hypothetical temperature profile. The reactor oven temperature was lowest in this system; the core temperature was the highest. Since 1-butene isomerization over a solid acid catalyst is exothermic [Kalló and Preszler, 1968], the highest temperature exists at the center of the catalyst bed. Heating the oven to the target temperature increased the bed temperature of the reactor.

When the mixture is first introduced into the reactor, the bed temperature increased sharply for the first few minutes until a maximum temperature was reached (Figure 4.2). Thereafter, the bed temperature decreased until it reached a steady value. Usually the bed temperature would stabilize about 2°C above the preset value for the reactor jacket heaters. This temperature increase was influenced by the concentration of the feed, the type of reactor used (5 cc or 20 cc reactor) and flow rate of the reactant. The maximum temperature reached was greater for the 20 cc reactor than the 5 cc reactor.

The pressure, maintained throughout the experiment by a back-pressure regulator, showed small fluctuations during the experiment (Figure 4.3). The graph shows a system

Table 4.1 Set Point Temperatures for Various Heaters; 150°C Experimental Run.

Heater	**T (°C)**
Valve Oven Heater	130
Reactor Oven Heater	140
Top Reactor Jacket Heater	150
Middle Reactor Jacket Heater	150
Bottom Reactor Jacket Heater	150
Gas-Liquid Separator	50
GC Transfer Line	50

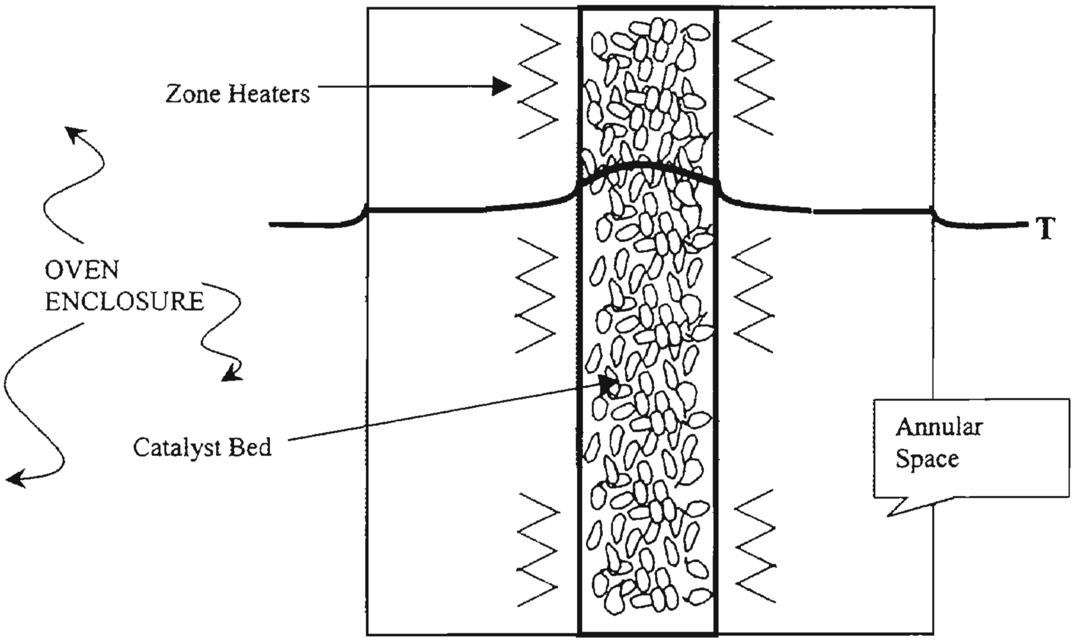


Figure 4.1 Schematic of the Temperature Profile for the Reactor Loaded with Catalyst.

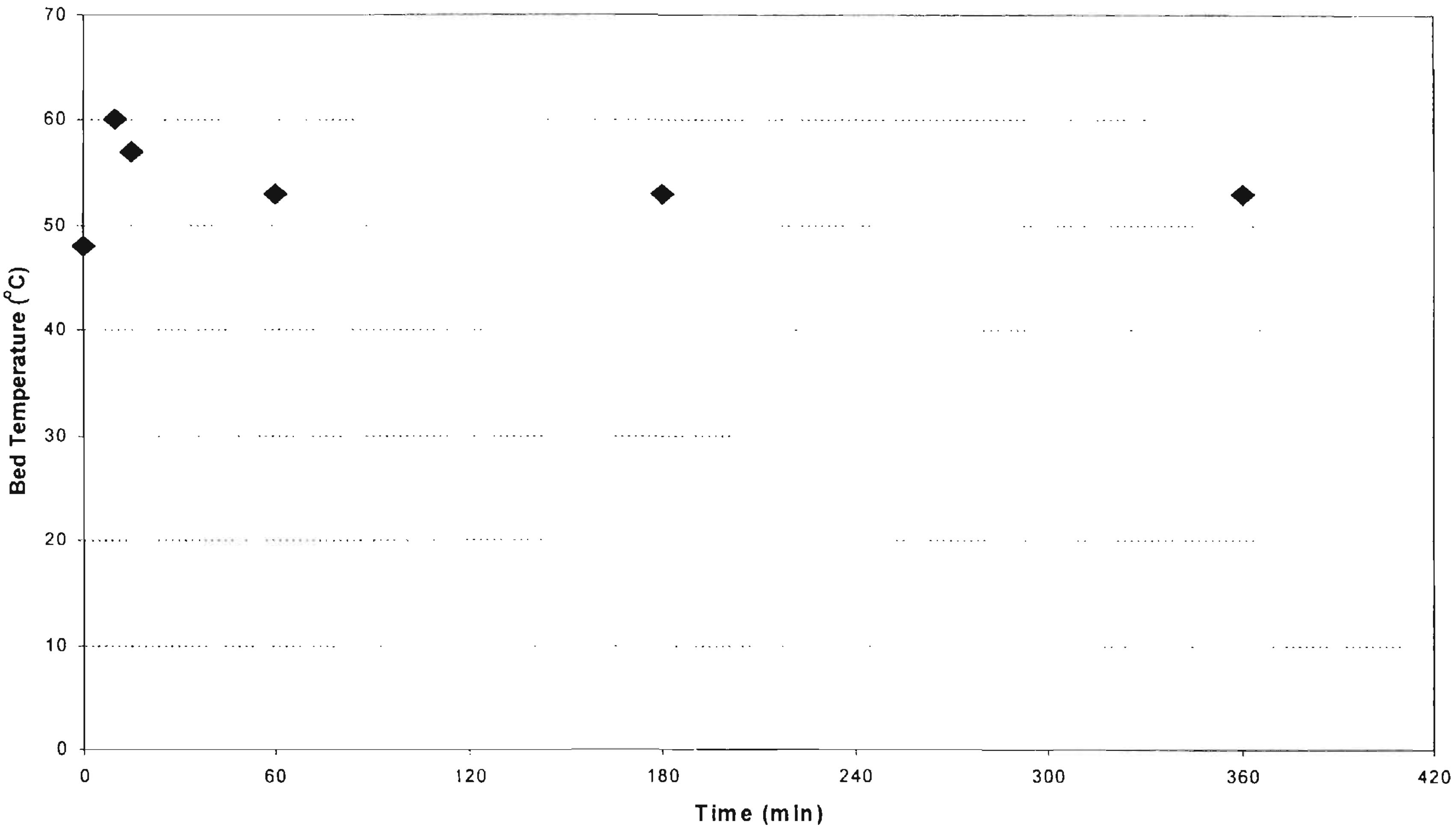


Figure 4.2 Bed Temperature Profile Versus Time for a Typical Reaction Experiment.

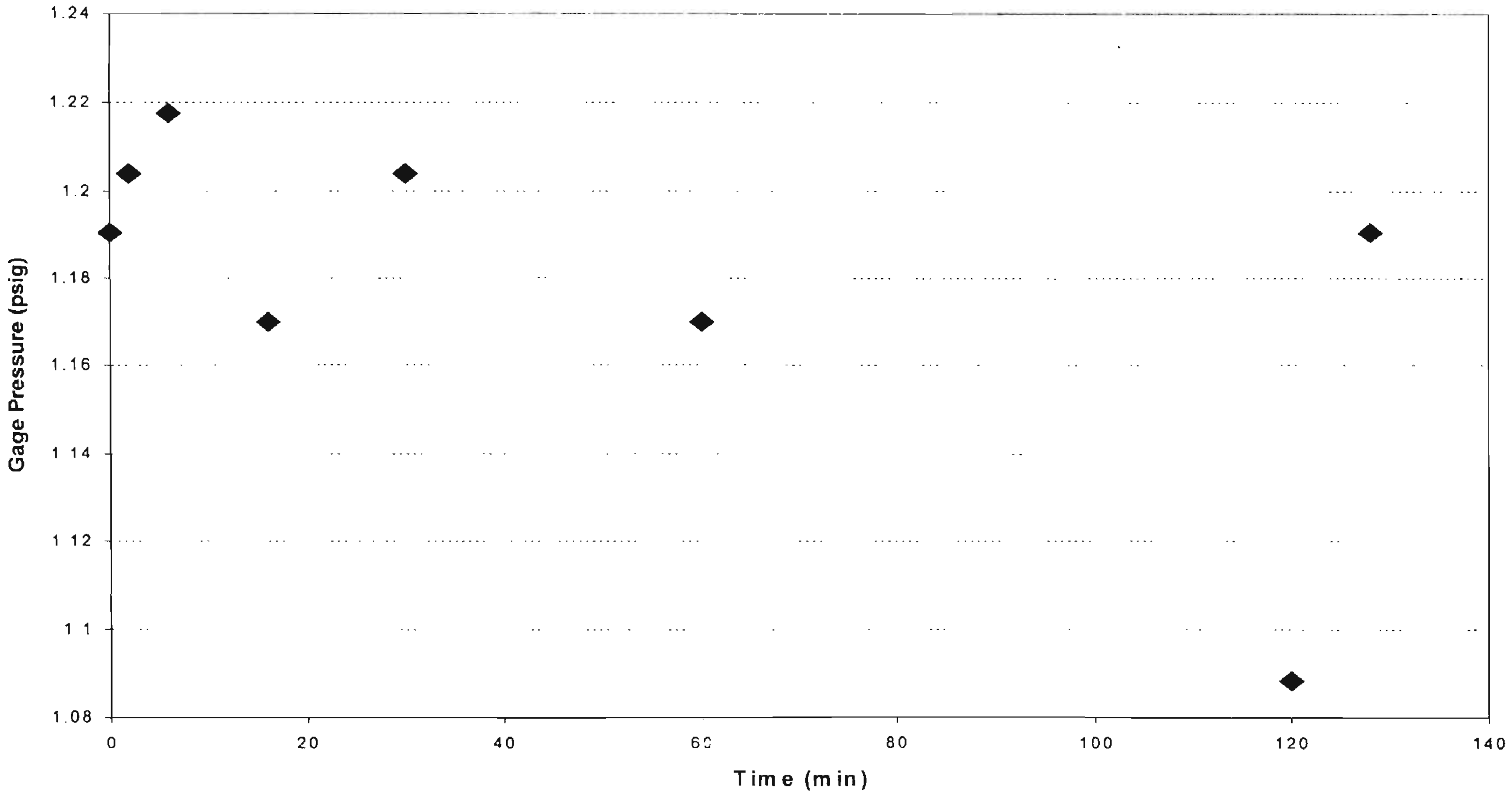


Figure 4.3 Gauge Pressure Readings Versus Time for a Reaction Experiment.

pressure behaving steadily, though slightly elevated from ambient pressure. Once the system showed slight or minimal variation in system parameters (e.g., temperature, pressure, concentration or flow) steady state was assumed to exist within the system.

Pressure versus volumetric flow rates for different experimental runs were plotted and are shown on Figure 4.4. The pressure is measured before the reactant is introduced into the alumina bed (see Figure 3.7).

The mixture was fed over Reactor #1 (filled with alumina) prior to entering the reactor (see Figure 3.1). The Nafion™ composite catalyst was loaded in Reactor 2. During this pretreatment operation, both materials were heated to 230°C with a helium flow of 150 sccm. Alumina is used to remove impurities, such as water or peroxides, from the reactant as described elsewhere [Clark and Subramaniam, 1999]. Impurities in the feed stream can deactivate the catalyst by hydrolysis and polymerization induced by peroxides [Clark and Subramaniam, 1999].

In Figure 4.5 the same relation is seen in a plot of pressure versus the volumetric flow rate per weight catalyst. These plots indicate a pressure drop for approximately 21 g of Nafion™ loaded into Reactor 2 together with 27 g of alumina loaded into Reactor 1 (see Figure 3.1). On this graph, with a smaller slope. 3.8 g of Nafion™ was loaded into Reactor 2 that followed 27 g of alumina loaded into Reactor 1. The same trend for pressure drop per volumetric flow per gram catalyst is observed. Here the 20 cc reactors were both used in series.

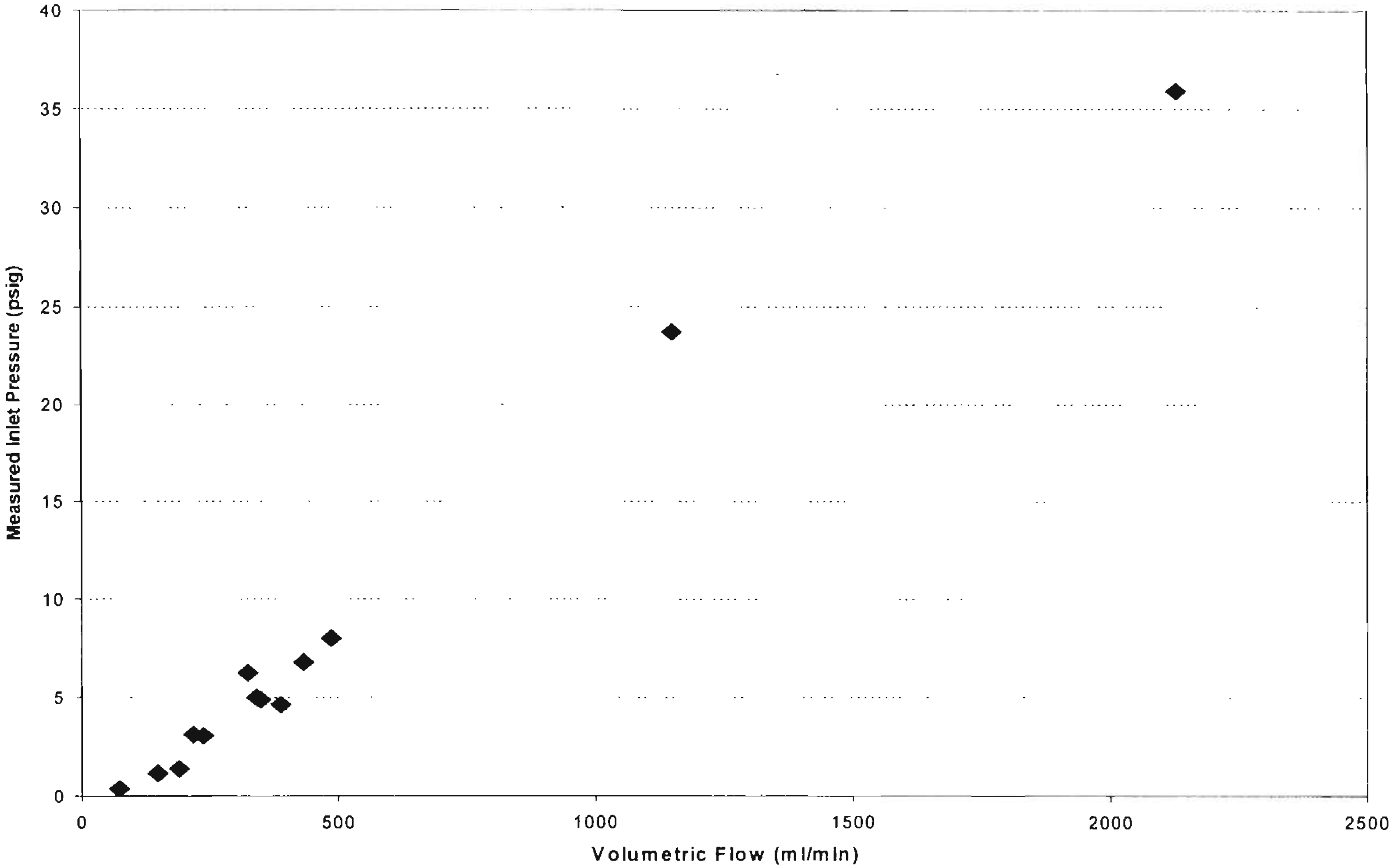


Figure 4.4 Measured Inlet Pressure Versus Volumentric (Feed) Flow Rate.

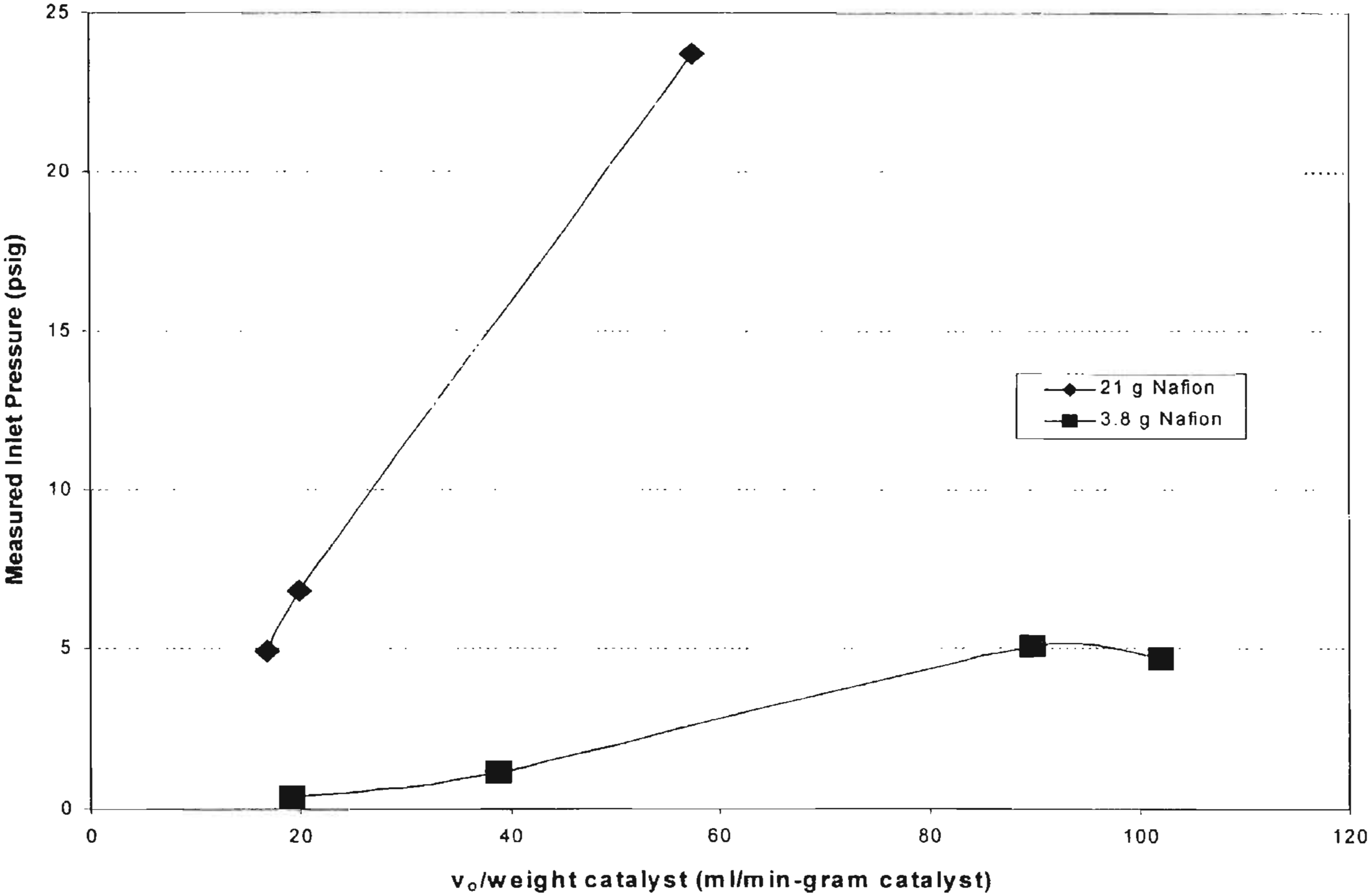


Figure 4.5 Measured Inlet Pressure Versus Volumetric Flow Per Weight Catalyst for a Reator Filled with Either 21 g Nafion™ Composite Catalyst or 3.8 g Composite Catalyst.

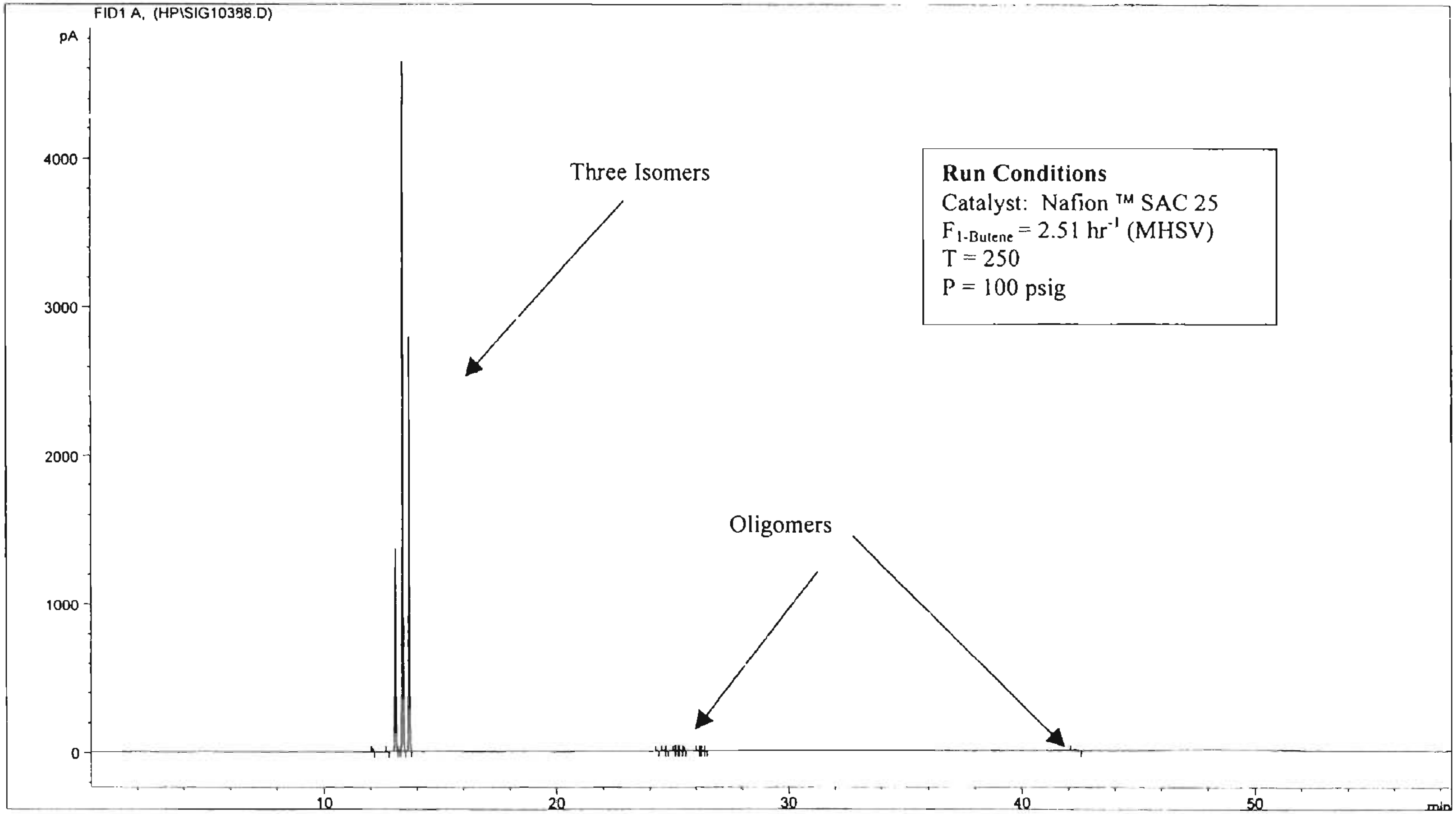
4.2 GAS CHROMATOGRAPHY

When evaluating the chromatograms for each experiment, the weight fraction of oligomers was usually less than 1.0 percent for experiments conducted at 50°C. The product oligomer concentration never exceeded 6% (see Appendix B, "%A olig"). The butene isomers comprised the majority of the product stream.

A response factor, RF_i, of unity was assumed for these lower chain olefins (e.g. 1-butene, trans- and cis-2-butene) which was also assumed previously for 1-hexene over a solid acid catalyst [Clark and Subramaniam, 1999]. These isomers have the same effective carbon number (ECN) [Grob 1995].

The Kovats Retention Index, introduced in Chapter 2. was used to identify the isomer peaks [Grob 1995; McNair and Miller, 1998]. Weight percent oligomers developed in this reaction, essentially less than 1% by weight, were also estimated using the area normalization technique with a response factor of one [Clark and Subramaniam. 1999]. The butene isomers in the product stream proved to be the only analytes where higher accuracy was needed. The oligomer peaks were not as distinct as the butene isomers. In essence, no additional effort was completed to improve the peak shape of these higher end hydrocarbons (Figure 4.6).

For qualitative analysis the Kovats Retention Index (KRI) was calculated for the three major peaks. The GC method used to determine the product distribution is shown previously (see Table 3.1). Table 4.2 shows the GC settings to conduct the peak identification analysis. The thermal conductivity detector was used for this qualitative



Run Conditions
Catalyst: Nafion ™ SAC 25
$F_{1\text{-Butene}} = 2.51\ hr^{-1}$ (MHSV)
T = 250
P = 100 psig

Figure 4.6 Chromatogram Indicating Peak Areas for Three Butene Iisomers and Oligomers.

Table 4.2 GC Method Used to Determine Retention Indices of Products from Butene Isomerization.

GC Component	Setting
Injector Type	Purged-Packed
Inlet Injector Temperature	150°C
Carrier Gas	Helium, Ultra-High Purity (App. D)**
Column Type	Supelco DH Petrocol Column
Column Size	100m x 0.25 mm ID, 0.5 µm film
Initial Oven Temperature	35°C
Ramp Rate	No ramp
Detector	Thermal Conductivity Detector
Detector Temperature	250°C
Make-up Gas	Helium, Ultra-High Purity (App. D)
Make-up Gas Flow	7.0 ml/min
Reference Flow (same as **)	40.0 ml/min
Split Ratio	1:100 for liquid injection and gas sample loop injection
	1:20 for Gas syringe injection

analysis since nitrogen was used to determine the retention time. Also the split ratio was altered to improve peak shape (see Table 4.2).

First nitrogen was injected into the column (via gas sample valve) to determine the retention time, t_R, for a non-adsorbing gas. This retention value was subtracted from the retention time for each analyte (peak) to obtain the adjusted retention time, t'_R, of the compound of interest.

Pentane and butane were injected (via syringe) into the column and the retention time was determined for each analyte by an integration algorithm inherent in the HP Chemstation software. The adjusted retention time, t'_R, for butane and pentane constituted the reference indices utilized for this analysis and are given as 400 and 500, respectively (Table 4.3).

The KRI values were calculated using Equation 2.38 (Chapter 2) for each of the three assumed isomers and are given in Table 4.4. The retention time for 1-butene is less than butane and the calculated KRI values somewhat deviate from the KRI values reported previously [Supelco 1996].

Error generated with this method is probably due to the differences in the injection methods for the compounds of interest and the compounds used to determine the retention indices. The gas sample loop was used to inject the isomer and the nitrogen samples. A pressure tight syringe was used to inject butane and pentane. The gas sample loop has approximately 30 cm of 1/16 inch tubing that the analyte must traverse before it reaches the head space of the injector (GC inlet).

Table 4.3 Retention Time and Retention Indices of N_2, Butane and Pentane.

Component	Retention Time, t_R (Min)	Adjusted Retention Time t'_R(min)	Log t'_R	Kovats Retention Index (KRI)
Nitrogen	11.4	-	-	-
Butane	13.3	1.96	0.292	400
Pentane	16.9	5.50	0.740	500

Table 4.4 Retention Times, and Kovats Retention Indices (KRI) for Lower Chain Products from Butene Isomerization.

Component	**Retention Time, t_R (Min)**	**Adjusted Retention Time t'_R(min)**	**Log t'_R**	**Calculated Kovats Retention Index (KRI)**	**Kovats Retention Index (KRI) given from Supelco**	**Precent Error (%)**
1-Butene	13.213	1.8110	0.25792	392.24	391.8	0.11
Trans-2-butene	13.664	2.2620	0.35449	413.78	411.1	0.65
Cis-2-butene	14.015	2.6130	0.41714	427.76	426.0	0.41

This method is adequate to qualitatively identify the hydrocarbons of interest, namely the three butene isomers. KRI values for oligomer compounds were not completed since the weight fraction of product oligomers were essentially negligible.

4.3 MIXTURE CALCULATION

An equimolar mixture of 1-butene and helium was charged over the reactor for each experiment. As stated previously (Chapter 3), helium as a diluent was used to aid in intraparticle diffusion and heat transfer within the particle.

The Benedict-Webb-Rubin equation of state was used to determine the vapor density of 1-butene (Equation 2.4). The density of 1-butene generated by the BWR equation was compared to experimental values of saturation vapor density [Hewitt 1998]. These are given in Table 4.5. Comparing the experimental versus the predicted value of the 1-butene vapor indicates that the BWR equation is adequate to determine the 1-butene vapor density. The percent error increases as the system approaches critical, but only by a factor of 1.42%.

The ideal gas equation was used to determine the volumetric flow of helium (Equations 2.2 and 2.3). This ideal gas correlation was also used to evaluate the volume of helium at the system temperature and pressure.

For the 1-butene/helium mixture, Amagat's law of additive volumes was assumed since, at low to moderate pressure, gaseous or vapor mixtures typically obey the Lewis-Randall rule [Balzhiser *et al.*, 1972]. Hence the partial fugacity of each component in the mixture is equivalent to the total fugacity multiplied by its vapor component fraction

Table 4.5 Experimental Versus Predicted Vapor Density of 1-Butene Using the Benedict-Webb-Rubin Equation of State.

Temperature (^{o}C)	**Pressure (atm)**	**BWR Predicted Density (mol/dm^3)**	**Experimental Value (mol/dm^3)**	**% Error**
-6.25	1	0.047659	0.0476	0.12
-3.15	1.127	0.05332	0.0531	0.41
36.85	4.139	0.1828	0.1823	0.27
76.85	11.046	0.4875	0.4876	-0.021
116.85	24.111	1.1905	1.2075	-1.42

(Lewis and Randall Rule). With these assumptions, and where minimal data is available to determine the mixture properties, Amagat's law of additive volumes can be assumed.

A typical empirical method to determine the deviation from Amagat's law is to calculate the compressibility factor, Z_m, based on the summation of compressibility of each component in the mixture. From thermodynamic tables [Balzhiser *et al.*, 1972] the compressibility factors for helium and 1-butene at 50°C and at ambient pressure are both approximately equivalent to unity. Therefore, the mixture compressibility factor will also be equivalent to unity.

4.4 THERMODYNAMIC EQUILIBRIUM

As stated previously (Chapter 2), the weight concentration of the butene isomers at equilibrium (at 50°C and ambient pressure) is 4.1, 70.5, and 25.4% for 1-butene, *trans*-2-butene and *cis*-2-butene, respectively [Sun *et al.*, 1996]. The equilibrium concentration was also calculated using Equations 2.10 through 2.15 (Chapter 2) and were compared to these values.

Considering the multiple reactions annotated in Table 2.1 (Chapter 2), three individual reactions take place, which are steps 4 and 5 (Table 2.1) together with a reversible reaction between the secondary olefin pairs. Development of a matrix using stoichiometric coefficients for the three reactions proceeded as follows:

1. 1-butene → *cis*-2-butene
2. 1-butene → *trans*-2-butene
3. *cis*-2-butene → *trans*-2-butene

The above equations form a coefficient matrix in the following manner:

$$\begin{array}{c} \\ 1 \\ 2 \\ 3 \end{array}\begin{array}{c} \begin{array}{ccc} \text{1-B} & \text{cis} & \text{trans} \end{array} \\ \begin{bmatrix} -1 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 1 \end{bmatrix} \end{array}$$

Using algebra, the above matrix is converted into a diagonal matrix with 1's down the diagonal and zeros beneath [Hill 1977]. When this is accomplished, the resultant matrix is shown:

$$\begin{array}{c} \\ 1 \\ 2 \\ 3 \end{array}\begin{array}{c} \begin{array}{ccc} \text{1-B} & \text{cis} & \text{trans} \end{array} \\ \begin{bmatrix} 1 & -1 & 0 \\ 0 & 1 & -1 \\ 0 & 0 & 0 \end{bmatrix} \end{array}$$

The number of 1's in the diagonal is equivalent to the number of independent reactions [Hill 1977]. Hence, the independent reactions for determining equilibrium concentration were reactions 1 and 2 (above) which was the same result assumed in a previous effort [Eliyas *et al.*, 1987]. Any choice of reactions would give similar results.

The enthalpy change, ΔH^o, for the reaction is assumed to be constant over the temperature interval. In essence, the change of enthalpy can be calculated by a negligible heat capacity term [Hill 1977]. Table 4.6 shows thermodynamic data, enthalpy, and free energy of activation for each reaction. Using the extent of reaction, Table 4.7 lists each component of the reaction together with the extent for each separate reaction.

Table 4.6 Enthalpy, Free Energy and the Equilibrium Concentration Coefficients for 1-Butene Isomerization.

Reaction	ΔH^o **kcal/gmole**	ΔG^o **kcal/gmole**	$K_{(T=298)}$	$K_{Temp.}$
1-b → t-b	-2.64	-2.04	3.4452	22.2
1-b → c-b	-1.64	-1.35	9.632	7.78

Table 4.7 Final Concentration Calculation Using the Calculated Extents of Reaction for Two Independent Reactions Responsible for 1-Butene Isomerization.

Compound	**Initial**	**Equilibrium**	**Final Concentration**	**As reported from Sun et al., 1996**
1-b	1	$1-\xi_1-\xi_2$	0.033	0.041
c-b	0	ξ_1	0.252	0.254
t-b	0	ξ_2	0.715	0.705
Total			1.000	1.000

Using the following relations, the values of the extent of reaction for both reactions can be calculated using an iterative method:

$$K_1 = 7.78 = \frac{\xi_2}{1 - \xi_1 - \xi_2} \tag{4.1}$$

$$K_2 = 22.2 = \frac{\xi_1}{1 - \xi_1 - \xi_2} \tag{4.2}$$

Here, ξ_1 and ξ_2 are equivalent to 0.715 and 0.252, respectively.

4.5 CONVERIONS OF DIFFERENT NAFION™ CATALYST

Experiments for 1-butene isomerization were carried out using three types of Nafion™ catalysts. Reaction conditions were carried out at 50°C, ambient pressure, with approximately 5 to 5.5 grams of catalyst, and with a space velocity of approximately 2.5 hr^{-1} of 1-butene charged over the catalyst. The results are given in Table 4.8.

As the data indicate, no activity was observed using Nafion™ SAC 13 catalyst. Nafion™ SAC 13-531 indicated about one-half the activity as the Nafion SAC 25 counterpart. The remainder of these experiments was conducted using Nafion SAC 25; no other experiments were conducted using Nafion™ SAC 13 or Nafion™ SAC 13-531. It is important to note that both Nafion™ SAC 13 composites utilized for these experiments of were quadralobe, extruded rods. Nafion SAC 25 was a spherical pellet.

Table 4.8 Comparison of Three Types of Nafion™ Composite Catalyst (SAC 25, SAC 13, SAC 13-531) for the Conversion of 1-Butene (T=50°c, P=Ambient, MHSV = 2.5hr^{-1}).

Catalyst	X_A	**Wt% 1-butene**	**Wt% trans-butene**	**Wt% cis-butene**	**Wt% olig.**
Nafion SAC 25	.91	9.98	61.4	26.1	2.48
Nafion SAC 13	0	~99	0	0	0
Nafion SAC 13-531	0.52	47.4	28.7	22.9	0.92

4.6 TRANSIENT REACTOR BEHAVIOR

For one experiment, (T = 250°C, P = 100 psig, $MSHV_{1\text{-butene}} = 0.98\ hr^{-1}$, 21.7 grams SAC 25), chromatograms were taken at three different time intervals (Figure 4.7). These chromatograms were generated after one hour, three hours, and six hours, respectively. The initial three sharp peaks constitute the three butene isomers as identified by the Kovats Retention Index. These chromatograms indicate that the reaction selectivity favors isomerization over oligomerization as the reaction approaches steady state. Figure 4.8 also shows the weight percent of butene isomers and oligomers of the effluent stream at varying time intervals. Again the selectivity for secondary isomers was favored with time on stream even at these higher temperatures.

After each run, the BTRS system was allowed to cool to room temperature. The catalyst was then removed from the reactor for observation. With experiments conducted at lower temperatures (i.e. 50°C), the catalyst was slightly discolored, giving a pinkish to light brown color. For experiments conducted at higher temperatures (i.e. 200°C) the catalyst was highly discolored with a black color. The discoloration of the catalyst at the lower temperature runs was more pronounced at the inlet; the intensity of discoloration of the catalyst decreased as the catalyst pellet was positioned further from the inlet.

Butene isomerization at higher temperatures using the Nafion™ resin/silica nanocomposite as a reacting medium gave 1-butene conversions somewhat equivalent to the 50°C and ambient pressure runs. The conversion of 1-butene to *trans*-2-butene was the favored reaction and is commensurate with thermodynamic data [Kallo and Preszler, 1968]. The concentration of oligomers (assuming from olefin polymerization and

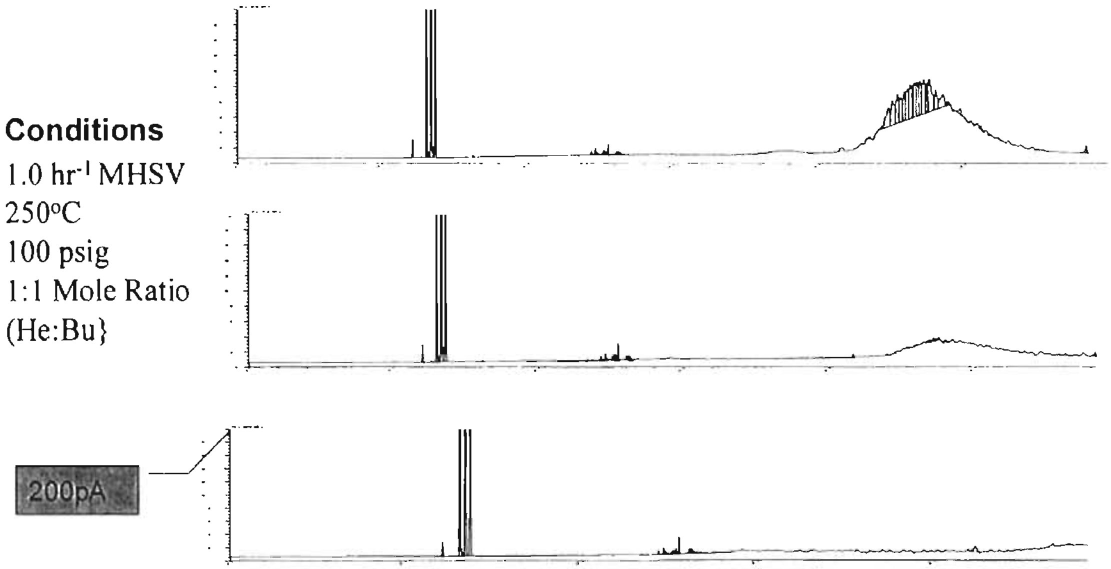


Figure 4.7 Three GC Chromatograms for an Experimental Run Taken After One, Three, and Six Hours Indicating the Lessening of Weight Percent Oligomers in the Product Stream.

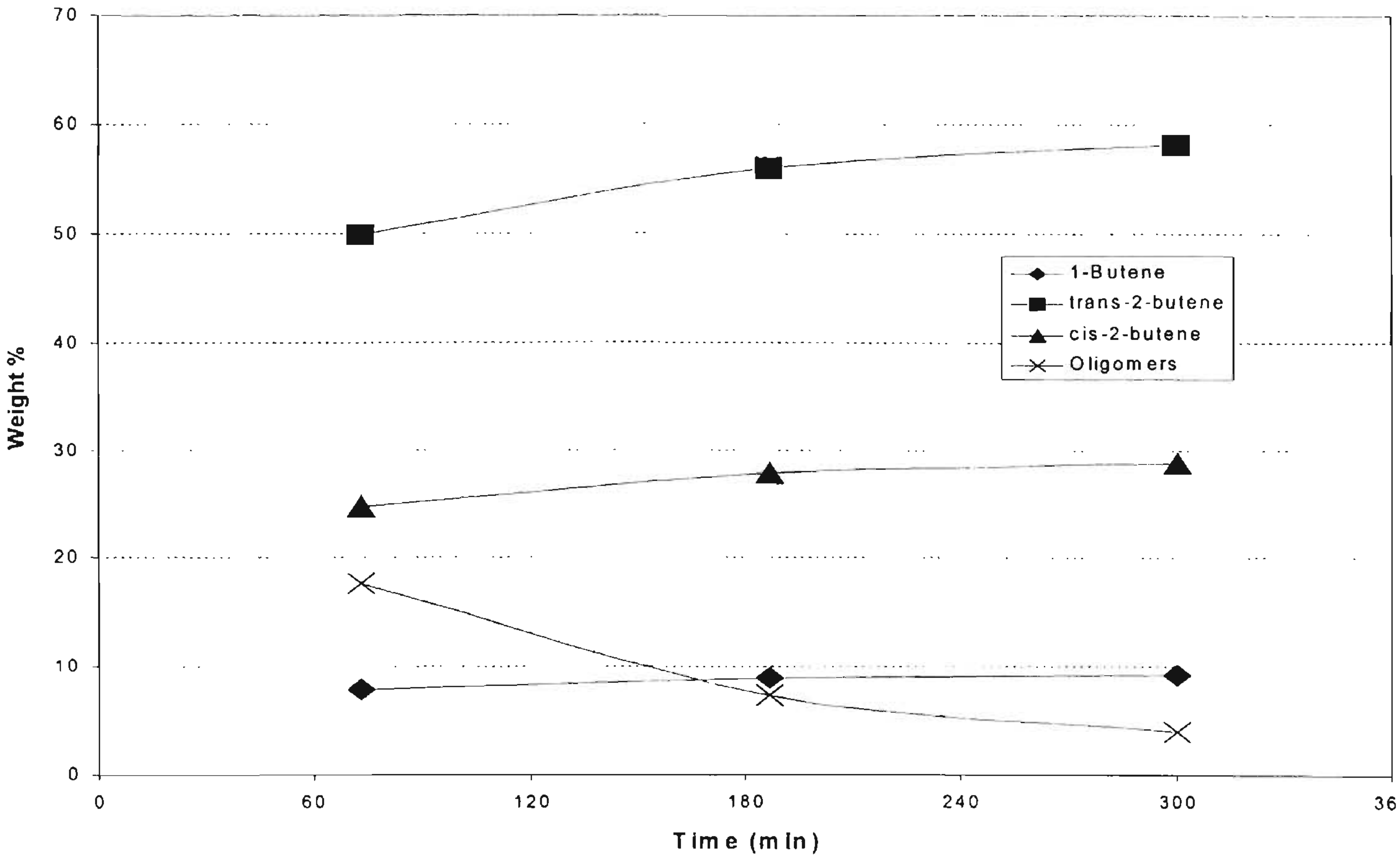


Figure 4.8 Weight % Butene Isomers And Oligomers In The Product Stream As A Function Of Time (T-50°c, P=Ambient, MHSV(1-Butene) = 1.0 Hr^{-1}.

cracking of these products) was higher in the product stream with increased system temperature. Lower temperature reaction conditions produced negligible (< 1.0%) oligomers.

4.7 WEIGHT-TIME ANALYSIS

For a tubular reactor, the optimal analysis rests in the weight-time, or equivalent reactor length (or charge of catalyst) that is effective in converting reactants to products [Levenspiel 1996]. Figure 4.9 shows the conversion of 1-butene versus weight-time at different temperatures. At 50°C, the conversion of 1-butene has a typical response of weight-time to conversion plots as generated for other tubular flow reactions [Satterfield 1980]. Here the leveling off of the conversion with increasing weight-time (at 50°C) reflects the approach to equilibrium [Satterfield 1980]. Unique methods are developed to extrapolate these curves through the origin [Froment and Bischoff, 1979]. The reaction appears to behave isothermally since the conversion versus weight-time curve (at 50°C) continues through the origin [Froment and Bischoff, 1979].

For reactions carried out at elevated temperatures, oligomer production increased with increasing temperature (Table 4.9). However, oligomer weight percent never increased beyond 6% of the total in any case (Appendix B). Figure 4.10 shows the weight percent of oligomers for various reactions carried out between 50°C and 250°C. The experiment that produced the highest weight percent oligomers was at 150°C and ambient pressure. Weight percent oligomers tended to reach a maximum and then

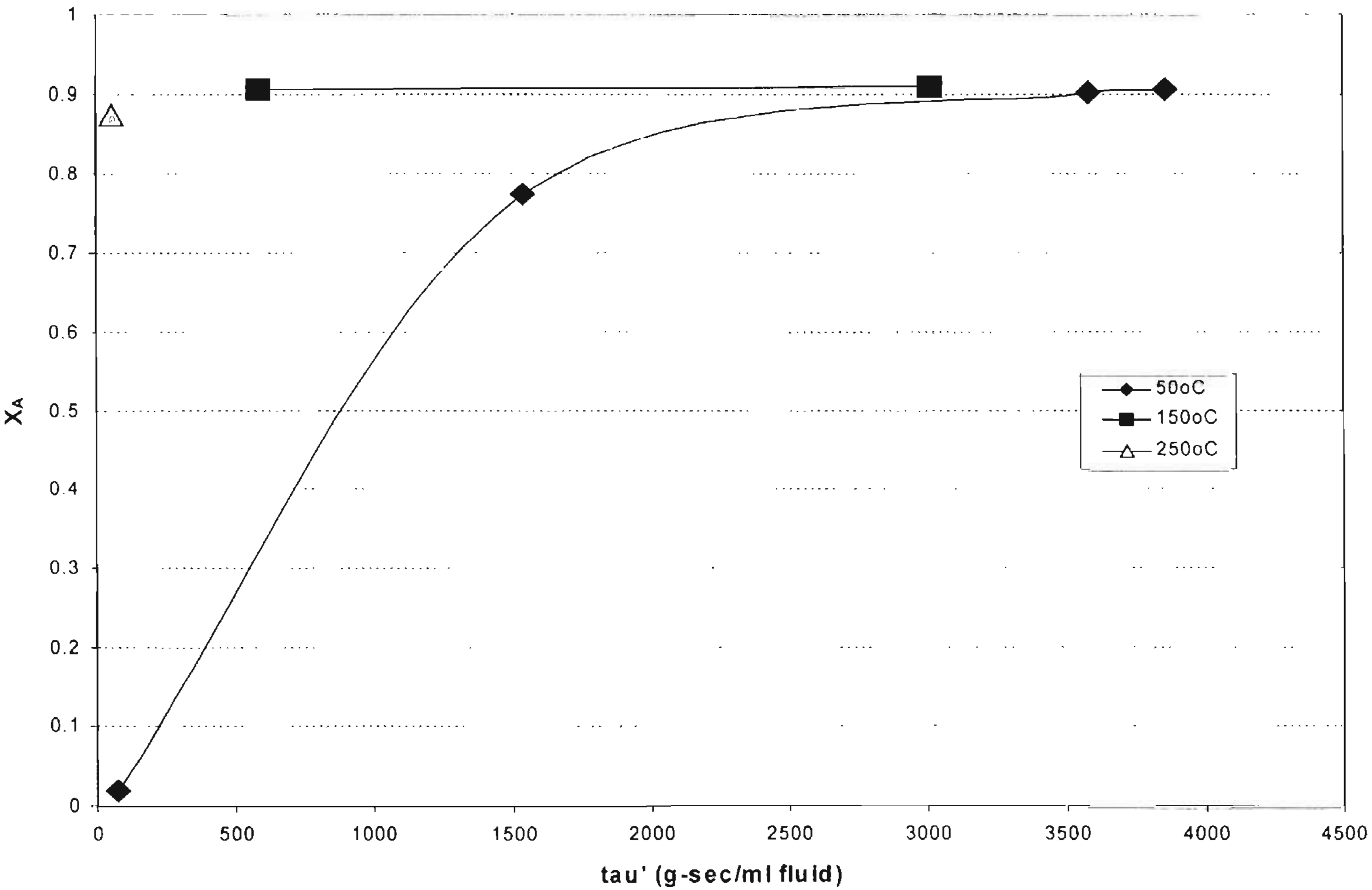


Figure 4.9 1-Butene Conversion Versus Weight Time (τ') for 50, 150 And 250°C.

Table 4.9 Product Weight Concentrations of 1-Butene Reaction over Nafion SAC 25 Composite Catalyst at Varying Temperatures.

Temp (°C)	**X_A**	**Wt% 1-butene**	**Wt% trans-2-butene**	**Wt% cis-2-butene**	**Wt% Oligomers**
50	0.905	9.42	62.08	27.32	0.92
150	0.908	9.13	58.17	28.74	3.65
250	0.855	14.39	50.11	30.89	4.385

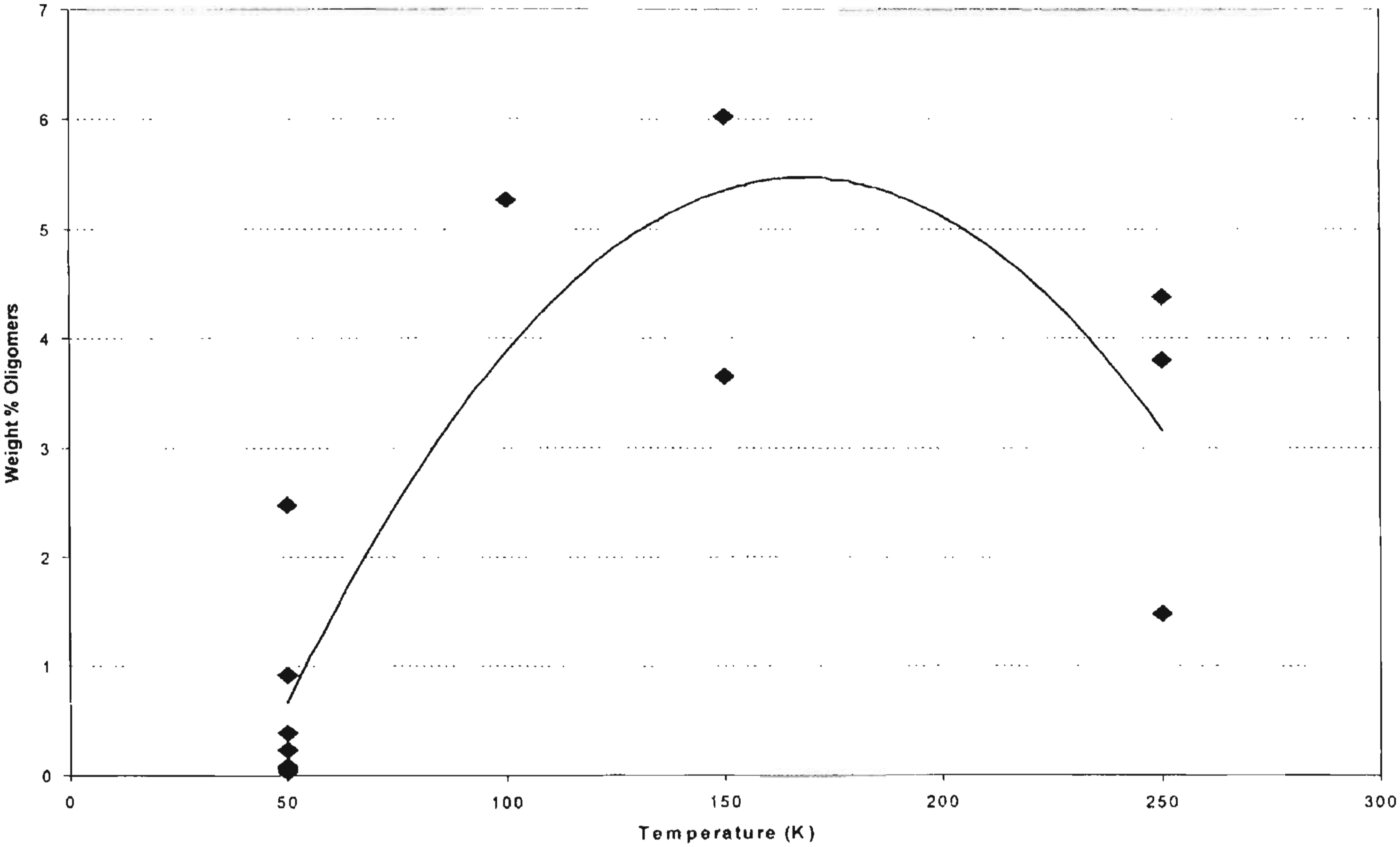


Figure 4.10 Wt% Oligomer Versus Temperature for Various Runs Where Increasing Temperature Indicates an Increase in Oligomer Weight Percent.

diminish with either increasing or decreasing temperature. This analysis may not be accurate and more detailed experiments may be warranted before this conclusion can be justified.

The weight percent of the three isomers, together with the oligomers, changes as the weight time, τ', is increased. Figure 4.11 shows that the weight percent of 1-butene in the product stream approaches equilibrium at about one-half the weight time (catalyst load) of a fully loaded reactor. Considering that the concentration of products changes as it traverses through the reactor, the mixture approaches equilibrium where the mixture concentration does not change with increasing weight time.

4.8 PLUG FLOW PERFORMANCE

As stated in Chapter 2, the equation to determine the effective rate constant utilized in this effort was derived from the integrated plug flow equation (Equation 2.18). Listed below is an integrated form of the plug flow equation for a first order, irreversible reaction [Levenspiel 1996]:

$$k\tau = \ln\left(\frac{1}{1-X_A}\right) = \ln\left(\frac{C_{Ao}}{C_A}\right) = -\ln\left(\frac{C_A}{C_{Ao}}\right) \qquad \textbf{(4.3)}$$

Considering the total volume of the reactor, τ is equivalent to the V/v_o, where v_o is the volumetric flow rate of the reactant fluid and V is the bed volume and was calculated by:

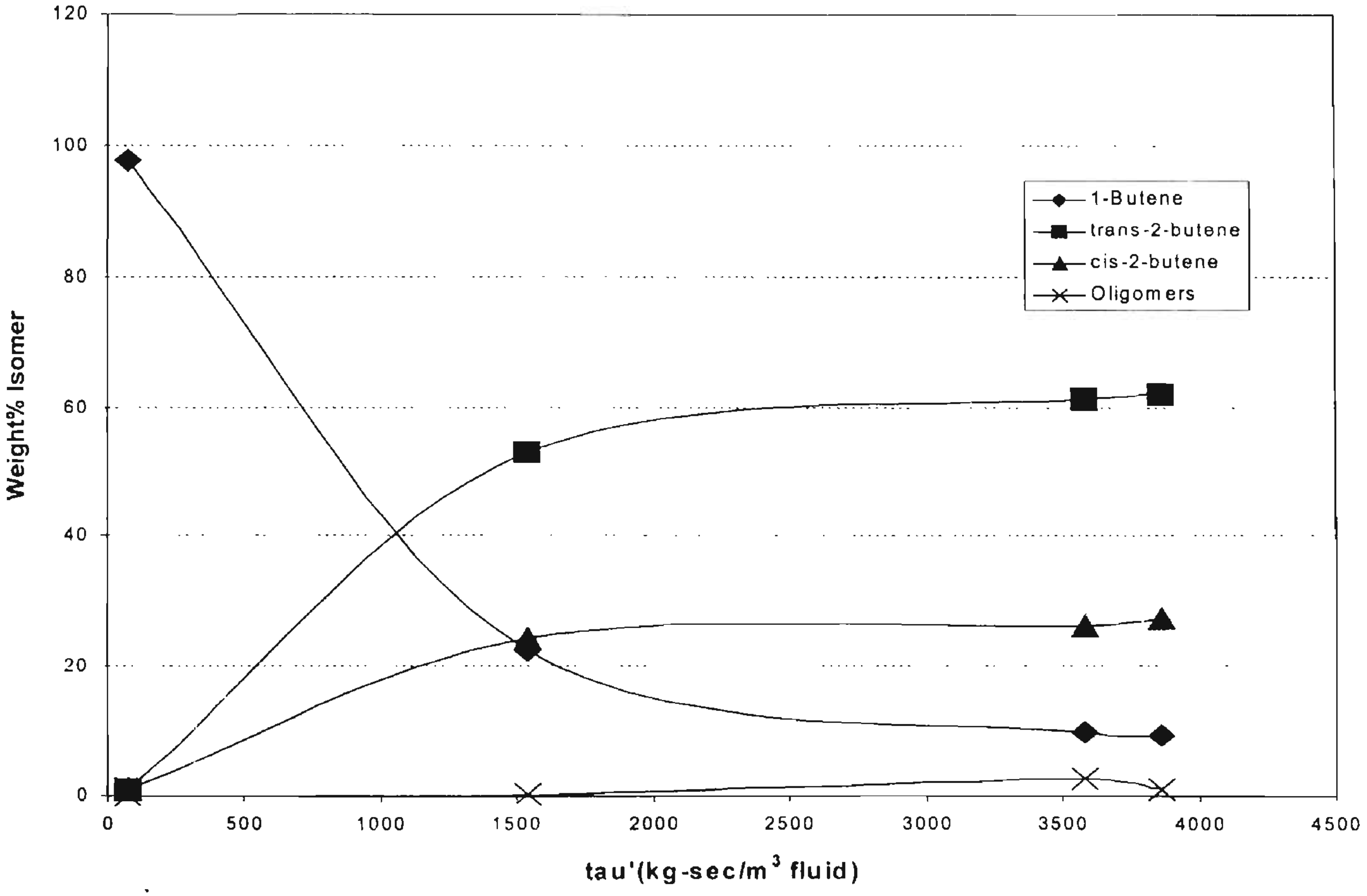


Figure 4.11 Wt% isomer (including oligomers) versus τ'.

$$V = \frac{W}{\rho_b} \tag{4.4}$$

Here, W is the weight of the catalyst in the bed and ρ_b is the bulk density of the catalyst pellet. Considering the above equations, and Equation 2.19, the equation generated for analysis includes the effectiveness factor, η:

$$\eta k = -\left\{ \ln\left(\frac{X_e}{X_o} \right) \right\} \left(\frac{\mathrm{v}}{W} \right) \rho_b \tag{4.5}$$

Here, X_e is the concentration of 1-butene leaving the reactor, and X_o is the concentration of 1-butene entering the reactor. With all butene isomer peaks having an equivalent response factor, and negligible oligomers weight percent, the area percent of 1-butene generated in each chromatogram was equivalent to the outlet concentration of 1-butene. The inlet concentration of 1-butene was extracted from a GC chromatogram when the reactant feed bypassed the reactor bed (refer to Figure 3.1).

At increased space velocities and reduced catalyst loading, the reaction did not reach equilibrium (Appendix B; Run # 17–20 and 23– 25). Experiments were conducted at a space velocity of 1-butene of 50 hr^{-1} and a catalyst loading of 0.3 grams while varying the system temperature. The plot generated from these data (Figure 4.12) was similar to findings from another effort (e.g. 1-hexene isomerization over an acid catalyst) [Clark and Subramaniam, 1999]. Here, the slope of the curve is equivalent to -(E/R) and

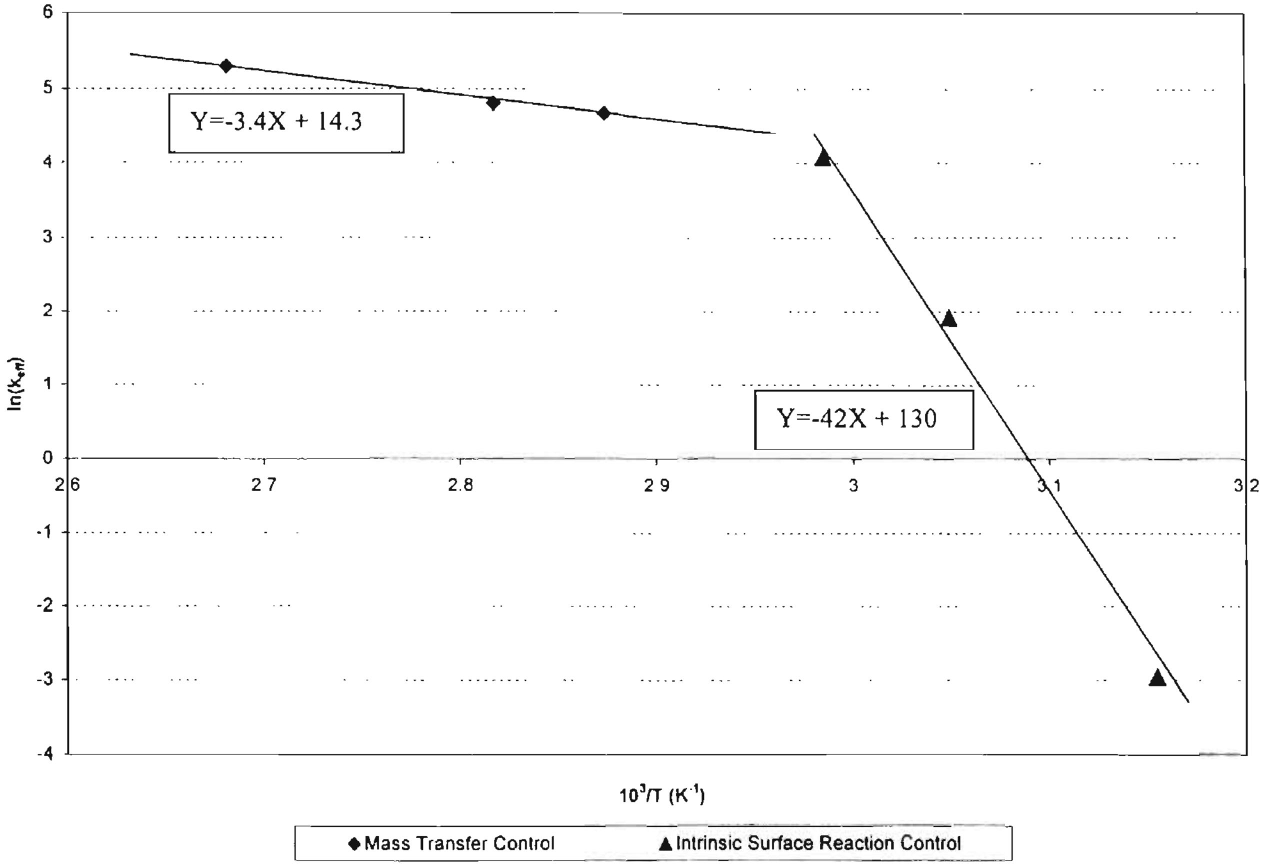


Figure 4.12 Plot Of Ln(Keff) Versus 10^3/T With A Space Velocity Of 50 Hr^{-1} And 0.3 G Nafion™ Composite Catalyst; Varying Temperature.

the ordinate intercept is equivalent to $\ln(k_o)$ [Hill 1977]. Using linear regression, the coefficient of determination, R^2, (which compares estimated and actual y-values and ranges in value from 0 to 1; also quantifies a difference parameter between the estimated y-value and the actual y-value) showed values greater than 99% for all values generated.

The first equation annotated in Figure 4.12 indicates a slope of -3.4. This corresponds to an effective activation energy of 6.8 kcal/mol which is less than the energy of activation of 16 kcal/mol previously reported [Sun *et al.*, 1996]. The ordinate intercept from this linear equation is equivalent to the logarithmic frequency factor of 1.6×10^6/min. Figure 4.12 also shows the slope of the linear equation begins to fall off with increasing temperature. The slope in the second equation is equivalent to –42, which correspond to an effective activation energy of 84 kcal/mol, somewhat larger than the energy of activation of 16 kcal/mol reported previously [Sun *et al.*, 1996]. These differing slopes indicate an activation energy, and temperature, where intraparticle diffusion influences the energy of activation and the calculated or effective energy of activation is removed from the true or intrinsic value [Hill 1977; Satterfield 1980].

The temperature difference for the set of data used to calculate this effective energy of activation was less than 50°C (Figure 4.12). In a similar effort [Clark and Subramaniam, 1999], the temperature difference for the data used to obtain the linear equation via regression was approximately 38°C. In this similar effort, a space velocity of 1-hexene of 138 hr^{-1} over a catalyst loading of 1.0 grams was utilized. It is important for the reaction to be removed from equilibrium for kinetic data to be extracted. When dealing with space velocities of this nature, the axial diffusion becomes significant thereby influencing the external mass transfer limitations for the reaction.

If the Reynolds number, Re, is greater than 10^4 and if the L/D ratio is at least 50, deviations from plug flow because of longitudinal dispersion may be neglected [Hill 1977]. Table 4.10 shows the Reynolds number and the L/D ratio for the data used to extract the effective rate constant and the effective energy of activation.

For the above requirement the Reynolds number, Re, for each experiment to extract the effective energy of activation (Appendix B; Run # 17-20, 23-25) was above 10^3, however, the L/D ratio was extremely low (<<50). Also the D_L/uL ratio is extremely high and is characteristic of large dispersion [Hill 1977]. Hence the performance equation for the plug flow model will not be accurate since the dispersion heavily contributes to mass transfer.

For radial dispersion, the dispersion parameter, D_r, can give an indication if radial dispersion is contributing to mass transfer in the tubular reactor and thus contributes to deviation from plug flow (i.e. radial concentration gradients within the plug or piston flow exists and contributes to mass transfer). A criterion used to determine the effect of radial dispersion is given elsewhere [Sie 1996]. It is shown as follows:

$$L * D_r / (R^2 * u) \gg 1/8 \qquad \mathbf{(4.6)}$$

For the experiments used to determine the effective rate constant and the effective energy of activation, the above parameter equaled 0.5, which is larger than 0.125, so the effect of radial dispersion can be ignored in this case (see Appendix B for data).

Table 4.10 Comparison of Dimensionless Parameters (Re, Pe', And D_L/Ul) for Experiments Aimed to Determine the Effective Rate Constant and the Effective Activation Energy.

Catalyst (g)	**G (g/s-cm^2)**	**Re**	**L/D**	**Pe'**	**D_L (cm^2/sec)**	**D_L/uL**
0.3	1.08	1693	2	0.5	1370	2.2
0.3	1.08	1259	2	0.5	1472	2.2
0.3	1.08	1630	2	0.5	1487	2.2
0.3	1.08	1630	2	0.5	1487	2.2
0.32	1.16	1760	2	0.5	1529	2.1

Hence, a more appropriate material balance equation for the tubular reactor, considering substantial longitudinal dispersion but negligible radial dispersion would be as follows [Hill 1977]:

$$D_L \frac{\partial^2 C_A}{\partial z^2} - \frac{\partial (C_A u_z)}{\partial z} + v_A r_v = 0 \qquad \textbf{(4.7)}$$

For all experiments where data was extracted for the effective rate constant and the effective energy of activation, the longitudinal Peclet number, *Pe'*, is an excellent parameter to gage the degree of longitudinal mixing and deviation from piston or plug flow manner. Figure 4.13 indicates this relationship graphically for a first order reaction [Sie 1996]. Table 4.11 summaries this qualitative description.

As Table 4.11 indicates, the plug flow model can be assumed to exist in the above experiments even though all experimental runs indicate a Peclet number lower than the minimum required for plug flow behavior. Hence Equation 4.5 is a good approximation of the performance of the reactor for these experiments.

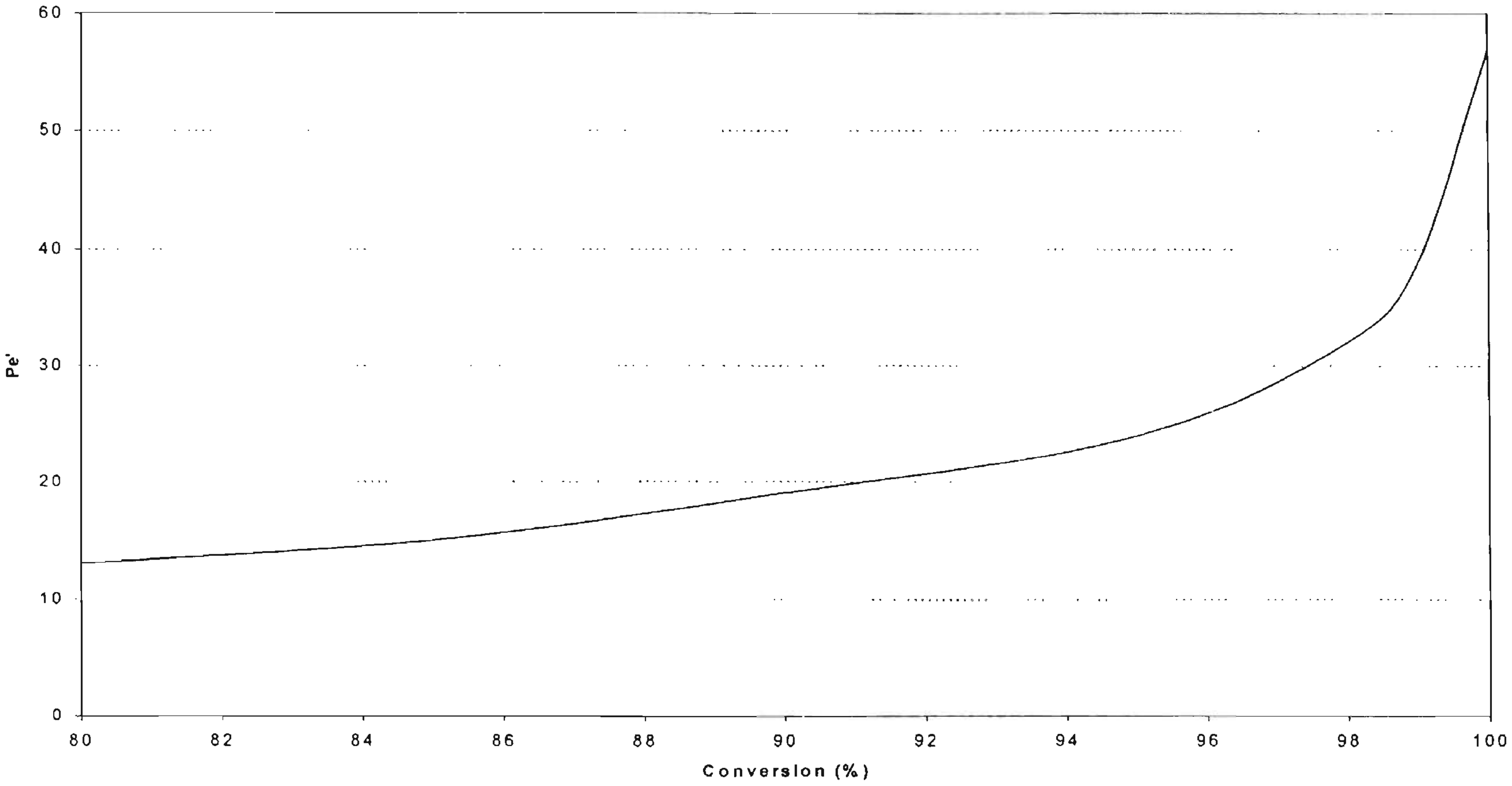


Figure 4.13 Minimum Required Peclet Number, Pe', as a Function of Conversion for a First Order Reaction [Sie 1996].

Table 4.11 Using The Peclet Number, Pe', to Determine Deviation from Plug Flow Assumption for Experiments with Conversions Above 80%.

Run #	$\mathbf{X_A}$	**Pe'**	**Minimum**	**Plug Flow?**
1	.87	11.4	16	Slightly below
3	.905	12.4	19	Slightly below
6	.908	12.3	19	Slightly below
11	.855	11.4	15	Ok
12	.854	10.5	15	Slightly below
13	.85	10.5	15	Slightly below
15	.902	11.9	19	Slightly below
16	.906	2.2	19	Below
18	.874	1.1	16	Below
21	.877	11.4	17	Slightly below
22	.855	5.7	15	Below

CHAPTER 5 – CONCLUSIONS AND RECOMMENDATIONS

The performance of the Nafion™ SAC 25 composite catalyst converted 1-butene to near equilibrium concentration at lower temperatures, pressures and flow rates. Also oligomer production was minimized at these conditions (e.g. 50°C, ambient pressure, and 1.0 $hr^{(-1)}$ mass hourly space velocity of 1-butene). For all flow rates, concentrations, pressures and temperatures tested, the reaction system produced less than 6% oligomers by weight.

Specific conclusions concerning the performance of the reactor and Nafion™ resin/silica nanocomposite as catalyst for this 1-butene isomerization reaction are as follows:

1. Of the three types of catalysts analyzed, Nafion SAC 25, a spherical catalyst bead, converted 1-butene to 2-butenes to near equilibrium concentration matching the results of an earlier examination.
2. At higher temperatures and pressures, the oligomer weight percent was increased in the product stream.
2. The oligomer concentration in the product stream at steady state was negligible at lower temperature (i.e. 50°C) and ambient pressure.
3. Product oligomer concentration decreased with time at all temperatures and pressures tested.
4. The highest production of oligomers, by weight, was six weight percent at a system temperature of 150°C and ambient pressure. The most extreme reaction conditions were carried out at 250°C and 100 psig. Here the weight % of

oligomers in the product stream was 1.5%. Oligomer weight percent for 50°C and ambient pressure with a space velocity of 1.0 hr^{-1} was less than 1%.

5. Nafion™ SAC 13 catalyst (an extruded rod) did not convert 1-butene at 50°C and ambient pressure. At 50°C and ambient pressure, Nafion SAC 13-531 catalyst (an extruded rod) converted 1-butene to product isomers at approximately half the Nafion™ SAC 25 counterpart.
6. The conversion of 1-butene using Nafion™ SAC 25 reached equilibrium concentration and was not affected by the high temperature (230°C) drying process.
7. The integral plug flow model, used to develop kinetic data, proved to be good assumption for fully charged micro flow reactors and with a length to diameter ratio approaching 50.
8. The Peclet number and the axial diffusion coefficient indicated that the integral plug model was not the ideal performance equation to reaction conversion in the system with higher flow rates and reduced length-to-diameter ratios.
9. In all systems tested, radial diffusion was not appreciable and the term could be neglected in the reactor performance equation.
10. 1-butene isomerization with the Nafion™ composite proved to be a durable system; not requiring an exorbitant effort to purify reactants, catalyst or feedstock. The reaction showed almost no dramatic temperature or pressure sensitivity at the conditions tested (i.e. 50°C and ambient pressure to 250°C and 150 psi).
11. At 50°C and ambient pressure, Nafion SAC 25 nanocomposite catalyst converted 1-butene to equilibrium concentration at approximately one-half the weight-time

of a fully charged reactor. The weight-time needed to convert these primary olefins to equilibrium concentration was reduced with increased system temperature.

12. The energy of activation estimated in this effort was 5 times higher than the energy of activation reported previously.

Considering the above conclusions, the following recommendations are included:

1. 1-Butene isomerization using Nafion SAC 25 spherical catalyst should be explored with a mixture composition of 66 weight percent 2-butene and 33 weight percent 1-butene to determine if equilibrium concentration could still be reached at the same conditions tested in this effort.
2. To completely understand the activity and catalyst deactivation of the Nafion™ composite, 1-butene isomerization over this composite catalyst should be conducted for a longer period of time (more than 10 hours obtained in this survey).
3. Deactivation of the catalyst should be reviewed. The activity and kinetic data derived using the Nafion™ composite could be more closely approximated. A deactivation model could be developed and incorporated into the performance equation for industrial operations.
4. This 1-butene isomerization over Nafion™ nanocomposite catalyst should be reviewed in a liquid phase that closely approximates industrial applications.

5. Crush test and attrition tests should be conducted to determine the radial strength and influence on flow during compression.
6. Mercury penetration tests should be conducted on the catalyst to determine the macro pore size distribution. These macropores are instrumental in removing intraparticle mass transfer influences.
7. The tubular reactor design of the BTRS, which is less than optimum for determining the intrinsic kinetic data of a particular system, should be compared to 1-butene conversion over Nafion™ composite catalyst in a differential reactor. This effort would generate intrinsic kinetic parameters for comparison.
8. Experimental dispersion coefficient, from RTD tracer curves, should be generated for a tubular reactor packed with Nafion™ composite catalyst. These axial and radial dispersion parameters would increase the accuracy of the developed reactor performance equation.
9. Surface analysis, including various electron spectroscopic methods, x-ray diffraction crystallography, calorimetry and gravimetric methods should be conducted on the Nafion™ nanocomposite catalyst at different run lengths and various feed rates, temperatures, and pressures. These would be instrumental in showing the possibility of destructive catalytic phenomenon such as sulfonyl acid removal, carbonaceous build up, and deactivation by sintering and calcining effects.
10. Since the maximum operating temperature of Nafion™ nanocomposite catalyst is 280°C, a literature research should be conducted to explore possible reactivation strategies.

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APPENDIX A

Operating Procedures

Start Up Procedure

1. Make sure sufficient gases are available, particularly GC carrier gas.
2. Turn on all gas cylinders
3. Before conducting chemical reaction studies, a thorough review of the following materials should be done:
   a. Autoclave Engineers Benchtop Reactor System Operating Manual, 1991 complete with flow diagrams and schematics. (**A**)
   b. Logicmaster™ 90 Series –30/20/Micro Programming Software User's Manual, (GFK-0466K), 1997. (**B**)
   c. Series 90-30/20/Micro Programmable Controllers, Reference Manual (GFK-0467J), 1997. (**C**)
   d. HP 6890 Series Gas Chromatography
      Volume 1. General Information (**D**)
      Volume 2. Inlets (**E**)
      Volume 3. Detectors (**F**)
   e. HP ChemStation, Understanding Your ChemStation (**G**)
   f. Instruction Manual for Operation and Maintenance of Ruska Positive Displacement Pumps (**H**)

In the steps that follow, the bold faced letters will annotate which guidance document should be reviewed. The page number will be annotated directly after (e.g. H-15 would refer to page 15 of the Ruska Positive Displacement pump guiding document).

Action	Response/Discussion
Develop Experimental Plan	
Identify proposed reaction mechanisms operating conditions and catalyst type	Mechanisms should be used to visualize reaction under study.
Identify proposed reaction mechanisms operating conditions and catalyst type	Should compare the reaction system with the system details. Refer to A - 40 for system settings, gas flow rates, and compatabilities of reactants, products, catalysts, etc.
Determine if flowrates, temperatures, pressures and volume of BTRS is suitable	Compare with system limits, A-15
Determine if products generated would be considered hazardous	Refer to A-40
Determine if reactants are incompatable with BTRS system and hardware	
Load Ruska Pump	
See Valves at positions 1, 2, and 3 Figure 3.2.	
Before mounting the but-1-ene tank, Valves 1, 2, and 3 (see figure 3.2) must be closed	
With Valve-1 closed turn butene tank carefully upside-down	
Place butene tank on stand	Wooden stand should be above the liquid line in on the Ruska Cylinder.
Fit the 1/8th inch stainless steel tubing (with Swagelok fitting) and tightened to the gas regulator.	
Connect vacuum pump to the 1/8th inch stainless steel tubing from the Ruska Pump	
Fill dewar flask with liquid nitrogen.	
Open Valve #3	
Start the vacuum pump and slowly evacuate the Ruska pump cylinder.	
Turn the manual wheel of the Ruska pump until the manual wheel stops.	The plunger should be backed out from the cylinder. Ruska venier scale should read 0 ml.
Allow the vacuum pump to run for several minutes.	This should evacuate the cylinder. This evacuation step is needed to initialize the flow from butene tank to the cylinder. Once a liquid holdup is in the 1/8" line, the cryogenic procedure will not have to be conducted.
Close Valve-3.	
Place ten pounds (10 lbs.) of ice in a 13 gallon garbage bag on the Ruska cylinder	
Allow the ice remain on the Ruska Chamber for approximately one hour to cool with the vacuum pump running	
Return the piston in the Ruska pump fully until the volume reads 250ml	
SCR Motor Control Device	
Set the power switch to the on position	
Place its control knob to "60."	
Close Valve-3	
Open Valve-1 (Figure 3.2).	

Press the "Reverse" button on the SCR control panel	
Allow the Ruska cylinder to operate for about 45 minutes or until the piston is fully withdrawn.	
Close Valve-1.	The volume index on the Ruska Pump should read "0" ml before this step. Ruska should automatically turn off.
Turn the hand wheel in the clockwise direction until pressure increases rapidly	This step is a check to see if if Ruska pump cylinder is filled with liquid but-1-ene. The pressure gauge down stream from the Ruska pump should rapidly increase in pressure.
Turn on GC air, GC Helium, GC Hydrogen, and Process Helium	
Turn main power reactor switch on	
Check for reactor shutdown warning signals	The Hoffman box, and three warning lights are located on the back side of the BTRS. These should not be activated. If these are activated, reset these.
Check hoffman box for down signals, all lights should be green	All lights should be green.
Turn on HP Chemstation workstation and GC	The HP Chemstation is a stand alone PC. Simply turn on the PC and wait for windows to start up.
Open chemstation II for GC operation	After windows in opened, click on the "start" button, click on "programs", click on "HP Chemstations," and click on "Instrument 2 Online"
Open new.m method	With HP Chemstation opened, the method run and analysis window should be activated. There are three list boxes located directly under the Graphical User Interface (GUI) tool bar. These are for click on the Method
Turn on GC HP 6890	The GC 6890 Should be turned on after HP Chemstation. This will allow HP Chemstation to load configuration settings into the GC
On the HP 6890 GC, Press blue button on Keyboard that reads "Front Inlet"	
Use wrench to slightly open union fitting nut to for exit gas coming from purged packed inlet on the gc to the manifold until flow rate reads approximately "100"	Use two 3/8" wrench to slightly open union fitting nut to for exit gas coming from PP on the gc to the manifold. This couple is colored red. Should be attached directly behind the front injector.
Notice flow rate in window; slightly open nut until flow rate reads approximately "100"	
Turn on switch to variac, turn control knob on variac to "42"	
Load catalyst into the reactor	
Remove the upper and lower adaptor coupling to the reactor (20cc)	At this step, the reactor should be stripped down to a stainless steel pipe. Ensure the reactor is clean of debris. You may wish to clean it with soap and water.
Place glass wool in the reactor tube and connect coupling to reactor	
Replace the upper adaptor to the reactor	The thermocouple should be attached to the adaptor device.
Place reactor with funnel attached (use masking taped) on the mass balance	The stand, reactor, adaptor, thermocouple, glass wool, and the tee should be together on the balance at this point.
Tare the balance until the weight equals zero	
Add catalyst until balance reaches targeted weight	

Remove reactor from balance and place reactor back into BTRS	The bottom adapter of the reactor should not be attached. Here the bare-end is then slid into the heating jacket in the BTRS oven. Attach the bottom adapter after the reactor is inside the heating jacket. Refer to A-Drawing 20B-9103.
Preheat catalyst	
Turn on LM90 logicmaster	
Double click the LM-90 Logicmaster icon in the Desktop Window	
Press "F1" to get into Logicmaster Programming Software	
Press "F2" to get into reference tables	
Enter "13q" into status bar	
Ensure that reference table system is in "online" mode	If the LM-90 is not in "online" mode, nothing will happen when data is entered. Refer to B-4-1 for more details.
press <ctrl-m> at the same time to change mode: Press "-" (minus sign) in numeric keypad to start reactor	
Preheat catalyst (reaction run at 150°C)	
Type "1r" in status bar to get to "r" reference tables and press enter	
Type "SP1TOP" into status bar and press enter	
Type "150" and press enter	This sets the upper jacket heater to desired temperature (°C)
Type "SP1MID" in status bar and press enter	
Type "150" and press enter	This sets the upper jacket heater to desired temperature (°C)
Type "SP1BOT" in status bar and press enter	
Type "150" and press enter	This sets the upper jacket heater to desired temperature (°C)
Preheat GC transfer line	
make sure reference table is in view	Refer to B-4-1 for more details.
type "GCX_SP" in status bar and press enter	
type "400"	Sets the effluent product line to the GC to 400. This value is not accurate. The actual temperature is about 50°C.
Preheat Gas Liquid Separator	
make sure reference table is in view	Refer to B-4-1 for more details.
type "GLS_SP" in status bar and press enter	
type "50" and press enter	Sets Gas-liquid separator to 50°C
Set Preheat outgass flow rate	
make sure reference table is in view	Refer to B-4-1 for more details.
type "FEED1" in status bar and press enter	
type "100"	Sets flow rate to approximately 150 sccm
Set oven to preheat temperature	
Make sure reference table is in view	Refer to B-4-1 for more details.
type "VO_SP" in status bar and press enter	
type "200"	This is the maximum temperature that can be written to the valve oven heater. The temperature of the Valve oven box only fluctuates at higher set-point temperatures.
type "ROVN_SP" in status bar and press	

enter	
type "240" and press enter	This step provides all the energy to preheat. The reactor oven is set to this value and maintained during the heating process.
Direct flow rate to both reactor and adsorption chambers	
Make sure reference table is in view	Refer to B-4-1 for more details.
Type "1t" and press enter	
Press "-" (minus sign) in numeric keypad	Sends flow to the first reactor
Type "2t" and press enter	
Press "-" (minus sign) in numeric keypad	Sends flow to the second reactor
NOTE: allow system to achieve temperatures overnight	
Start Reactor for Experimental Run	Reactor conditions T= 150°C P=Ambient Pressure Flow Rate = 5.0 hr^{-1} Gram Catalyst = 3.8 grams Helium to Butene Molar Ration = 1.0:1.0
Make sure the LM90 reference table is in view	Refer to B-4-1 for more details.
Type "1r" on the status line and press enter	Takes you to R reference tables.
Type "rovn_sp" in the status line and press enter	ROVN_SP is the setpoint reference variable for the Reactor oven setpoint.
Type "140" and press enter	Sets the reactor oven setpoint to 140°C. 10°C below reaction temperature. Temperature gradient needed to establish a gradient to remove heat for an exothermic reaction.
Make sure the LM90 reference table is in view	Refer to B-4-1 for more details.
Type "vo_sp" in the status line and press enter	VO_SP is the setpoint reference variable for the valve oven heater.
Type "130" and press enter	Sets the valve oven heater to setpoint = 130°C.
Allow 4 hours for temperatures to reach steady state.	
Experiment with Higher than Ambient Pressure (if pressure is at ambient, skip this section).	If the experiment calls for system pressure is higher than ambient, some alterations are needed.
Remove ball valve directly down line from the gas-liquid separator assembly at the hub fittings attached at the interior BTRS walls.	For ambient pressure, the back pressure regulator (BPR) is bypassed. Hence for higher than ambient system pressure, the Back pressure regulator should be placed back online. Refer to A-Drawing 30A-6199-6 for more details.
Connect the inlet and outlet lines leading to the Back Pressure Regulator.	Refer to A-Drawing 30A-6199-6 for more details. The inlet port should connect directly to the gas-liquid separator; the outlet port to the GC transfer line.
Connect the BPR coil to the BPR power source.	Refer to A-Drawing 40A-6006-1, Item # 36 and 37. NOTE: the power sources elevates the shell temperature of the BPR. If the temperature inceases above fail-safe, the system will shut down.
Make sure the LM90 reference table is in view	Refer to B-4-1 for more details.
Type "1r"	
Type "press"	
Enter (psig) X 10(e.g. 500 for 50 psig)	For instance, for an operating pressure of 50 psig, press = 500
Start Experiment	
Make sure the LM90 reference table is in	Refer to B-4-1 for more details.

view	
Type "1t" and press enter	Gets you to the temporary reference tables
Hit the "-" (minus) sign on the numberic keyboard	Turns on Reactor 1 status valve, sends inlet mixture to reactor 1. Refer to A-Drawing 50-1637-5 (1 of 2)
Type "2t" and press enter	Turns on Reactor 2 status valve, sends inlet mixture to reactor 2. Refer to A-Drawing 50-1637-5 (1 of 2)
Type "1r"	
Analyze temperatures, pressures, and flowrates of different components.	%R0001 to %R0021 are reference variable for these temperatures and pressures. Scroll down these to determine which values are annotated as such.
Conduct Sampling Event	
Record the time of the sampling event in notebook.	
Ensure manual injection valve on top of the GC 6890 is in "bypass" mode	
Press "Front Inlet" button.	Blue button located on GC6890 Keyboard
Ensure "Total Flow" approximately equals 100.	Ensures a 1:100 split in the purged-packed inlet. If this step is not done, severe tailing on the chromatogram will result. Refer to F-58 for details on the Purged-Packed inlet.
Simultaneously press the "Start" button and turn the manual gas valve to "inject"	Starts run. The "ready to inject" status bar will immediately turn to "run in progress"
After a few minutes, return the manual gas injection valve back to "bypass"	This action ensures thorough mixing for next run.
Shutdown Procedure	
Make sure the LM90 reference table is in view	Refer to B-4-1 for more details.
Type "75q" in the status line and press enter	
Press "-" (minus sign) on the numeric keyboard.	This action is preferable for shut down since it assigns all setpoints and flowrates to zero. To turn on system, enter "13q" and press "-" (minus sign).
Turn off all gas cylinders	
On the HP 6890 GC, in the "Method and run control menu," click and drag on the method list-box and until "shutdown.m" method is highlighted.	
Release the left click button.	"Shutdown.m" method is loaded into the GC
Allow 2 hours for GC oven, injectors and detectors to cool to room temperaturer.	
Turn off power to GC	
Exit HP Chemstation	

NOTES

A.1 Loading But-1-ene into the Ruska Pump

- Loaded liquid but-1-ene in the Ruska pump ensures about a six to ten hour reaction runtime.
- But-1-ene, at ambient pressure and temperature, is thermodynamically close to vapor-liquid transition; either the temperature of but-1-ene is lowered or the pressure increased to liquefy the but-1-ene.
- A gas regulator was attached to the but-1-ene tank and placed above the elevation of the inlet opening for the Ruska Pump for to increase head pressure of outlet butene.
- The but-1-ene chamber is mounted in a holding stand upside-down and a 1/8" stainless steel tubing was attached to the gas regulator of the but-1-ene tank.

A. 2 ESTABLISHING HELIUM VOLUMETRIC FLOW

- Standard grade helium was obtained from Sooner Airgas Southwest located in Stillwater, Oklahoma.
- The helium tank was fitted with a gas regulator and connected to a steel 1/8" tubing which was then connected to the mass flow controller system.
- The mass flow controller was calibrated using a bubble-flow meter.

A.3 THE LM90-30 PROGRAMMING CONTROLLER

- For this project the BTRS and attached hardware is controlled by the GE Fanuc Programming Logic Controller (PLC).
- Logicmaster™ LM 90-30 programming software was used to configure and program the PLC.
- Custom designed screens developed by Autoclave Engineers included programming and instrumentation to run the BTRS system at specified operating conditions.
- FIX DMACS software by Intellution was the original supervisory computer software used to operate the BTRS.
- The research team hired a master candidate in electrical engineering with PLC programming experience to rewrite the PLC program originally developed for the BTRS. This student redeveloped the programming sequence to fit the needs of this research effort.
- The developed sequential program used with this BTRS system is manipulated by LM90-30 reference tables.
- Utilizing reference screens in the PLC LM90-30 are outlined in Chapter 4 of the GE Fanuc, Logicmaster™ 90 Series 90TM-30/20/Micro Programming Software User's Manual, *GFK-0466K*.
- In utilizing the reference screen for operation, the operator must use extreme care in effecting changes to the PLC program. The possibility of changing the

programming steps, formally developed by Autoclave Engineers and the OSU-Conoco design group, can be accomplished with relative ease.

- Any inadvertent pressed key can induce a PLC program change thwarting future execution of the BTRS if the operator is not careful.
- System overrides prevent coil operation, which will suspend the output signal sent to an output device.
- Coils for heating were overridden for some tests for various reasons. Overrides must be enacted with extreme care since improper use of the override feature can damage equipment or cause personal injury. Overrides enacted in the program will be felt throughout the program and not just at the cursor location.
- To review more information about system overrides, refer to Section 4-9, GE Fanuc, Logicmaster^{TM} 90 Series 90TM-30/20/Micro Programming Software User's Manual, *GFK-0466K*.

A.4 REFERENCE TABLE MANIPULATION

- Reference table manipulation is operating the BTRS in the programming mode.
- Display formats in reference screens are usually in single integer mode (see page 4-11, GE Fanuc, Logicmaster^{TM} 90 Series 90TM-30/20/Micro Programming Software User's Manual, GFK-0466K).

A.4 VALVE OPENINGS

- The BTRS system was originally designed to operate using two gaseous and two liquid flow streams.
- For this study only one gas inlet and one liquid inlet was utilized.
- Valves for the other inlet ports were placed in the closed position. Closing unneeded valves further eliminated the possibility of leaks.
- Inlet control valves (Table A.2) are located above the feed ports outside the BTRS shell or housing unit. For ease in location, the valves are listed in top-down fashion, as they are located on the BTRS system. For this study, valves are adjusted as annotated in Table A.2. The operator must verify that the gases are supplied at the appropriate pressure.
- The status valve connected to the gas chromatograph (GC) carrier system was bypassed. The carrier gas and analytical valves attached to the BTRS system were closed for this study.

A.5 INLET AIR

- The PLC system utilizes digital-to-pneumatic relays to activate air-actuated valves (AOV).
- An analog coil output is sent to the requisite AOV via analog signal distributed by the PLC. The AOV utilize a pressure gradient to provide sufficient mechanical energy to move valves.
- House air is connected to a port from the ATRC building via a ¾" copper tubing with is connected to a ¾" ball valve. This valve is then connected to a

reduced ½" black steel pipe which is then connected to a compressed air P-trap to knock off precipitation and debris from entering the air system. This system is then connected to ¼" copper tubing which is then connected to the air feed port (B/H-1) of the BTRS (see drawing 50-1637-5).

- The operator should insure that the house air is compressed to at least 90 psig.

A.6 UTILITY SUPPLY

- Utilities needed to operate the BTRS and the gas chromatography system effectively are outlined in the Reaction-Chromatography Systems, Autoclave Engineers Micro-Scale Bench-Top Reaction System Installation, Operation and Maintenance Manual, *July 1991*).

A.7 VOLUMETRIC FLOW

- In this study the mixture flow rates, or mass hour space velocity was calculated using catalyst weight-time.
- A pre-weighed amount of Nafion™ catalyst loaded into either the 5ml or the 20ml tubular reactor. After carefully packing catalyst into the tubular reactor, the reactor tube was weight an a Mettler balance.
- The Nafion™ was then dried in a continuous flow of helium at approximately 230°C with approximately 150 ml/min of helium was charged over the Nafion™ catalyst to remove any additional adsorbed water.

A.8 HEAT TRANSFER

- The BTRS has three distinct systems to provide energy as heat to the reactor system. These are:
  - Valve oven heater – assembly provided heat for the premixing section of the BTRS.
  - Reactor Oven assembly – to provide a stable thermal environment.
  - Reactor tube-jacket heaters – provide direct energy to the reactor for Isothermal operation and stability.
  - Gas/liquid separator box heater – assembly provided heat to ensure a stable thermal environment for gas/liquid separation in the headspace of the separator. This essentially knocked out by-product liquid which could clog transfer lines, hinder product vapor transport and introduce error in analysis.
  - Gas transfer line heater (segment #1). This system provided heat to the gas (vapor) transfer line where continuous energy is provided to maintain steady temperature. The PLC is programmed to ensures steady an isothermal transfer of product. The apparatus is insulated with asbestos.
  - Transfer line heater (segment #2) – the segment is heated by heating tape wrapped around the 1/8th inch stainless steel tubing. Tubing is insulated with poly-foam pipe insulation. The segment is approximately four feet in length.

- Valco box heater – internal heating element provides heat and insulation to stabilize the sample segment prior to its entrance into the GC column. The power source is adjusted by a variac.

- For system temperatures below 100°C, the heating elements for the reactor jackets were turned off. The operator can achieve this in either two ways. First the operator may complete a system override; essentially assigning a "0" or turning off the analog output signals which is sent directly from the PLC unit to the heating element. This action leaves the heating elements off during the PLC sweep, thereby insuring the PLC sequential program and other parameters are not affected by the override. For BTRS system temperatures 100°C or above, the operator simply utilizes the PLC program, utilizing encoded set-points, to establish a correct temperature setting within the BTRS.

A.9 MECHANICAL SAFETY FEATURES

- Before operation, the operator should ensure that BTRS equipment meet specifications for the reaction conditions identified.
- Operating temperatures and pressures of reactants and products should be reviewed to determine if these would potentially harm equipment and personnel.
- Rupture disks of sufficient quality and design should be checked for the intended experiment to be run.

- Information on rupture disks are outlined in the flow schematic (see drawing 50-1637-5 of the Reaction-Chromatography Systems, Autoclave Engineers Micro-Scale Bench-Top Reaction System).

A.10 SETTING GAS FLOW RATES

- Inlet gas flows for purging the two ovens, tubular reactor systems, gas and liquid inlet flow systems, and analytical systems must be set to approximately 30 ml/min for each line receiving purge gas.
- A bubble flow meter and the three way ball valves were set to flow rates as described (Table A.2). These valves were set to "vent" with a bubble flow meter attached to the exit conduit. Flow rates were then set to 30 ml/min. The "metering" valve next to three way ball valves was used to set flow rates. After these rates were set, the three-way valves was returned to the "SYS" position.
- Utility gases are connected to the BTRS system via 1/8" flow stainless-steel or copper tubing. Gases are stored in vertical gas cylinders that are provided by an outside supplier. Each vertical cylinder is fitted with a compressed gas regulator. These regulators are set using set-points described in Table A.3.
- After connecting gas cylinders to the BTRS via 1/8" tubing the operator should check for leaks using a portable gas leak detector or soap film detector. All fittings, regulators and connections should be tested for leaks.

Table A.1 Subsystems and components of the BTRS

Component
I. Feed Preparation
Mass Flow Controller
N_2 Purge Port 3-Way Valve
N_2 Calibration Needle Valve
Ball Valve, Whitey Type, 1/8"
Ruska Positive Displacement Pump w/ Ultracon II Variable Flow Controller
Butene Cylinder Holding Stand
Gas Regulator (30 lb. max.)
Toggle Handle Valve, 1/8"
Pressure Gauge, Ashcroft Type 1008, 5000 lb. Max
Manual Pressure Regulator, Go Inc.
Ball Valve (1), 1/8"
Ball Valve (2), 1/8"
HPLC Liquid Pump
II. BTRS Reactor System
Reactor Oven Assembly
Reactor Assembly
Furnace Assembly
Heater Assembly
Valve Oven Assembly
Mixer Assembly
Furnace Assembly
Heater Assembly
Injection Port Assembly
Automatic Separator Assembly
Liquid Level Controller
Back Pressure Regulator
Inlet/Outlet Pressure Gauge Assembly
Gas Transfer Line
III. HP 6890 Gas Chromatograph
Packed Inlet
Supelco DH Petrocol Capillary Column, 100m x 250μm x .5μm,
Flame Ionization Detector
HP Chemstation Software
VICI 2-Way Gas Sampling Valve (#3C6WP) w/ HVE-B Heated Valve Enclosure

Table A.2 Valve Position Settings for BTRS During Experiment.

VALVE	SYSTEM	OPERATION	SETTING
V-S23	Reactor 1 Purge Vent	Reactor purge outlet flow adjust	Adjusted open
V-S43	Reactor 2 Purge Vent	Reactor purge outlet flow adjust	Adjusted open
V-S22	Reactor 1 Purge Feed	Inlet flow adjust	"ON"
V-S42	Reactor 2 Purge Feed	Inlet flow adjust	"ON"
V-S21	Reactor 1 Purge Feed	System failsafe purge	Adjusted open
V-S41	Reactor 2 Purge Feed	System failsafe purge	Adjusted open
V-S12	System Failsafe Purge Feed	System purge feed (mixer box purge gas ball valve)	Adjusted open
V-S13	System Failsafe Purge Feed	System purge feed (mixer box purge gas 3 way valve)	"SYS"
V-F12	Feed 1	Gas Feed 1 adjustable ball valve	Adjusted open
V-F13	Feed 1	Gas Feed 1 three way valve	"SYS"
V-F12	Feed 2	Gas Feed 2 adjustable ball valve	Closed
V-F23	Feed 2	Gas Feed 2 three way valve	"OFF"
V-F32	Feed 3	Gas Feed 3 adjustable ball valve	Closed
V-F33	Feed 3	Gas Feed 3 three way valve	"OFF"
V-F42	Feed 4	Gas Feed 4 adjustable ball valve	Closed
V-F43	Feed 4	Gas Feed 4 three way valve	"OFF"
V-S31	Reactor Oven Purge Feed	Reactor oven purge ball valve	Adjusted open
V-S32	Reactor Oven Purge Feed	Reactor oven purge three-way valve	"SYS"
(no name)	Valve Oven Purge Feed	Valve oven purge ball valve	Adjusted open
(no name)	Valve Oven Purge Feed	Valve oven purge three-way valve	"SYS"
V-A12	GC Carrier Input	GC carrier gas input three-way valve	"OFF"
(no name)	GC Carrier Input	GC carrier gas input ball valve	Closed

Table A.3 Flow Rate Settings for BTRS

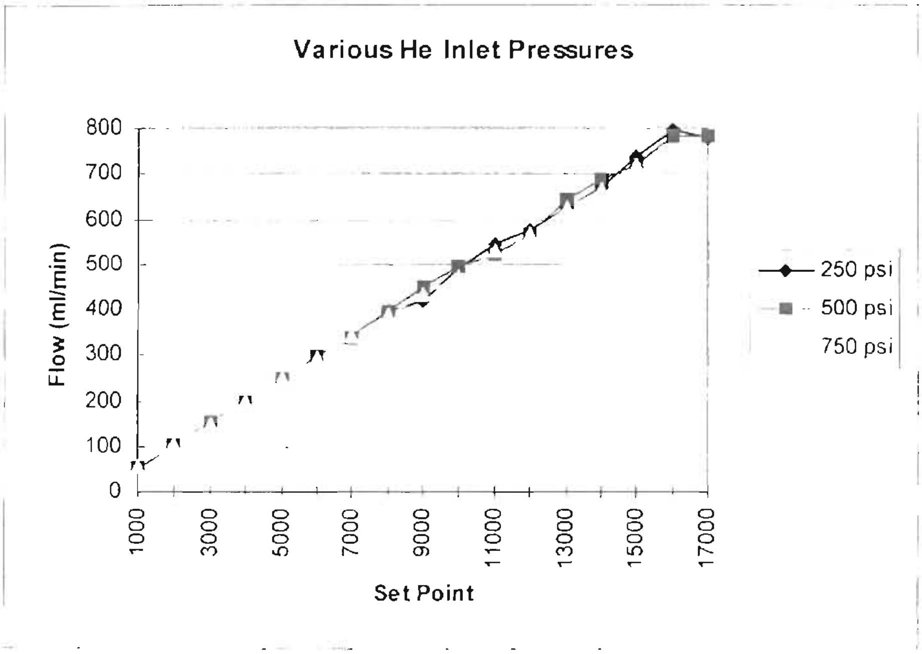
SUPPLY	PURPOSE	PRESSURE (PSIG)	TYPICAL USAGE
Air	Valve Actuators	90	2cyl/yr
He	Cap. GC Carrier	80-100	30 cc/min
He	Pack. GC Carrier	80-100	30 cc/min
N_2	HTS Carrier	80-100	30 cc/min
N_2	H.P. Purge (Reactor & System Failsafe)	20 PSI Above Reaction Pressure	30 cc/min
N_2	Reactor Oven Purge	80-100	30 cc/min
N_2	Valve Oven Purge	80-100	30 cc/min
N_2	GC Valve Oven Purge	80-100	30 cc/min
CO_2	Cryogenic Cooling	800-1200 (liquid)	30 LB/day
H_2	Flame Ionization Detector	25	30 cc/day
Air	Flame Ionization Detector	30	300 cc/min
Liquids	Reactants	0-10	< 3 ml/min
Gases	Reactants	50 PSI or Greater Above Reaction Pressure	cc/min

A.2 Calibrating the Mass Flow Controller

I conducted various inlet pressure tests for the Mass Flow Controller. By varying the pressure of inlet gas, in this case standard helium, I was able to make some determinations about the Mass Flow Controller, namely the effects of varying inlet pressure to outlet stream flow.

The inlet pressure was varied between 250, 500 and 750 psig and inlet set-point flow rates were initiated at 1000 and increased to 15,000 (some instances higher). I used a stop watch and a flow meter to determine the flow of helium as it exited the Mass Flow Controller before it entered the reactor. With these I calculated the flow rate (ml/min).

The results - varying inlet pressure to the Mass Flow Controller has no effect on outlet flow rate. The graph below indicates that the data are quite similar in regions between set point values from 1000-7000. However, at higher values of set-point (above 7000) the calculated flow was less accurate. These errors were attributed to reaction time of the stopwatch, the time between formulation of a bubble in the flow meter and the initiation of the stopwatch. Human reaction time produced significant error, especially at higher set-points.



The set point actual value posed some questions. The value jumps in multiples of 16. In other words, the actual flow reading (to the Logic Master 90 interface) would jump from 10,000 to 10,016 to 9,884 and back to 10,000. When I would increase the flow rate from 1000 set-point to 2000, the MFCACT (Mass Flow Controller Actual) would jump to 2064, decrease to 2048, then to 2032 before resting at 2000. The data indicate that all actual even-numbered values would finally rest on the set-point value, but the odd-numbered values would rest on other values (e.g. for 3000 set-point, the final resting point would be 2992 or 3008).

APPENDIX B

Run Matrix

Variable	Units	Description
#		Run Number
Date		Date run was conducted
CAT.		Catalyst type: SAC 25; SAC 13; SAC 131-531
Weight Cat	(grams)	Dry weight of catalyst in grams
Cat Mix		The mixture mass ratio of catalyst to inert
MHSV	(hr^{-1})	Mass hourly space velocity for 1-Butene
Flow Ratio	(he:bu)	Molar flow ratio of helium to butene
T	(^{o}C)	Target temperature
P	(psig)	Target pressure
V_{He}	(ml/min)	Calculated volumetric flow of helium
V_{1-B}	(ml/min)	Calculated volumetric flow of 1-butene
F_{He}	(mol/hr)	Calculated molar flow of helium
F_{1-B}	(mol/hr)	Calculated molar flow of 1-butene
t_{sample}	(min)	Time elapsed after fluid stream was sent to reactor
TC1	(^{o}C)	Temperature of the reactor bed temperature
TC2	(^{o}C)	Temperature of the Alumina bed temperature
rovn	(^{o}C)	Temperature of the reactor oven
vo	(^{o}C)	Temperature of the valve oven
R1t	(^{o}C)	Temperature of the zone closest to the inlet
R1m	(^{o}C)	Temperature of the zone in the middle of the reactor
R1b	(^{o}C)	Temperature of the zone at the bottom of the reactor
AIPTV	(psig*10)	System pressure at reactor inlet
GC		GC Run number
%A 1-b		Wt% 1-butene in product stream
%A t-b		Wt% of t-2-butene in product stream
%A c-b		Wt% of c-2-butene in product stream
%A 1iso		Wt% of first butene isomer in product stream (Isobutene)
%A olig		Wt% all other (oligomers)
Type		20 cc or 5 cc reactor
$X_{A,butene}$		Calculated conversion of 1-butene
k_{eff}	(min^{-1})	Calculated value for the effective rate constant
C_{A0}	(mol/m^3)	Inlet 1-butene concentration
(tau)'	(kg-s/m^{3}fluid)	Weight time of 1-butene over catalyst and at flow conditions
ln(k)		Natural log of the effective rate constant k_{eff}
Ave P	(psig*10)	Pressure reading sent back from PLC; equivalent to P_{sys} * 10
G	(g/sec-cm^2)	Superficial gas velocity
T_c'	(K)	Combined critical temperature of the mixture in the system
p_c'	(atm)	Combined critical pressure of the mixture in the system
u_c'	(g/cm-sec)	Combined critical viscosity of the mixture in the system
T_r'		Reduced temperature of the mixture in the system
p_r'		Reduced pressure of the mixture in the system
u_r	(table)	Reduced viscosity of the mixture in the system
u	(g/cm-sec)	Actual viscosity of the mixture in the system
Re		Reynolds number
L/D		Length to diameter ratio of the reactor
L/d_p		Ratio of the length of the reactor to the diameter of the catalyst particle
kT/E_{AB}		Boltzmann constant, Temperature, and energy of mol. Interaction
Omega$_D$	(Table)	Collision integral
D_{AB}	(cm^2/sec)	Molecular diffusion coefficient
den	(g/ml)	Density
Sc		Schmidt Number

Variable	Units	Description
$Pe_{,Dp}$		Pectlet number for using catalyst particle diameter as a length reference
D_L	(cm^2/sec)	Calculated axial dispersion parameter
Pe'		Radial Peclet correction parameter
Pe_f		Radial Peclet correction parameter
Pe_r		Radial Peclet number
D_r	(cm^2/sec)	Calculated radial dispersion parameter
D_L/uL		Inverse Peclet number using the length of reactor as a reference
$L*D_r/(R^2*u)$		Correlation to detemine degree of radial dispersion that affects plug flow

#	Date	CAT.	Weight Cat (grams)	Cat Mix	MHSV (hr^{-1})	Flow Ratio (he:bu)	T (°C)	P (psig)	V_{He} (ml/min)	V_{1-B} (ml/min)
1	5/15/00	SAC 25	20.0076	1	2.5	1.0:1.0	200	0	575.347	574.0809
			20.0076						575.347	574.0809
2	5/19/00	SAC 13-1	5.6	1	2.51	1.0:1.0	200	0	161.967	160.5826
			5.6						161.967	160.5826
3	5/24/00	SAC 25	21.7	1	0.99	1.0:2.01	50	0	84.6584	166.3371
			21.7						170.655	166.3371
4	5/25/00	SAC 25	21.7	1	0.98	1.21:1.0	50	50	45.9193	34.1176
			21.7						45.9193	34.1176
5	5/26/00	SAC 25	21.7	1	0.99	1.21:1.0	50	100	26.2456	17.43084
			21.7						26.2456	17.43084
6	5/28/00	SAC 25	21.7	1	0.98	1.0:1.0	150	0	216.825	216.0618
			21.7						216.825	216.0618
7	5/30/00	SAC 13-1	5.56	1	2.5	1.0:1.0	50	0	109.808	107.2656
			5.56						109.808	107.2656
8	6/2/00	SAC 25	3.8	1	2.51	0.0:1.0	50	0	0	72.68284
			3.8						0	72.68284
9	6/3/00	SAC 25	3.8	1	2.51	1.0:1.0	50	0	74.9229	72.68284
			3.8						74.9229	72.68284
10	7/3/00	SAC 25	3.8	1	4.97	1.0:1.0	100	0	171.766	169.6909
			3.8						171.766	169.6909
11	7/5/00	SAC 25	7.6	1	2.51	1.0:1.0	250	0	243.44	241.5626
			7.6						243.44	241.5626
12	7/6/00	SAC 25	7	1	2.51	1 0:1.0	250	50	51.3546	49.97639
			7						51.3546	49.97639
13	7/7/00	SAC 25	7	1	2.51	1.0:1.0	250	100	34.6087	33.81657
			7						34.6087	33.81657
14	7/9/00	SAC 13-2	4.9	1	2.46	1.0:1.0	50	0	97.639	92.85202
			4.9						97.639	92.85202
15	7/10/00	SAC 25	20.8	1	0.96	1.24:1.0	50	0	194.994	153.562
			20.8					bypas	194.994	153.562
16	8/11/00	SAC 25	3.8	1	4.96	1.01:1.0	150	0	195.844	192.6737
			3.8						195.844	192.6737
17	8/13/00	SAC 25	0.3	1	50.8	1.0:1.0	50	0	118.733	117.4907
			0.3						118.733	117.4907
18	8/15/00	SAC 25	2		50.8	1.0:1.22	200	0	962.594	1165.14
			2						962.594	1165.14
19	8/16/00	SAC 25	0.3		50.8	1.0:1.0	200	0	129.755	123.5304
			0.3						129.755	123.5304
20	8/17/00	SAC 25	0.3		49.39	1.02:1.00	75	0	127.918	123.6727
			0.3				75		127.918	123.6727
			0.3				100		137.104	133.0164
21	3/31/00	SAC 25	20.0076	1	1.2	1.0.1.0	200	0	271.252	268.7539
22	8/30/00	SAC 25	10	1	1	1.2:1.0	50	0	83.0358	81.58652
			10						83.0358	81.58652
23	9/1/00	SAC 25	0.32	1	50.27	1.0:1.0	63	0	131.948	129.3661
			0.32						131.948	129.3661
24	9/7/00	SAC 25	0.32	1	50.27	1.0:1.0	83	0	139.799	137.5308
25	9/7/00	SAC 25	0.3	1	50.27	1.0:1.0	44	0	116.161	113.1514
KU	KU	KU	1	1	137.59		50	0	1079	1060.432

#	F_{He} (mol/hr)	$F_{1\text{-}B}$ (mol/hr)	t_{sample} (min)	TC1 (°C)	TC2 (°C)	rovn (°C)	vo (°C)	R1t (°C)
1	0.889133	8.94E-01	0	201	190	190	185	200
	0.889133	8.94E-01	65.05	-	-	-	-	-
2	0.250952	2.50E-01	0	199	190	190	185	200
	0.250952	2.50E-01	60	200	190	190	185	200
3	0.189835	3.81E-01	0	50	51	51	44	51
	0.38267	3.81E-01	159	55	50	51	44	54
4	0.456964	3.77E-01	0	48	48	51	44	50
	0.456964	3.77E-01	60	54	52	52	44	52
5	0.462781	3.81E-01	0	50	43	42	35	50
	0.462781	3.81E-01	180	50	42	42	35	50
6	3.75E-01	3.77E-01	0	149	132	130	125	150
	3.75E-01	3.77E-01	300	155	131	130	125	150
7	0.247969	2.47E-01	0	50	52	50	42	50
	0.247969	2.47E-01	123	49	50	50	42	50
8	0	1.70E-01	0	49	50	50	42	50
	0	1.70E-01	150	49	50	50	42	50
9	0.171225	1.70E-01	0	49	49	50	42	50
	0.171225	1.70E-01	600	49	49	50	42	50
10	0.336581	3.37E-01	0	97	99	100	76	98
	0.336581	3.37E-01	210	98	97	100	76	98
11	0.340831	3.40E-01	0					
	0.340831	3.40E-01	380	248	233	240	200	250
12	0.316087	3.13E-01	0	247	234	239	200	249
	0.316087	3.13E-01	360	248	233	240	200	250
13	0.377786	3.81E-01	0	247	234	240	200	250
	0.377786	3.81E-01	375	248	234	240	200	250
14	0.221306	2.15E-01	0	50	39	45	36	51
	0.221306	2.15E-01	360	52	44	44	36	50
15	0.440776	3.55E-01	0	48	43	40	32	50
	0.440776	3.55E-01	360	54	44	45	37	52
16	0.338416	3.36E-01	0	156	141	139	129	154
	0.338416	3.36E-01	330	156	141	140	130	154
17	0.268659	2.72E-01	0	53	48	50	41	53
	0.268659	2.72E-01	240	55	50	50	40	54
18	1.487579	1.81	0	202	190	190	180	201
	1.487579	1.81	85	207	190	190	180	204
19	0.268659	0.268	0	70	50	60	50	61
	0.268659	0.268	150	79	60	60	50	77
20	0.268659	0.264	0	69	39	50	40	76
	0.268659	0.264	300	74	74	75	65	74
	0.268659	2.64E-01	344	100	83	90	80	97
21	0.420278	4.19E-01	90	203	190	190	185	202
22	0.187887	1.89E-01	0	47	50	50	40	48
	0.187887	1.89E-01	540	51	50	50	40	51
23	0.287016	2.87E-01	0	62	63	63	53	63
	0.287016	2.87E-01	540	62	63	63	53	63
24	0.287016	2.87E-01	450	82	83	83	73	83
25	0.268659	2.68E-01	155	44	44		53	
KU	2.442455	2.45						

#	R1m (°C)	R1b (°C)	AIPTV (psig*10)	GC	%A 1-b	%A t-b	%A c-b	%A 1iso
1	204	202	237	-				
	-	-	-	sig10113.d	12.95318	55.56788	31.22422	0.25473
2	204	201	63	-				
	204	202	63	sig10114.d	98.87255	0.42504	0.46295	0.23946
3	51	51	47	-				
	54	53	50	sig10119.d	9.42022	62.08302	27.32795	0.25164
4	50	49	503	sig10122.d	99.63976	0	0	0.24217
	53	53	514	sig10123.d	37.79469	35.27347	26.58958	0.25318
5	52	51	969					
	52	51	1011	sig10126.d	63.74572	17.02888	18.34827	0.48163
6	153	149	62					
	154	150	65	sig10132.d	9.13963	58.17795	28.739	0.2892
7	50	50	26					
	50	49	31	sig10134.d	99.65876	0	0	0.23421
8	50	50	21					
	50	50	-2	sig10136.d	62.41764	20.97545	16.30375	0.24371
9	50	49	21					
	50	50	14	sig10142.d	22.39446	52.89118	24.24156	0.23928
10	98	98	53					
	98	98	45	sig10374.d	63.69886	14.58671	16.22068	0.21544
11								
	252	251	76	sig19379.d	14.39471	50.11186	30.89111	0.21633
12	252	250	499					
	252	251	497	sig10385.d	14.52037	50.53873	30.92155	0.21861
13	252	250	976					
	251	251	996	sig10388.d	14.983	51.76501	31.53132	0.2348
14	53	52						
	52	51	22	sig10391.d	47.22458	28.69223	22.94226	0.2201
15	51	49	67					
	55	54	50	sig10396.d	9.76053	61.39317	26.1434	0.22776
16	159	157	44					
	159	158	43	sig10401.d	9.36661	55.51897	28.87525	0.2224
17	55	55	29					
	57	56	30	sig10404.d	97.70633	1.00129	1.03389	0.22334
18	205	204	228					
	209	206	269	sig10405.d	12.55805	43.76404	26.5966	0.18396
19	77	76	18					
	84	83	24	sig10408.d	76.69044	13.58954	9.32434	0.22314
20	73	76	23					
	74	74	28	sig10411.d	75.20493	14.5318	9.95273	0.22387
	100	99	14	sig10412.d	60.77373	24.02122	14.79952	0.22258
21	206	203	76	conoco	12.3	53.9	29.8	
22	48	48	6					
	51	50	15	sig10420.d	11.43835	61.49087	25.30276	0.22679
23	63	62	28					
	63	62		sig10425.d	84.76896	8.40645	6.48956	0.22219
24	82	82	35	sig10441.d	73.03498	15.59352	11.10177	0.21834
25				sig10442.d	99.58842	0.05562	0.12609	0.21238
KU								

#	%A olig	Type	$X_{A,butene}$	k_{eff} (min^{-1})	C_{A0} (mol/m^3)	(tau)' ($kg\text{-}s/m^3$fluid)	ln(k)	Ave P (psig*10)	G ($g/sec\text{-}cm^2$)	T_c' (K)	p_c' (atm)
1		20						237.00	3.57	213	31.3
	0.00	20	0.870	5.27E+01	12.962966	1.04E+03	3.97				
2		5						63.00	1 01	212	31 2
	0.00	5	0.007	1.91E-01	12.9179019	1.04E+03	-1.66				
3		20							0.76	282	34 1
	0.92	20	0.905	1.65E+01	18.8431661	3.86E+03	2.80				
4	0.12	20						509.00	1.83	193	30.4
	0.09	20	0.621	1.61E+00	78.5054168	1.63E+04	0.48				
5		20						926.80	1.86	192	30.4
	0.40	20	0.360	4.04E-01	145.387407	2.98E+04	-0.91				
6		20						68.00	1.51	213	31.3
	3.65	20	0.908	2.14E+01	14.514947	3.01E+03	3.07				
7		5						31.50	1.00	212	31.2
	0.11	5									
8		20						3.75	0.00	420	39.9
	0.06	20	0 373	4.02E+00	38.9821495	3.14E+03	1.39				
9		20						11.25	0.69	212	31.2
	0.23	20	0.775	2.61E+01	19.1952749	1 54E+03	3.26				
10		20						50.29	1.35	213	31.3
	5.28	20	0.360	1.81E+01	16.4491282	6.68E+02	2.89				
11		5						80.00	1.37	212	31.2
	4.39	5	0.855	5.55E+01	11.6837934	9.40E+02	4.02				
12		5						501.6667	1.27	212	31.2
	3.80	5	0.854	1.25E+01	51.4814435	4.14E+03	2.53				
13		5						996.25	1.52	213	31.3
	1.49	5	0.850	8.33E+00	92.8019179	6.14E+03	2.12				
14		5						14.00	0.89	210	31.1
	0.92	5	0.526	1 31E+01	18.8110325	1.54E+03	2.57				
15		20						49.13	1.77	190	30 3
	2.48	20	0.902	1.75E+01	16.9748097	3.58E+03	2.86				
16		20						46.50	1.36	212	31.2
	6.02	20	0.906	1.09E+02	14.4137614	5.87E+02	4.69				
17		5						31.00	1.08	214	31.3
	0.04	5	0.019	6.81E+00	19.1908895	7.62E+01	1.92				
18		20							5.97	233	32.1
	16.90	20	0.874	9.91E+02	14.1778354	5.64E+01	6.90	358.80			
19		5							1.08	212	31.2
	0.17	5	0.230	9.93E+01	17.6349017	7.11E+01	4.60	21.50			
20		5							1.08	211	31.2
	0.09	5	0.245	1.06E+02	17.4887158	7.15E+01	4.66				
	0.18	5	0.390	2.00E+02	16.2890507	6.66E+01	5.30	24.5			
21	1.90	20	0.877	8.10E+01	12.9319671	2.22E+03	4.39	76	1.69	212	31.2
22		20						19.3	0.75	213	31.3
	1.54	20	0.885	1.60E+01	19.1347055	3.64E+03	2.77				
23		5						29	1.16	213	31.2
	0.11	5	0.149	5.93E+01	18.3048976	7.35E+01	4.08				
24	0.05	5	0.267	1.21E+02	17.2478221	6.92E+01	4.80	35	1 16	213	31.2
25	0.02	5	0.000	5.20E-02	19.4785561	7.85E+01	-2.96	35	1.08	212	31.2
KU		5							9.85	213	31.3

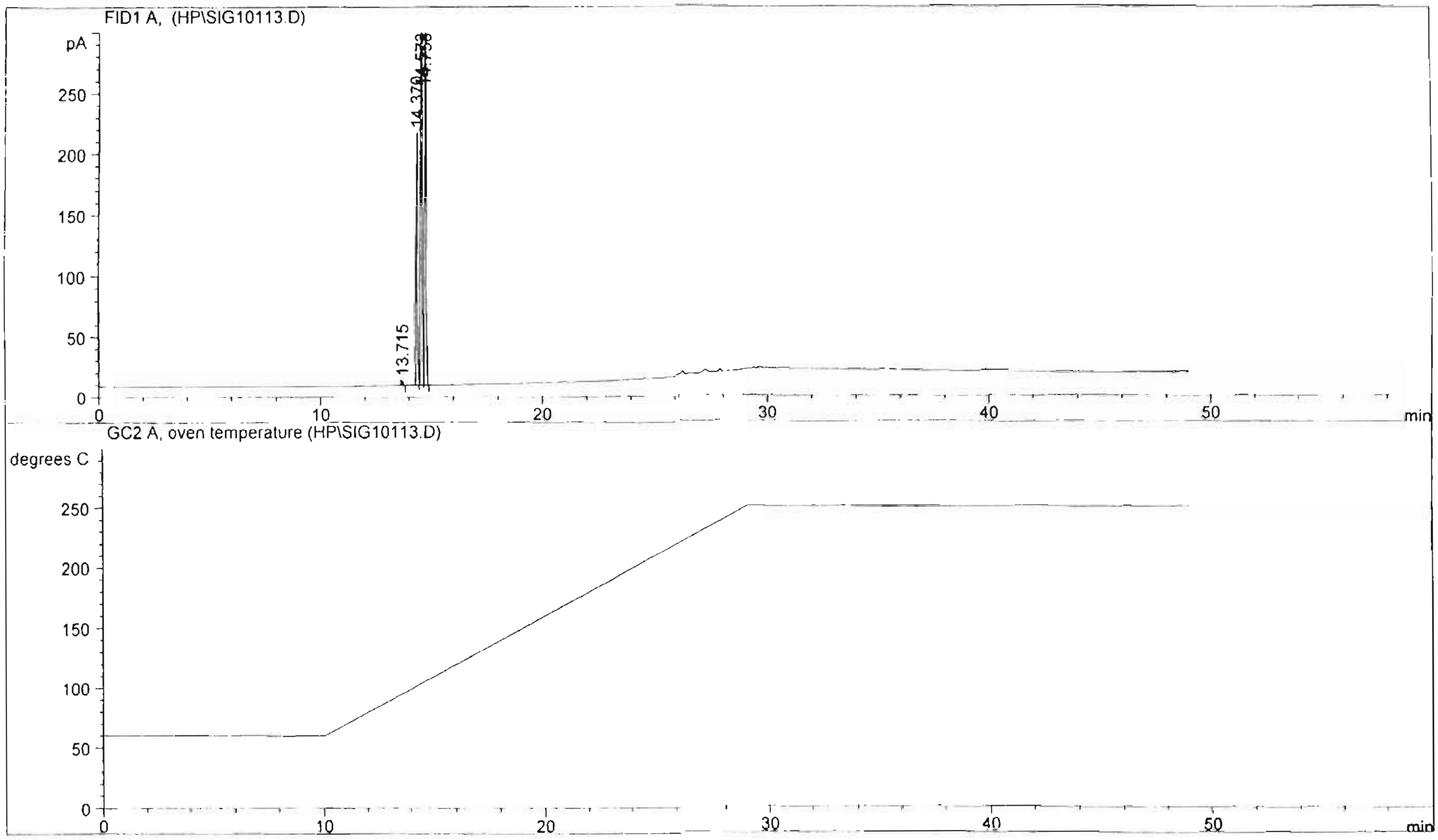
#	u_c' (g/cm-sec)	T_r'	p_r'	u_r (table)	u (g/cm-sec)	Re	L/D	L/d_p	kT/E_{AB}	Omega$_D$ (Table)	D_{AB} (cm^2/sec)
1	1.69E-04	2.22	0.032	0.91	1.54E-04	4050	26	191.5	13.18	0.717	7.95E-02
2	1.69E-04	2.23	0.032	0.91	1.54E-04	1151	31	141.5	13.18	0.717	7.95E-02
3	1.95E-04	1.15	0.029	0.6	1.17E-04	1145	28	207.7	9.00	0.7556	9.13E-02
4	1.62E-04	1.68	0.145	0.7	1.13E-04	2829	28	207.7	9.00	0.7556	2.07E-02
5	1.62E-04	1.68	0.257	0.7	1.13E-04	2867	28	207.7	9.00	0.7556	1.17E-02
6	1.69E-04	1.99	0.032	0.85	1.44E-04	1831	28	207.7	11.79	0.728	8.28E-02
7	1.69E-04	1.52	0.032	0.65	1.10E-04	1592	31	140.4	9.00	0.7556	9.13E-02
8	2.45E-04	0.77	0.025	0.34	8.33E-05	4	5	36.36	9.00	0.7556	9.13E-02
9	1.69E-04	1.53	0.032	0.65	1.10E-04	1095	5	36.36	9.00	0.7556	9.13E-02
10	1.69E-04	1.75	0.032	0.78	1.32E-04	1790	5	36.36	10.39	0.739	8.69E-02
11	1.69E-04	2.46	0.032	1	1.69E-04	1422	42	192	14.57	0.707	7.67E-02
12	1.69E-04	2.47	0.141	1	1.69E-04	1321	39	176.8	14.57	0.707	1.74E-02
13	1.70E-04	2.45	0.249	0.99	1.68E-04	1588	39	176.8	14.57	0.707	9.83E-03
14	1.68E-04	1.54	0.032	0.66	1.11E-04	1407	27	123.8	9.00	0.7556	9.13E-02
15	1.61E-04	1.70	0.033	0.7	1.13E-04	2744	27	199	9.00	0.7556	9.13E-02
16	1.69E-04	2.00	0.032	0.85	1.44E-04	1655	5	36.36	11.79	0.728	8.28E-02
17	1.70E-04	1.51	0.032	0.66	1.12E-04	1693	2	7.578	9.00	0.7556	9.13E-02
18	1.77E-04	2.03	0.031	0.85	1.50E-04	6962	3	19.14	13.18	0.717	7.95E-02
19	1.69E-04	2.23	0.032	0.89	1.50E-04	1259	2	7.578	13.18	0.717	7.95E-02
20	1.69E-04	1.65	0.032	0.69	1.16E-04	1630	2	7.578	9.70	0.746	8.91E-02
21	1.69E-04	2.23	0.032	0.89	1.50E-04	1961	26	191.5	13.18	0.717	7.95E-02
22	1.69E-04	1.52	0.032	0.65	1.10E-04	1198	13	95.69	9.00	0.7556	9.13E-02
23	1.69E-04	1.58	0.032	0.68	1.15E-04	1760	2	8.083	9.36	0.751	9.01E-02
24	1.69E-04	1.68	0.032	0.68	1.15E-04	1760	2	8.083	9.92	0.751	8.75E-02
25	1.69E-04	1.49	0.032	0.68	1.15E-04	1648	2	7.578	8.83	0.751	9.27E-02
KU	1.69E-04	1.52	0.032	0.68	1.15E-04	14967	6	25.26	9.00	0.751	9.19E-02

#	den (g/ml)	Sc	$Pe_{,Dp}$	D_L (cm^2/sec)	Pe'	Pe_f	Pe_r	D_r (cm^2/sec)	D_L/uL	$L*D_r/(R^2*u)$
1	1.56E-03	1.243	5033.384	6743	11.4	11.1	11.0	2287.5	0.088	34.91
2	1.56E-03	1.240	1427.528	1918	8.4	11.2	11.1	648.8	0.119	9.77
3	2.29E-03	0.558	638.7526	975	12.4	11.2	11.1	333.3	0.080	37.86
4	1.10E-02	0.497	1405.309	489	12.4	11.1	11.0	166.6	0.081	37.86
5	2.16E-02	0.448	1283.566	252	12.4	11.1	11.0	85.8	0.081	37.86
6	1.75E-03	0.995	1821.265	2541	12.3	11.1	11.1	862.0	0.081	37.86
7	2.30E-03	0.522	831.366	1270	8.4	11.1	11.1	433.8	0.119	9.70
8	2.19E-03	0.417	1.749353	0	16.9	34.5	3.7	0.9	0.059	6.63
9	2.34E-03	0.514	562.6123	857	2.2	11.2	11.1	293.6	0.459	6.63
10	1.99E-03	0.764	1368.051	1998	2.2	11.1	11.1	679.3	0.462	6.63
11	1.41E-03	1.564	2223.61	2883	11.4	11.1	11.1	974.7	0.088	13.27
12	6.27E-03	1.546	2041.287	602	10.5	11.2	11.1	203.3	0.096	12.22
13	1.13E-02	1.515	2406.853	400	10.5	11.1	11.1	135.2	0.096	12.22
14	2.32E-03	0.524	737.8153	1126	7.4	11.1	11.1	385.0	0.135	8.55
15	2.31E-03	0.534	1464.446	2243	11.9	11.1	11.0	764.2	0.084	36.29
16	1.75E-03	0.993	1642.777	2292	2.2	11.1	11.1	777.5	0.463	6.63
17	2.32E-03	0.529	896.2251	1370	0.5	11.1	11.1	467.7	2.209	0.52
18	1.56E-03	1.213	8445.697	11309	1.1	11.0	11.0	3838.3	0.880	3.49
19	2.17E-03	0.873	1099.672	1472	0.5	11.2	11.1	499.8	2.221	0.52
20	2.14E-03	0.611	995.3899	1487	0.5	11.1	11.1	506.9	2.212	0.52
21	1.56E-03	1.212	2376.197	3187	11.4	11.1	11.1	1079.9	0.088	34.91
22	2.32E-03	0.520	623.3596	950	5.7	11.2	11.1	325.3	0.174	17.45
23	2.22E-03	0.575	1012.528	1529	0.5	11.1	11.1	521.2	2.073	0.56
24	2.09E-03	0.629	1107.744	1626	0.5	11.1	11.1	554.0	2.075	0.56
25	2.37E-03	0.523	862.506	1338	0.5	11.1	11.1	457.1	2.208	0.52
KU	2.31E-03	0.542	8112.83	12535	1.5	11.0	11.0	4259.5	0.666	1.75

Run #1

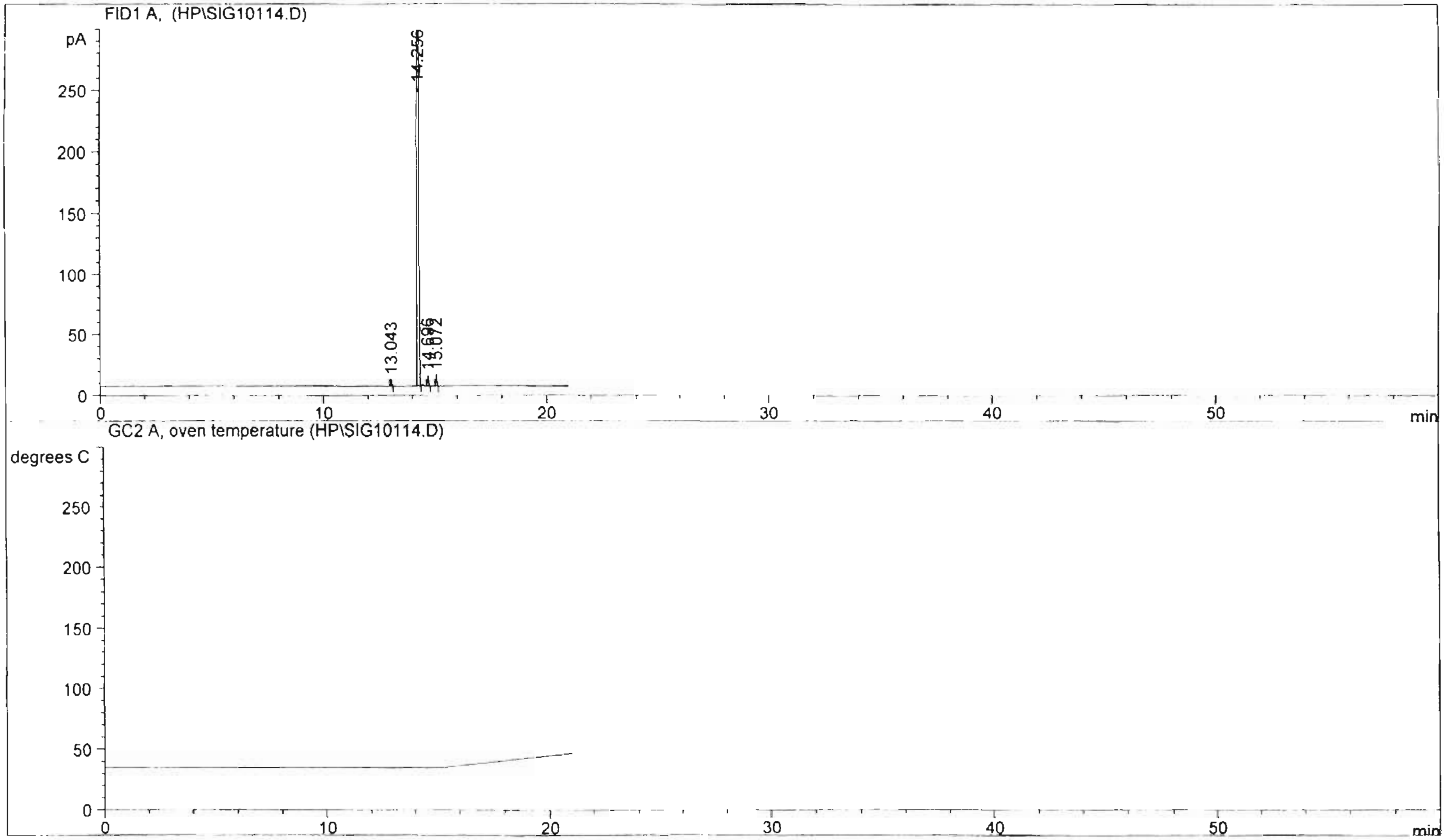
Data File C:\HPCHEM\2\DATA\HP\SIG10113.D Sample Name: 1-butene/NAFION

```
HP 6890 GC 8/30/00 3:19:49 PM MSH

=====================================================================
Injection Date    : 5/15/00 9:05:20 PM
Sample Name       : 1-butene/NAFION                        Vial :    -
Acq. Operator     : MSH                                     Inj :    1
                                                    Inj Volume : Manually
Acq. Method       : C:\HPCHEM\2\METHODS\NAFION2.M
Last changed      : 5/12/00 6:47:28 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed      : 8/30/00 3:11:58 PM by MSH
                    (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]    [pA*s]       [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  13.715 BB    0.0626   15.90936    4.07055  0.25473
   2  14.370 BV    0.0614  808.99298  207.97675 12.95318
   3  14.572 VV    0.0619 3470.50171  881.62299 55.56788
   4  14.758 VB    0.0629 1950.11401  484.78375 31.22422
Totals :                  6245.51806 1578.45404

=====================================================================
                        *** End of Report ***
```


FID1 A, (HP\SIG10113.D)
pA
250
200
150
100
50
0
13.715
14.370
14.573
14.738
0
10
20
30
40
50
min
GC2 A, oven temperature (HP\SIG10113.D)
degrees C
250
200
150
100
50
0
0
10
20
30
40
50
min

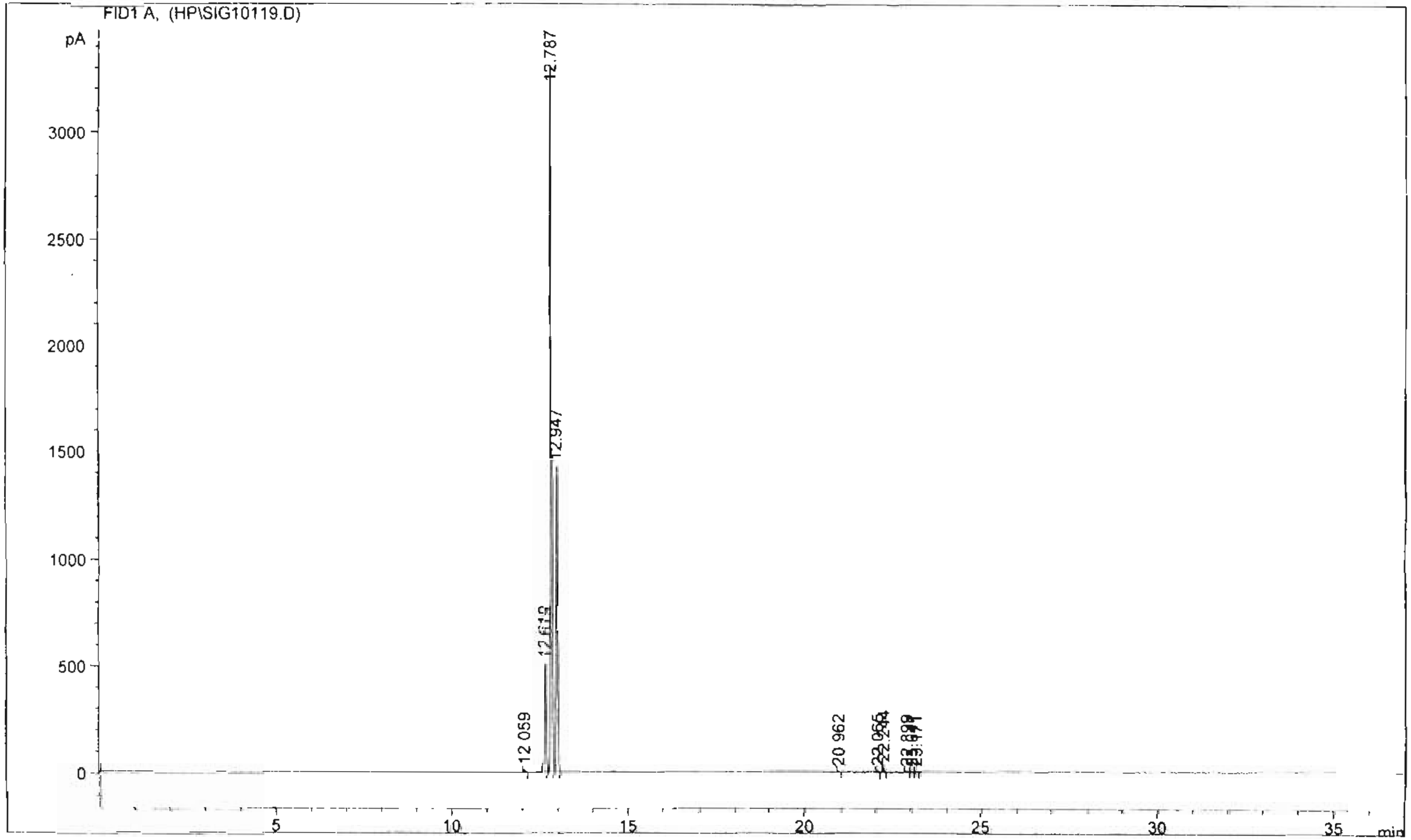
Run #2

```
Data File C:\HPCHEM\2\DATA\HP\SIG10114.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 3:50:10 PM MSH

=====================================================================
Injection Date    : 5/19/00 4:34:08 PM
Sample Name       : 1-butene/NAFION                        Vial :   -
Acq. Operator     : MSH                                     Inj :   1
                                                   Inj Volume : Manually
Acq. Method       : C:\HPCHEM\2\METHODS\NAFION.M
Last changed      : 5/19/00 1:42:09 PM by MSH
Analysis Method   : C:\HPCHEM\2\METHODS\NEW.M
Last changed      : 8/30/00 3:11:58 PM by MSH
                    (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]
----|-------|----|-------|----------|----------|--------|
   1  13.043 BP    0.0499   16.88208    5.19059  0.23946
   2  14.256 BP    0.0530 6970.46045 2031.88281 98.87255
   3  14.696 PP    0.0547   29.96494    8.59750  0.42504
   4  15.072 BP    0.0563   32.63737    8.99396  0.46295
Totals :                  7049.94485 2054.66486

=====================================================================
*** End of Report ***
```


FID1 A, (HP\SIG10114.D)
pA
250
200
150
100
50
0
14.256
13.043
14.696
15.072
0
10
20
30
40
50
min
GC2 A, oven temperature (HP\SIG10114.D)
degrees C
250
200
150
100
50
0
0
10
20
30
40
50
min

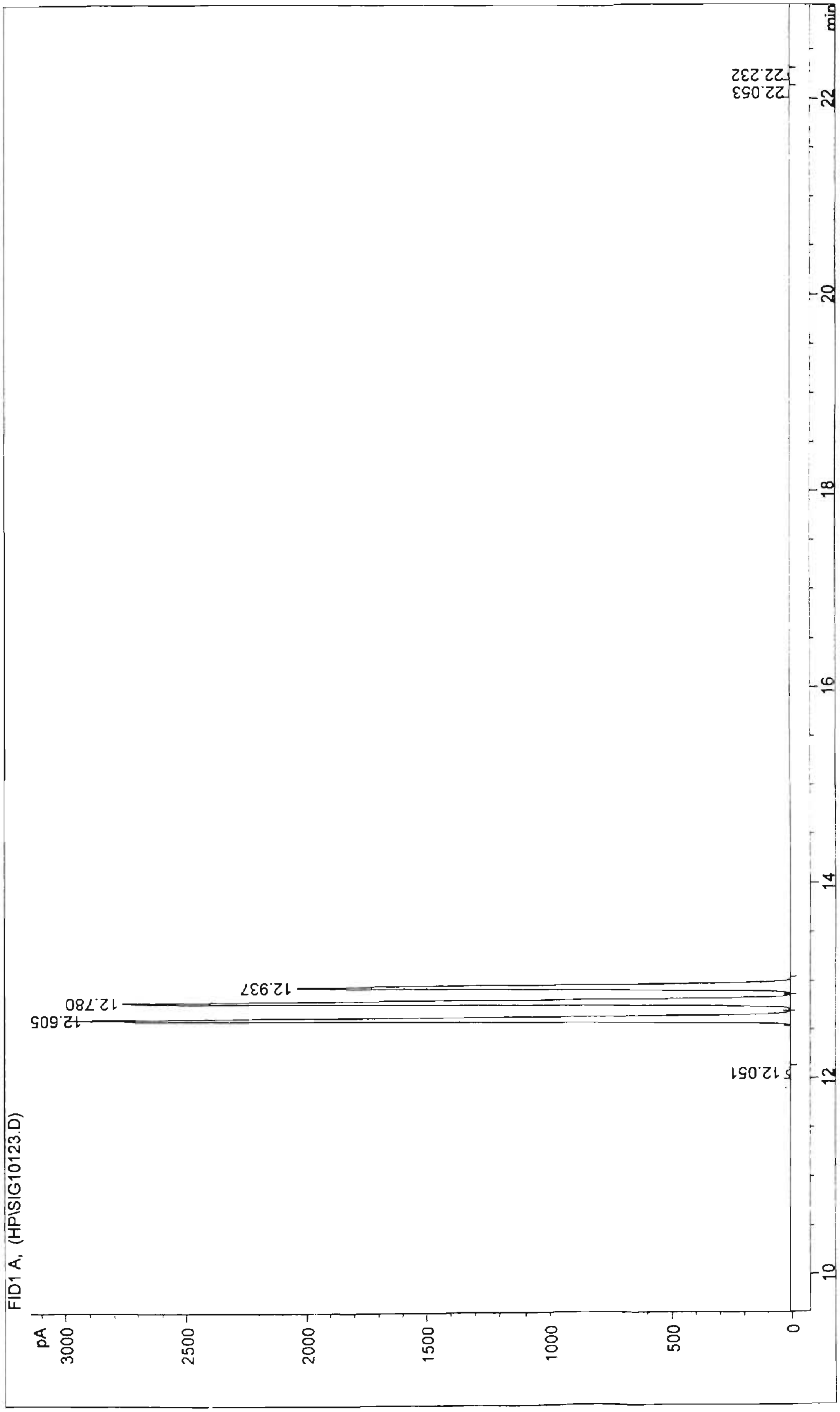
Run #3

```
Data File C:\HPCHEM\2\DATA\HP\SIG10119.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 3:52:23 PM MSH

======================================================================
Injection Date  : 5/24/00 4:18:19 PM
Sample Name     : 1-butene/NAFION                        Vial :   -
Acq. Operator   : MSH                                     Inj :   1
                                                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NAFION2.M
Last changed    : 5/24/00 4:03:28 PM by MSH
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.059 BP    0.0462   38.92650   13.26631  0.25164
   2  12.619 BV    0.0452 1457.24976  512.22449  9.42022
   3  12.787 VV    0.0450 9603.85547 3300.11987 62.08302
   4  12.947 VB    0.0466 4227.46289 1426.64624 27.32795
   5  20.962 BB    0.0429   14.41856    5.27741  0.09321
   6  22.065 PP    0.0457   23.52115    7.89942  0.15205
   7  22.244 BP    0.0427   66.35983   24.45527  0.42898
   8  22.899 PB    0.0515   16.02929    4.85419  0.10362
   9  23.041 BB    0.0427   10.55731    3.89105  0.06825
  10  23.171 BP    0.0426   10.99499    4.05974  0.07108
Totals :                   1.54694e4  5302.69400

======================================================================
                       *** End of Report ***
```


FID1 A, (HP\SIG10119.D)
pA
3000
2500
2000
1500
1000
500
0
5
10
15
20
25
30
35
min
12.787
12.947
12.619
12 059
20 962
22.065
22.244
22.899
23.171

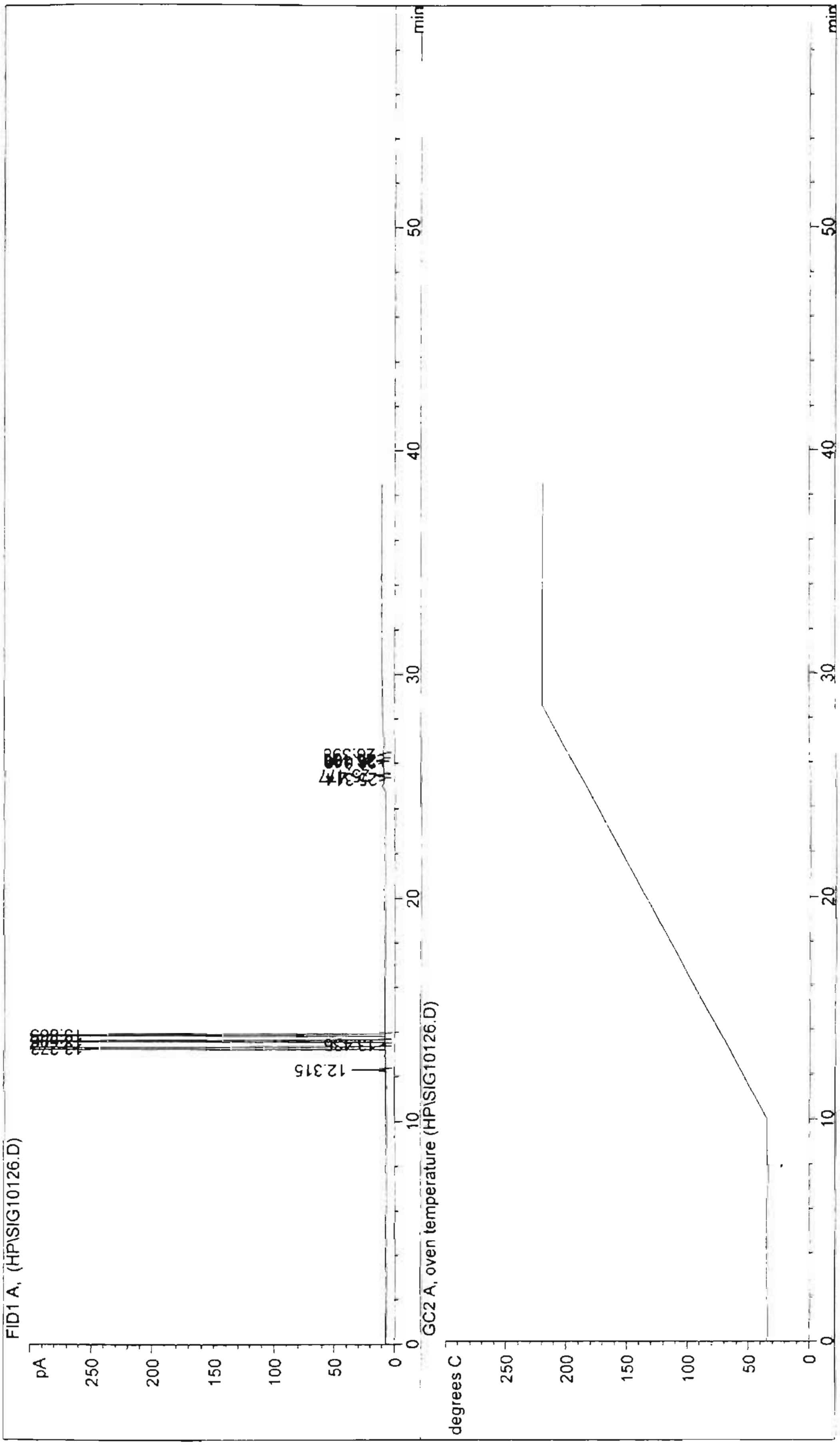
Run #4

```
Data File C:\HPCHEM\2\DATA\HP\SIG10123.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 3:59:05 PM MSH

======================================================================
Injection Date  : 5/25/00 5:51:34 PM
Sample Name     : 1-butene/NAFION                          Vial :   -
Acq. Operator   : MSH                                       Inj :   1
                                                   Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NAFION2.M
Last changed    : 5/24/00 7:14:55 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

======================================================================
                         Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.051 BP    0.0451   57.27559   19.60613  0.25318
   2  12.605 BV    0.0454 8550.16309 2988.60596 37.79469
   3  12.780 VV    0.0448 7979.79639 2754.21631 35.27347
   4  12.937 VB    0.0466 6015.27051 2030.81152 26.58958
   5  22.053 PB    0.0438    5.00399    1.77741  0.02212
   6  22.232 BP    0.0427   15.14869    5.56958  0.06696
Totals :                  2.26227e4  7800.58691

======================================================================
                          *** End of Report ***
```


FID1 A, (HP\SIG10123.D)
pA
3000
2500
2000
1500
1000
500
0
10
12
14
16
18
20
22
min
12.051
12.605
12.780
12.937
22.053
22.232

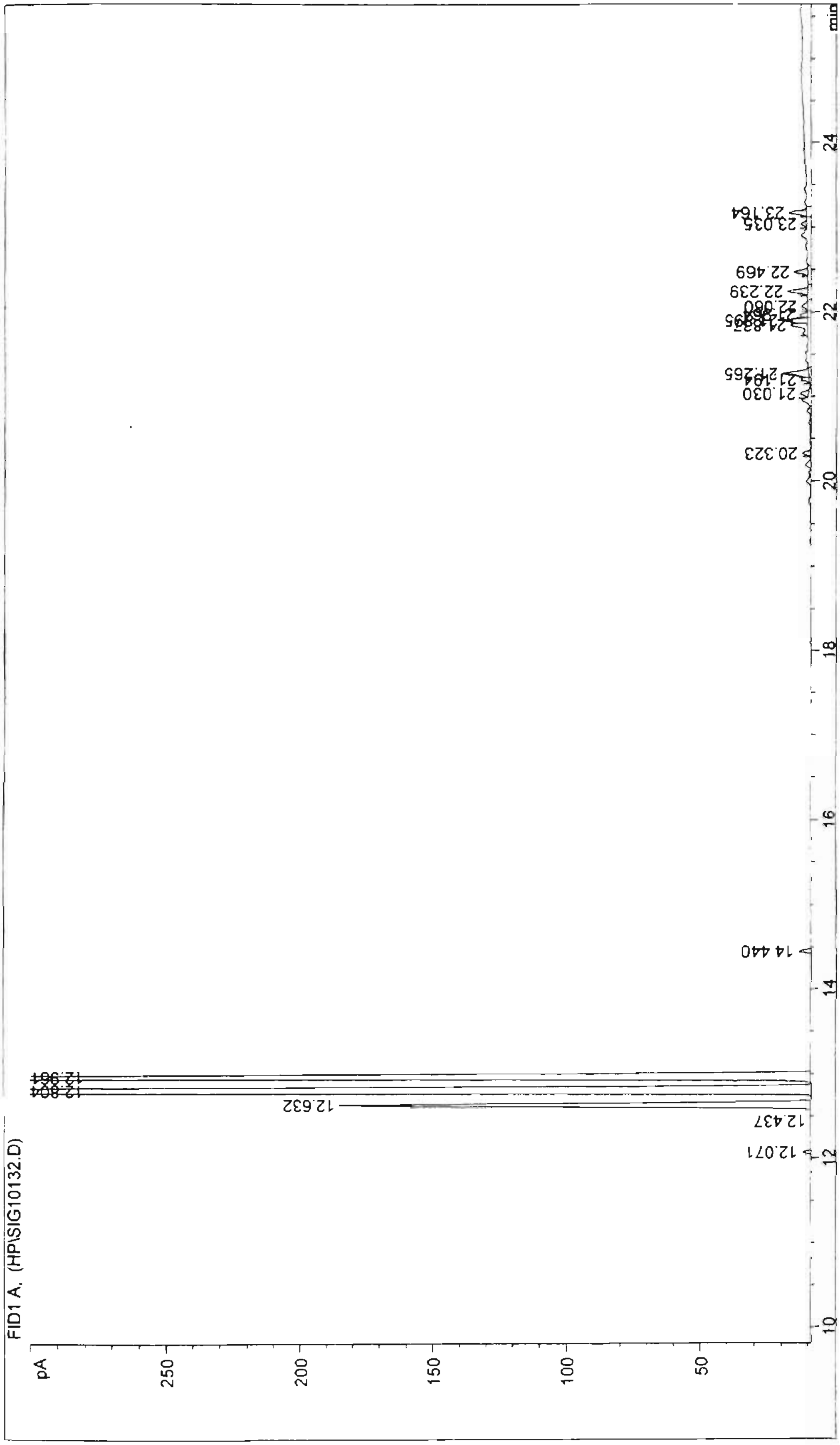
Run #5

```
Data File C:\HPCHEM\2\DATA\HP\SIG10126.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:00:43 PM MSH

=====================================================================
Injection Date  : 5/26/00 6:22:43 PM
Sample Name     : 1-butene/NAFION                        Vial :   -
Acq. Operator   : MSH                                     Inj :   1
                                                Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NAFION3.M
Last changed    : 5/26/00 4:11:07 PM by MSH
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.315 BB    0.0431   78.59048   28.55285  0.48163
   2  13.273 BB    0.0432 1.04017e4  3773.39160 63.74572
   3  13.436 BP    0.0431   10.57034    3.84490  0.06478
   4  13.596 BB    0.0431 2778.68408 1010.68231 17.02888
   5  13.865 BB    0.0436 2993.97632 1071.91626 18.34827
   6  25.314 PP    0.0379    4.74097    1.97929  0.02905
   7  25.477 BB    0.0399   19.89001    7.77049  0.12189
   8  26.046 PV    0.0397    5.56756    2.18747  0.03412
   9  26.109 VV    0.0378    6.70720    2.72110  0.04110
  10  26.165 VP    0.0403    9.06161    3.48850  0.05553
  11  26.398 PP    0.0372    7.99721    3.42783  0.04901
Totals :                  1.63175e4  5909.96260

=====================================================================
                         *** End of Report ***
```


FID1 A, (HP\SIG10126.D)
pA
250
200
150
100
50
0
12.315
13.436
25.347
26.398
0
10
20
30
40
50
min
GC2 A, oven temperature (HP\SIG10126.D)
degrees C
250
200
150
100
50
0
0
10
20
30
40
50
min

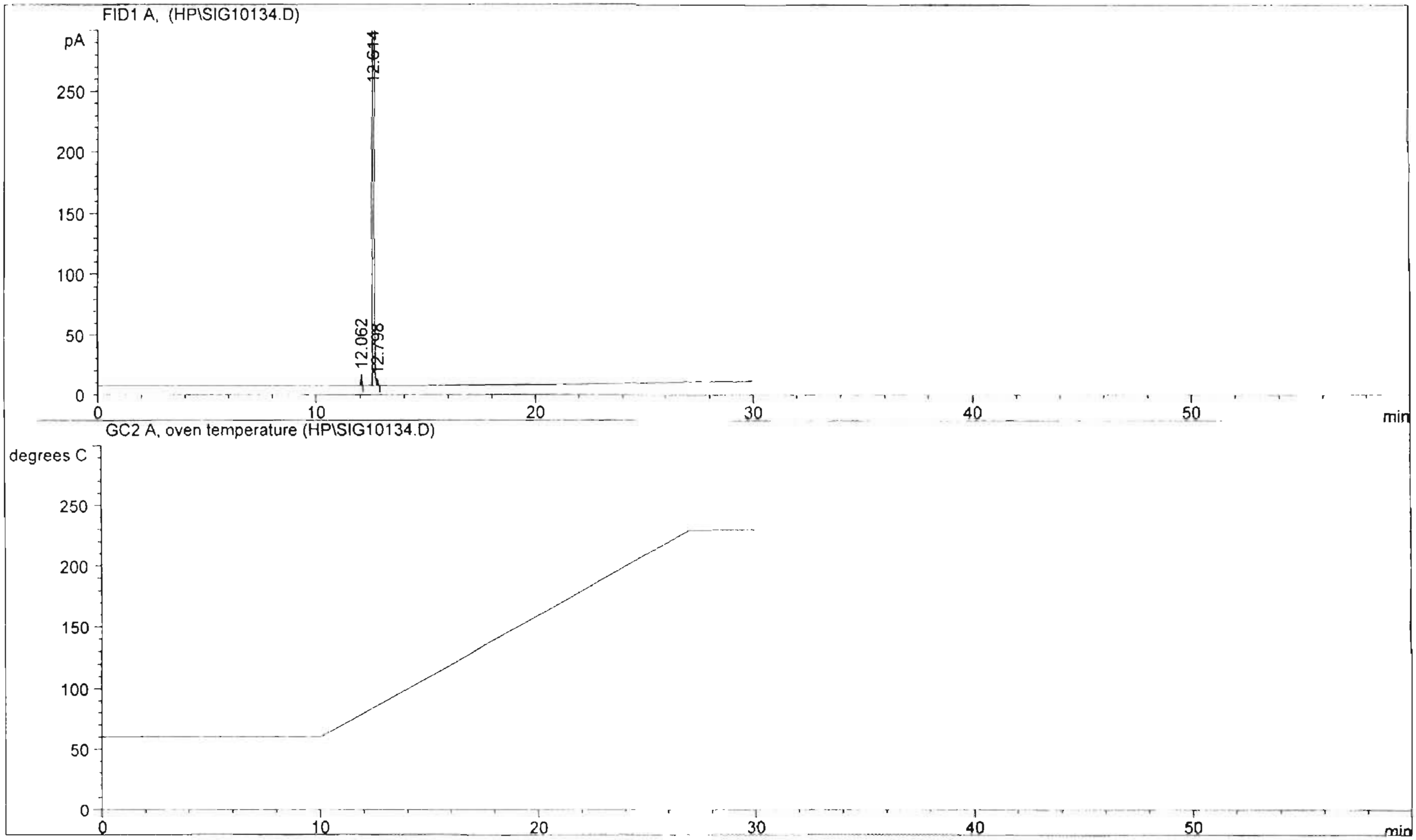
Run #6

```
Data File C:\HPCHEM\2\DATA\HP\SIG10132.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:02:32 PM MSH

=====================================================================
Injection Date   : 5/29/00 4:21:36 AM
Sample Name      : 1-butene/NAFION                    Vial :   -
Acq. Operator    : MSH                                 Inj :   1
                                             Inj Volume : Manually
Acq. Method      : C:\HPCHEM\2\METHODS\NAFION2.M
Last changed     : 5/26/00 4:06:52 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 8/30/00 3:11:58 PM by MSH
                   (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.071 BP    0.0466   16.07119    5.41817  0.28920
   2  12.437 BP    0.0439    5.65445    2.07075  0.10175
   3  12.632 BB    0.0442  507.89880  178.29909  9.13963
   4  12.804 BV    0.0441 3233.01050 1138.93958 58.17795
   5  12.961 VB    0.0456 1597.05652  553.85138 28.73900
   6  14.440 BP    0.0450   18.72498    6.61797  0.33696
   7  20.323 BP    0.0411    7.75999    3.00449  0.13964
   8  21.030 BP    0.0491    9.27071    2.99714  0.16683
   9  21.194 PV    0.0392    7.95981    3.18023  0.14324
  10  21.265 VB    0.0466   30.40587    9.96150  0.54715
  11  21.837 BV    0.0533   24.53514    6.45997  0.44151
  12  21.895 VV    0.0422   26.49516    9.60816  0.47678
  13  21.964 VP    0.0382    7.41437    2.96299  0.13342
  14  22.060 VP    0.0474    7.42776    2.31678  0.13366
  15  22.239 BP    0.0425   20.38113    7.55911  0.36676
  16  22.469 BP    0.0416   13.56514    5.17788  0.24410
  17  23.035 BB    0.0437    5.54324    2.03902  0.09975
  18  23.164 BP    0.0422   17.93133    6.69814  0.32267
Totals :                  5557.10608 1947.16234

=====================================================================
                         *** End of Report ***
```


FID1 A, (HP\SIG10132.D)
pA
250
200
150
100
50
10
12
14
16
18
20
22
24
min
12.071
12.437
12.632
12.804
12.961
14.440
20.323
21.030
21.164
21.265
21.837
21.895
22.060
22.239
22.469
23.035
23.164

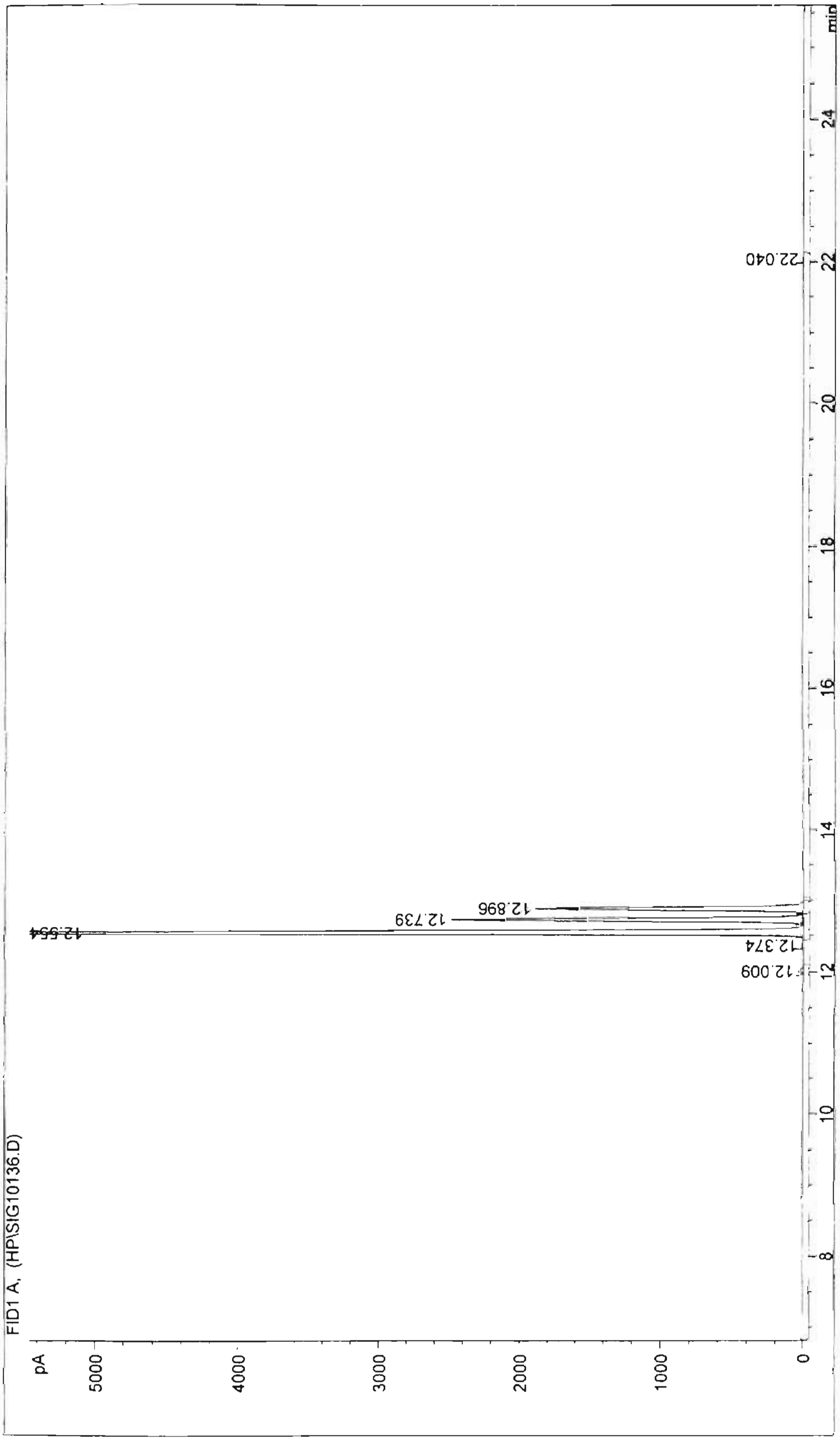
Run #7

```
Data File C:\HPCHEM\2\DATA\HP\SIG10134.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:09:47 PM MSH

=====================================================================
Injection Date  : 5/30/00 6:51:37 PM
Sample Name     : 1-butene/NAFION                       Vial :   -
Acq. Operator   : MSH                                    Inj :   1
                                                 Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NAFION2.M
Last changed    : 5/30/00 5:05:32 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.062 BP    0.0459   27.83659    9.58641  0.23421
   2  12.614 BB S  0.0446 1.18446e4  4109.10107 99.65876
   3  12.798 BB T  0.0423   12.71977    4.73757  0.10702
Totals :                  1.18851e4  4123.42505

=====================================================================
                         *** End of Report ***
```


FID1 A, (HP\SIG10134.D)
pA
250
200
150
100
50
0
12.614
12.062
12.798
0
10
20
30
40
50
min
GC2 A, oven temperature (HP\SIG10134.D)
degrees C
250
200
150
100
50
0
0
10
20
30
40
50
min

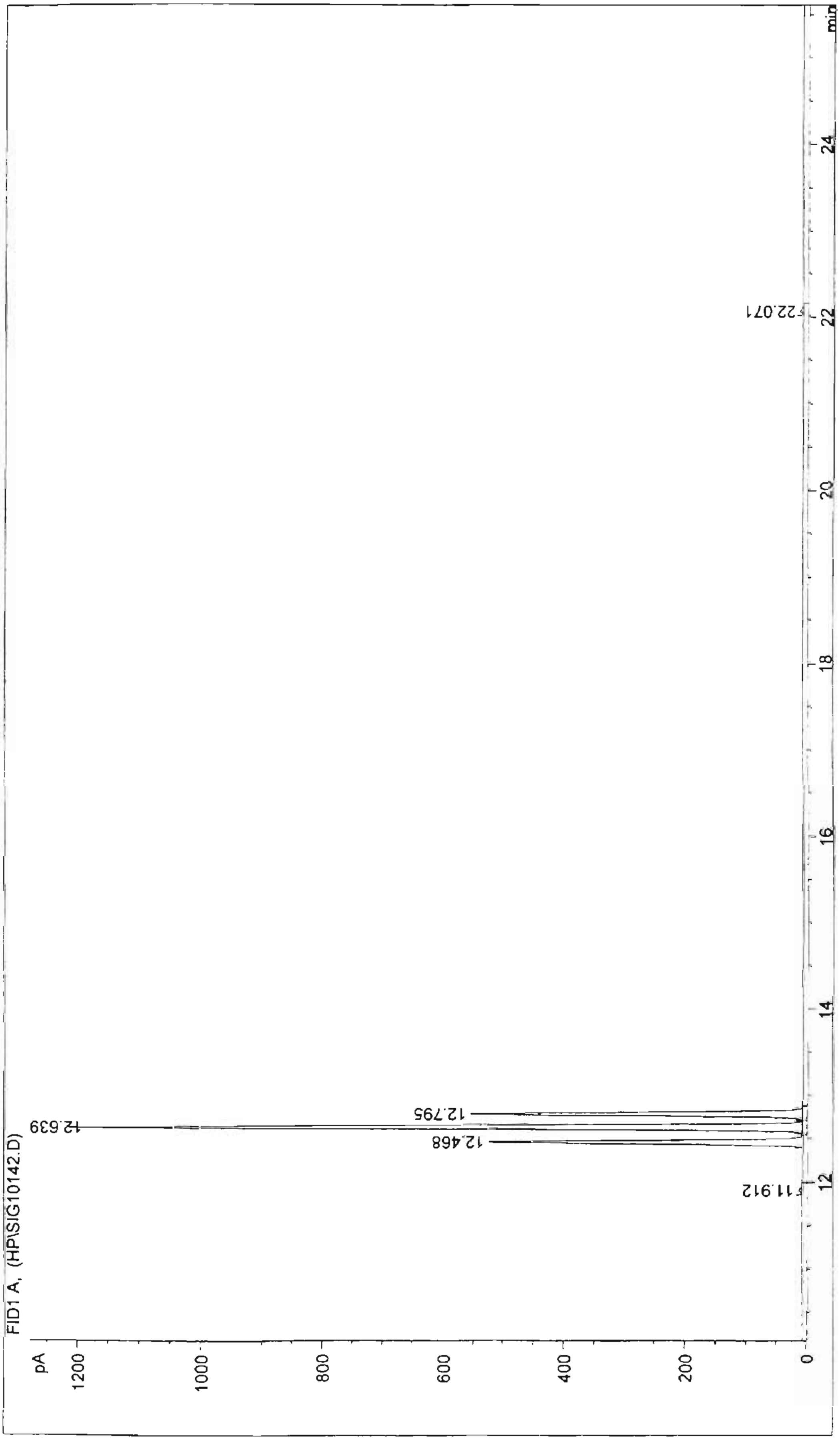
Run #8

```
Data File C:\HPCHEM\2\DATA\HP\SIG10136.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:11:33 PM MSH

=====================================================================
Injection Date  : 6/2/00 2:09:32 PM
Sample Name     : 1-butene/NAFION                     Vial :   -
Acq. Operator   : MSH                                  Inj :   1
                                               Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NAFION2.M
Last changed    : 6/2/00 2:02:13 PM by MSH
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.009 BP    0.0461   83.52676   28.61235  0.24371
   2  12.374 BP    0.0429    6.40058    2.34294  0.01868
   3  12.554 BB S  0.0464 2.13925e4  7258.96045 62.41764
   4  12.739 BV X  0.0460 7188.93555 2463.20776 20.97545
   5  12.896 VB T  0.0467 5587.79883 1878.65564 16.30375
   6  22.040 PP    0.0408   13.97705    5.28591  0.04078
Totals :                  3.42731e4  1.16371e4

=====================================================================
                         *** End of Report ***
```


FID1 A, (HP\SIG10136.D)
pA
5000
4000
3000
2000
1000
0
8
10
12
14
16
18
20
22
24
min
12.009
12.374
12.554
12.739
12.896
22.040

Run #9

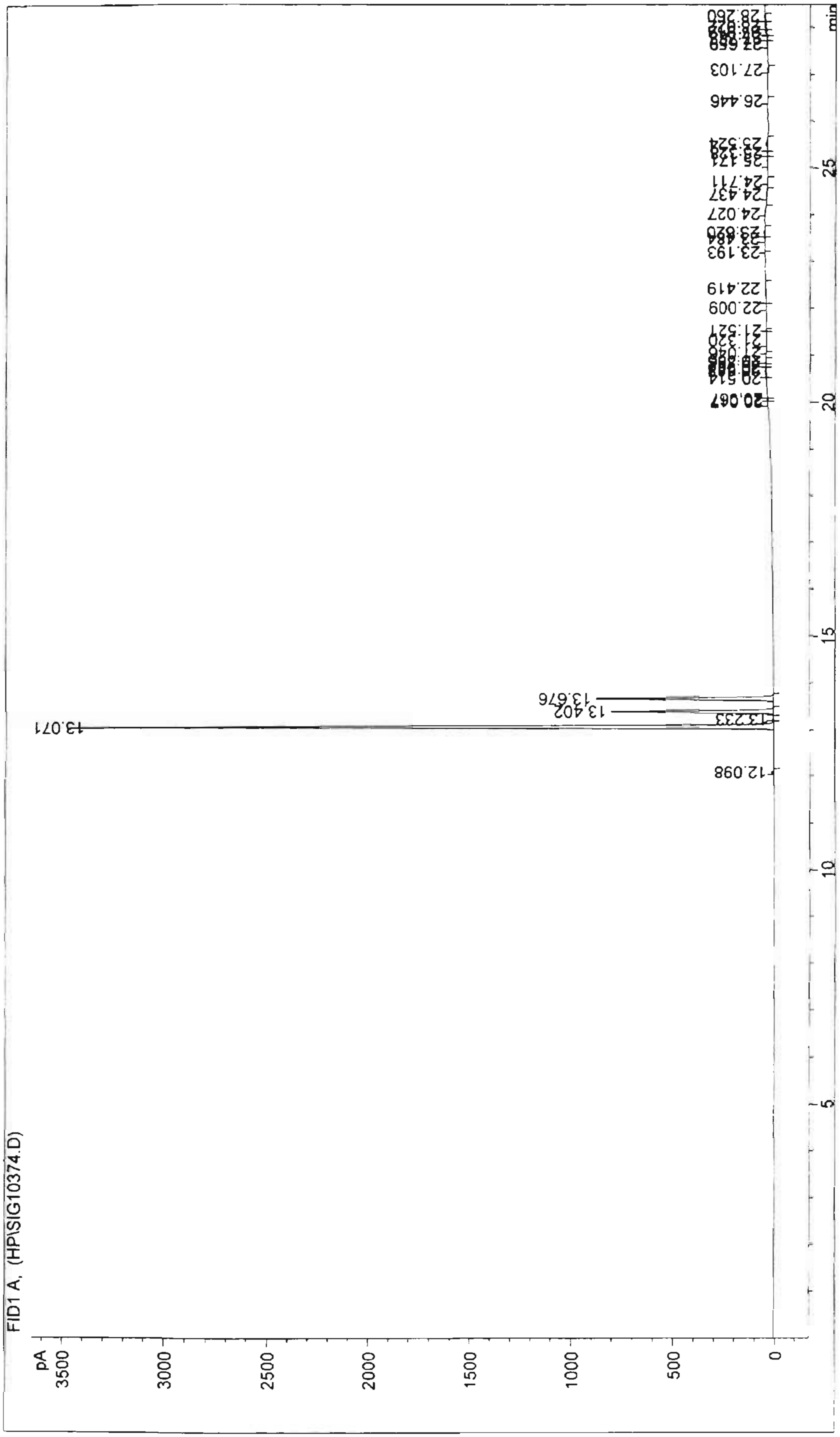
```
Data File C:\HPCHEM\2\DATA\HP\SIG10142.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:12:57 PM MSH

=====================================================================
Injection Date  : 6/3/00 2:26:20 AM
Sample Name     : 1-butene/NAFION                          Vial :   -
Acq. Operator   : MSH                                       Inj :   1
                                                 Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NAFION2.M
Last changed    : 6/2/00 2:02:13 PM by MSH
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.912 BP    0.0449   15.19671    5.38234  0.23928
   2  12.468 BB    0.0431 1422.25171  517.20044 22.39446
   3  12.639 BV    0.0444 3359.07104 1209.83301 52.89118
   4  12.795 VB    0.0439 1539.55933  546.49359 24.24156
   5  22.071 BP    0.0405   14.83057    5.66921  0.23352
Totals :                  6350.90936 2284.57859

=====================================================================
                         *** End of Report ***
```


FID1 A, (HP\SIG10142.D)
pA
1200
1000
800
600
400
200
0
12
14
16
18
20
22
24
min
11.912
12.468
12.639
12.795
22.071

Run #10

```
Data File C:\HPCHEM\2\DATA\HP\SIG10374.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:18:13 PM MSH

=====================================================================
Injection Date  : 7/3/00 10:02:50 PM
Sample Name     : 1-butene/NAFION                     Vial :   -
Acq. Operator   : MSH                                  Inj :   1
                                               Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 7/3/00 7:28:48 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.098 BP    0.0456   34.18630   11.86025  0.21544
   2  13.071 BB    0.0450 1.01079e4  3465.75635 63.69886
   3  13.233 BV    0.0522   17.82910    5.04390  0.11236
   4  13.402 VB    0.0450 2314.65527  794.60394 14.58671
   5  13.676 BB    0.0465 2573.93921  870.87573 16.22068
   6  20.017 BP    0.0353    3.39219    1.30409  0.02138
   7  20.067 VP    0.0200    1.86519    1.27728  0.01175
   8  20.514 VV    0.1396   61.23589    5.27031  0.38590
   9  20.688 VV    0.1297   75.90749    6.98922  0.47836
  10  20.761 VB    0.0406   13.87407    4.55098  0.08743
  11  20.866 BB    0.0469   14.37003    3.81473  0.09056
  12  21.046 PP    0.0160    1.65795    1.72958  0.01045
  13  21.320 PP    0.1044   26.35090    3.06064  0.16606
  14  21.521 VP    0.0232    1.87384    1.20075  0.01181
  15  22.009 BP    0.0554    7.16964    1.59719  0.04518
  16  22.419 VV    0.1620   95.60058    7.01480  0.60246
  17  23.193 BB    0.0189    2.26136    1.65739  0.01425
  18  23.484 BV    0.0504   13.09029    3.21941  0.08249
  19  23.620 VP    0.0808   38.93177    5.76613  0.24534
  20  24.027 BB    0.1179   31.49720    3.16948  0.19849
  21  24.437 BB    0.1081   34.87331    4.32341  0.21977
  22  24.711 BP    0.0691   13.15733    2.32088  0.08292
  23  25.171 BV    0.1008   41.16196    5.01221  0.25940
  24  25.328 VV    0.0604   21.89638    4.37170  0.13799
  25  25.524 VB    0.1159   92.77158    9.58427  0.58464
  26  26.446 BP    0.0595    9.18925    2.08041  0.05791
```

```
  27  27.103 BP    0.0648    30.18599     5.79531  0.19023
  28  27.659 PV    0.0630    27.50286     5.52884  0.17332
  29  27.783 VP    0.0499    16.20098     4.30408  0.10210
  30  27.912 VV    0.0599    35.75350     8.03965  0.22531
  31  28.022 VV    0.0884    56.27980     8.26941  0.35467
  32  28.260 VV    0.0941    51.69590     6.76715  0.32578
Totals :                   1.58683e4  5266.15948

=====================================================================
                       *** End of Report ***
```

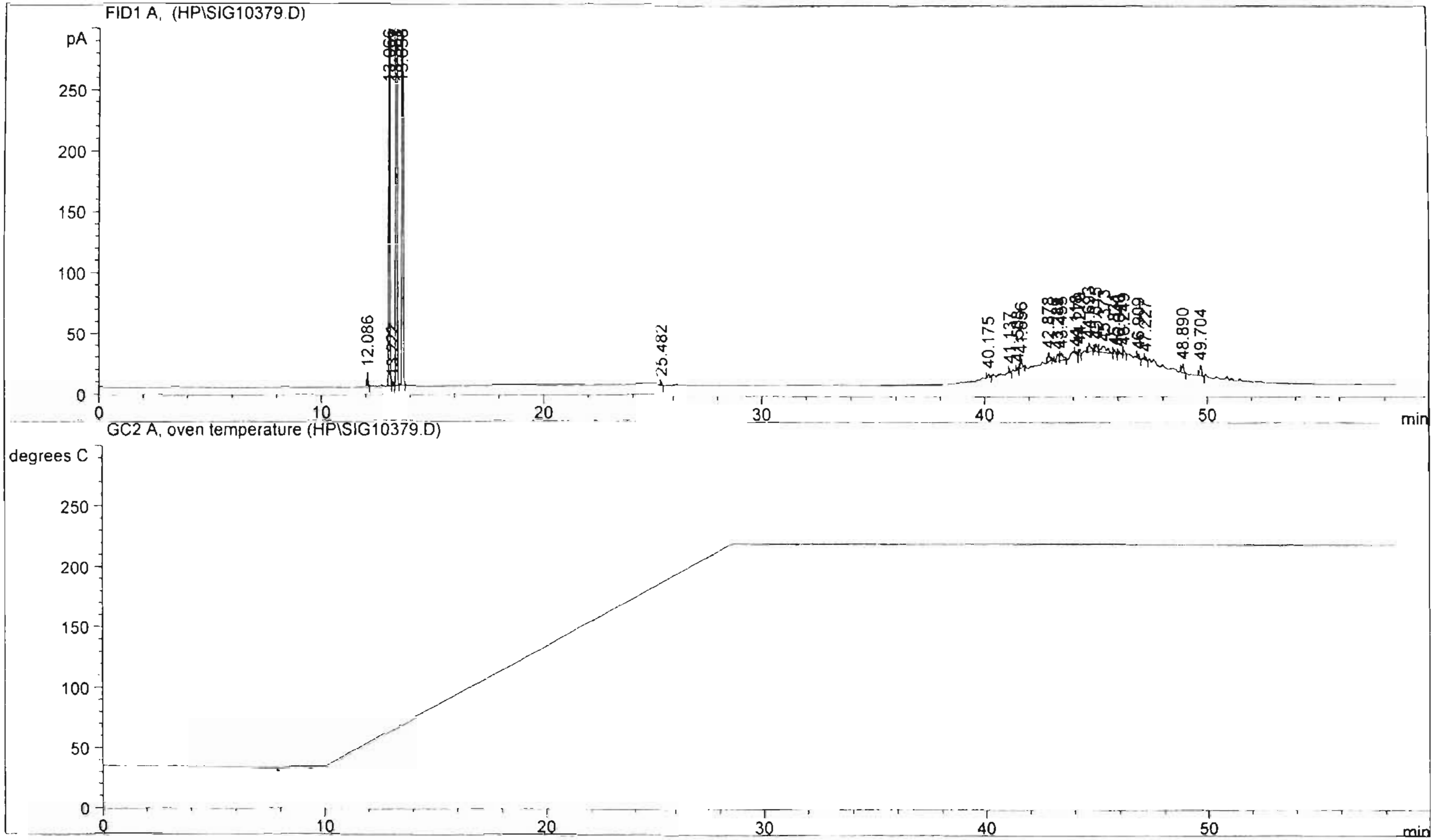


FID1 A, (HP\SIG10374.D)
pA
3500
3000
2500
2000
1500
1000
500
0
5
10
15
20
25
min
12.098
13.071
13.233
13.402
13.676
20.067
20.514
21.320
21.521
22.009
22.419
23.193
23.484
23.620
24.027
24.437
24.711
25.171
25.328
25.524
26.446
27.103
27.658
28.260

Run #11

```
Data File C:\HPCHEM\2\DATA\HP\SIG10379.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:19:51 PM MSH

=====================================================================
Injection Date  : 7/5/00 9:09:27 PM
Sample Name     : 1-butene/NAFION                        Vial :   -
Acq. Operator   : MSH                                     Inj :   1
                                                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 7/5/00 9:02:12 PM by MSH
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.086 BB    0.0458   32.71706   11.28977  0.21633
   2  13.066 BB    0.0454 2177.01294  760.40558 14.39471
   3  13.222 BP    0.0444    9.98459    3.48642  0.06602
   4  13.381 BB    0.0449 7578.76904 2608.14185 50.11186
   5  13.658 BB    0.0464 4671.87939 1583.62390 30.89111
   6  25.482 PB    0.0429    9.50292    3.47730  0.06283
   7  40.175 PB    0.0827   19.91114    3.42901  0.13166
   8  41.137 BP    0.0491   10.80782    3.48844  0.07146
   9  41.503 PP    0.0626    9.56275    2.44849  0.06323
  10  41.656 VB    0.0822   44.70036    8.12776  0.29556
  11  42.878 PB    0.0844   45.49083    7.32810  0.30079
  12  43.289 PV    0.0931   47.01738    6.37025  0.31089
  13  43.455 VB    0.1109   58.05313    6.27979  0.38386
  14  44.118 PP    0.0482    9.84289    2.71983  0.06508
  15  44.279 VP    0.0608   22.97605    5.61054  0.15192
  16  44.693 PB    0.0973   59.80121    7.90357  0.39541
  17  45.015 PV    0.0808   37.46047    6.44277  0.24769
  18  45.373 VV    0.2181   99.50316    5.49851  0.65793
  19  45.831 VP    0.0706   20.36004    3.56602  0.13462
  20  46.040 VB    0.0773   18.97416    3.06276  0.12546
  21  46.249 BB    0.0717   22.54977    4.06412  0.14910
  22  46.909 BP    0.0617   15.65297    3.82662  0.10350
  23  47.227 BP    0.0553   13.18427    2.99947  0.08718
  24  48.890 BP    0.0817   39.60358    6.93187  0.26186
```

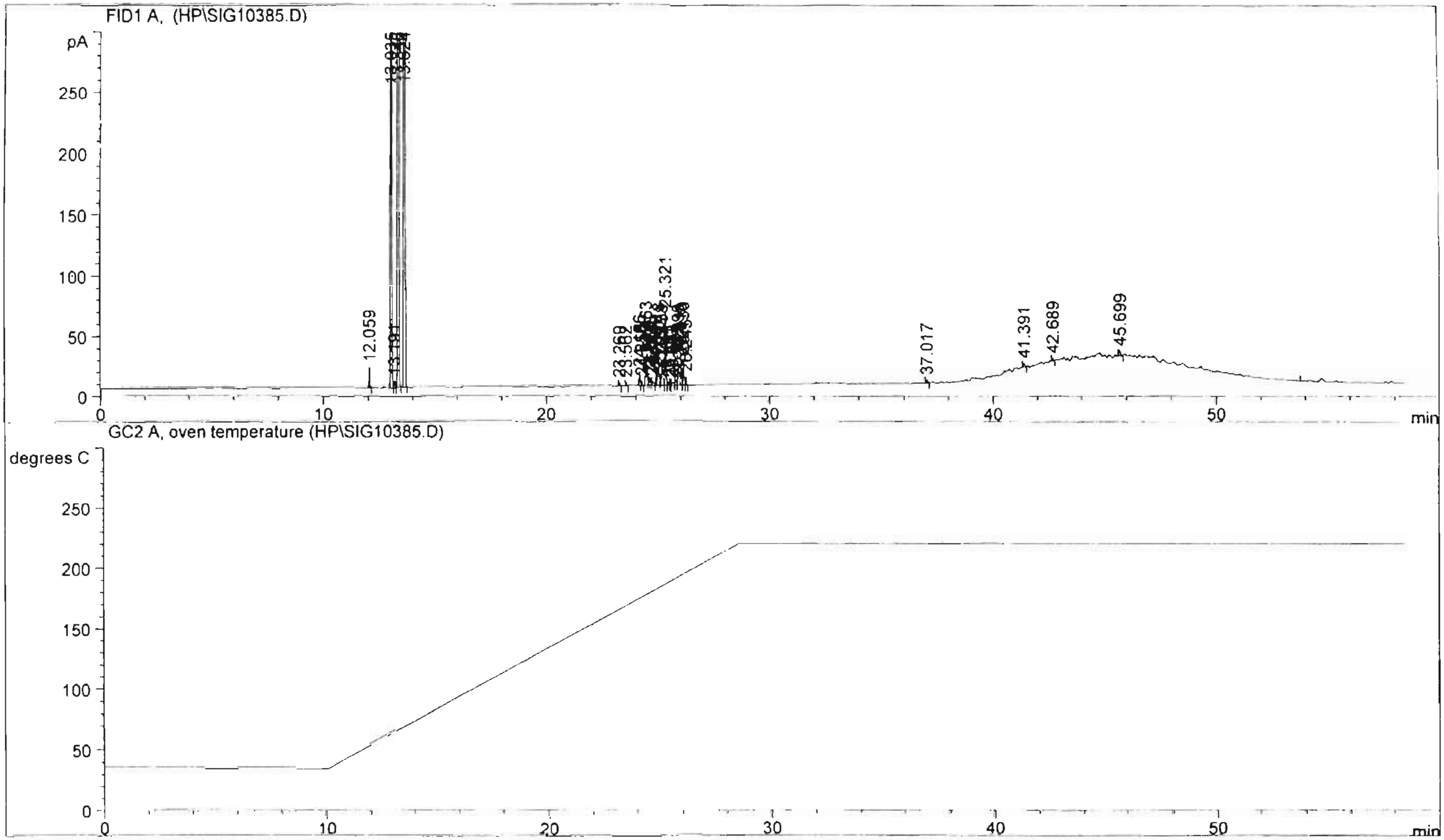
```
  25  49.704 BP     0.0851   48.38433    8.80468  0.31992
Totals :                  1.51237e4  5069.32741

==========================================================================
                          *** End of Report ***
```


FID1 A, (HP\SIG10379.D)
pA
250
200
150
100
50
0
0
10
20
30
40
50
min
12.086
13.066
13.222
25.482
40.175
41.137
42.878
44.148
46.249
46.909
47.227
48.890
49.704
GC2 A, oven temperature (HP\SIG10379.D)
degrees C
250
200
150
100
50
0
0
10
20
30
40
50
min

Run #12

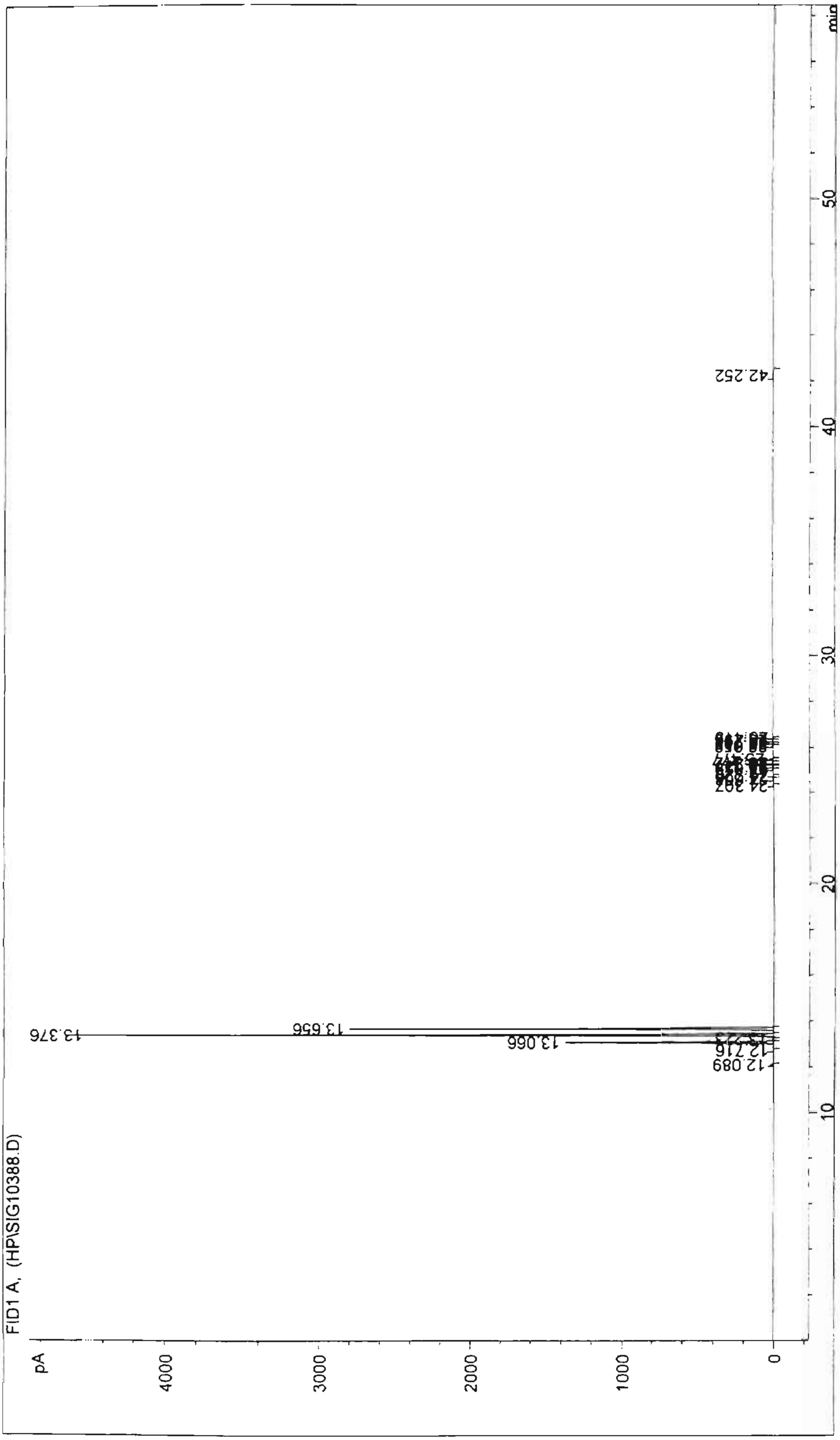
```
Data File C:\HPCHEM\2\DATA\HP\SIG10385.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:21:54 PM MSH

=====================================================================
Injection Date   : 7/6/00 11:17:29 PM
Sample Name      : 1-butene/NAFION                       Vial :   -
Acq. Operator    : MSH                                    Inj :   1
                                                Inj Volume : Manually
Acq. Method      : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 7/6/00 10:29:38 PM by MSH
                   (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 8/30/00 3:11:58 PM by MSH
                   (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.059 BB    0.0449   52.61185   18.12744  0.21861
   2  13.035 BB    0.0443 3494.50562 1223.46313 14.52037
   3  13.191 BP    0.0444   18.13825    6.34412  0.07537
   4  13.346 VB S  0.0449 1.21628e4  4190.76904 50.53873
   5  13.624 BB    0.0463 7441.64893 2529.22632 30.92155
   6  23.269 PP    0.0388    7.21607    3.02385  0.02998
   7  23.562 PB    0.0402    8.07379    3.23070  0.03355
   8  24.166 BV    0.0435   33.34698   11.96627  0.13856
   9  24.258 VP    0.0408   10.69143    4.18834  0.04443
  10  24.463 BV    0.0574   95.30691   23.45155  0.39602
  11  24.579 VV    0.0464   21.31222    6.83642  0.08856
  12  24.666 VV    0.0493   19.43033    5.77200  0.08074
  13  24.745 VB    0.0738   20.00363    3.96736  0.08312
  14  24.908 BV    0.0470   34.18357   10.76962  0.14204
  15  25.018 VV    0.0505   76.67786   22.10675  0.31861
  16  25.093 VV    0.0376   22.10168    9.00685  0.09184
  17  25.158 VV    0.0497   69.07719   20.31243  0.28703
  18  25.321 VB    0.0405  158.50565   60.62687  0.65862
  19  25.463 BV    0.0422    8.35324    3.02548  0.03471
  20  25.531 VV    0.0377    4.90074    1.99071  0.02036
  21  25.632 VV    0.0808   17.17977    2.83074  0.07139
  22  25.801 VV    0.0549   18.03068    3.97694  0.07492
  23  25.896 VV    0.0586   81.68788   20.43334  0.33943
  24  26.018 VV    0.0446   61.33037   21.28268  0.25484
  25  26.130 VB    0.0397   57.16589   22.42571  0.23754
```

```
  26  26.245 BB    0.0388   17.82973    7.21065  0.07409
  27  37.017 BP    0.0658   10.27348    2.45781  0.04269
  28  41.391 BP    0.0602   15.94205    3.85968  0.06624
  29  42.689 PP    0.0548    8.55042    2.38664  0.03553
  30  45.699 BP    0.0610   19.38283    4.35266  0.08054
Totals :                   2.40662e4  8249.42213

==========================================================================
                           *** End of Report ***
```


FID1 A, (HP\SIG10385.D)
pA
250
200
150
100
50
0
12.059
13.191
23.269
23.562
25.321
37.017
41.391
42.689
45.699
0
10
20
30
40
50
min
GC2 A, oven temperature (HP\SIG10385.D)
degrees C
250
200
150
100
50
0
0
10
20
30
40
50
min

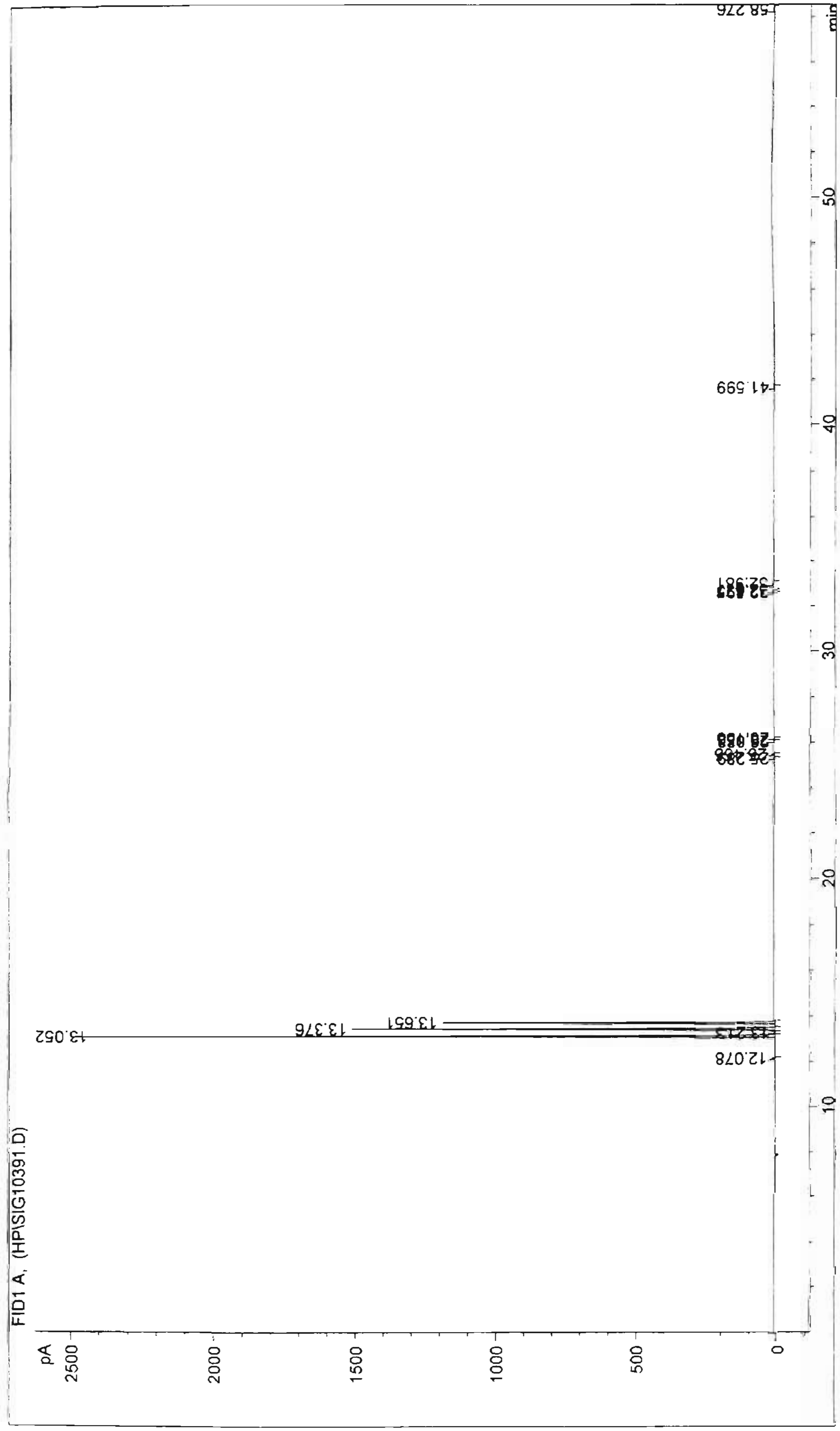
Run #13

```
Data File C:\HPCHEM\2\DATA\HP\SIG10388.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:23:26 PM MSH

=====================================================================
Injection Date  : 7/7/00 8:28:47 PM
Sample Name     : 1-butene/NAFION                          Vial :   -
Acq. Operator   : MSH                                       Inj :   1
                                                    Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 7/7/00 12:35:42 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.089 BB    0.0449   61.46968   21.16060  0.23480
   2  12.716 BP    0.0440    4.86938    1.77754  0.01860
   3  13.066 BB    0.0454 3922.42334 1370.61206 14.98300
   4  13.223 BP    0.0453   20.43221    7.14791  0.07805
   5  13.376 VB S  0.0451 1.35516e4  4631.38672 51.76501
   6  13.656 BB    0.0465 8254.63574 2791.58203 31.53132
   7  24.307 PB    0.0425   16.11263    5.95935  0.06155
   8  24.608 PV    0.0566   32.90289    8.05880  0.12568
   9  24.726 VB    0.0383    3.99887    1.64901  0.01528
  10  25.059 PV    0.0451   13.93147    4.77321  0.05322
  11  25.171 VV    0.0466   20.64393    6.76159  0.07886
  12  25.247 VV    0.0364    5.98161    2.54870  0.02285
  13  25.312 VP    0.0470   30.65013    9.40715  0.11708
  14  25.477 BP    0.0418   70.18050   26.56278  0.26808
  15  26.059 PV    0.0564   27.95823    7.35258  0.10680
  16  26.182 VV    0.0440   19.70309    6.96920  0.07526
  17  26.296 VB    0.0411   13.95069    5.24091  0.05329
  18  26.413 BB    0.0449    6.89560    2.24389  0.02634
  19  42.252 BB    0.1446  100.77953    8.42410  0.38496
Totals :                  2.61792e4  8919.61812

=====================================================================
                          *** End of Report ***
```


FID1 A, (HP\SIG10388.D)
pA
4000
3000
2000
1000
0
10
20
30
40
50
min
12.089
12.716
13.066
13.376
13.656
24.307
42.252

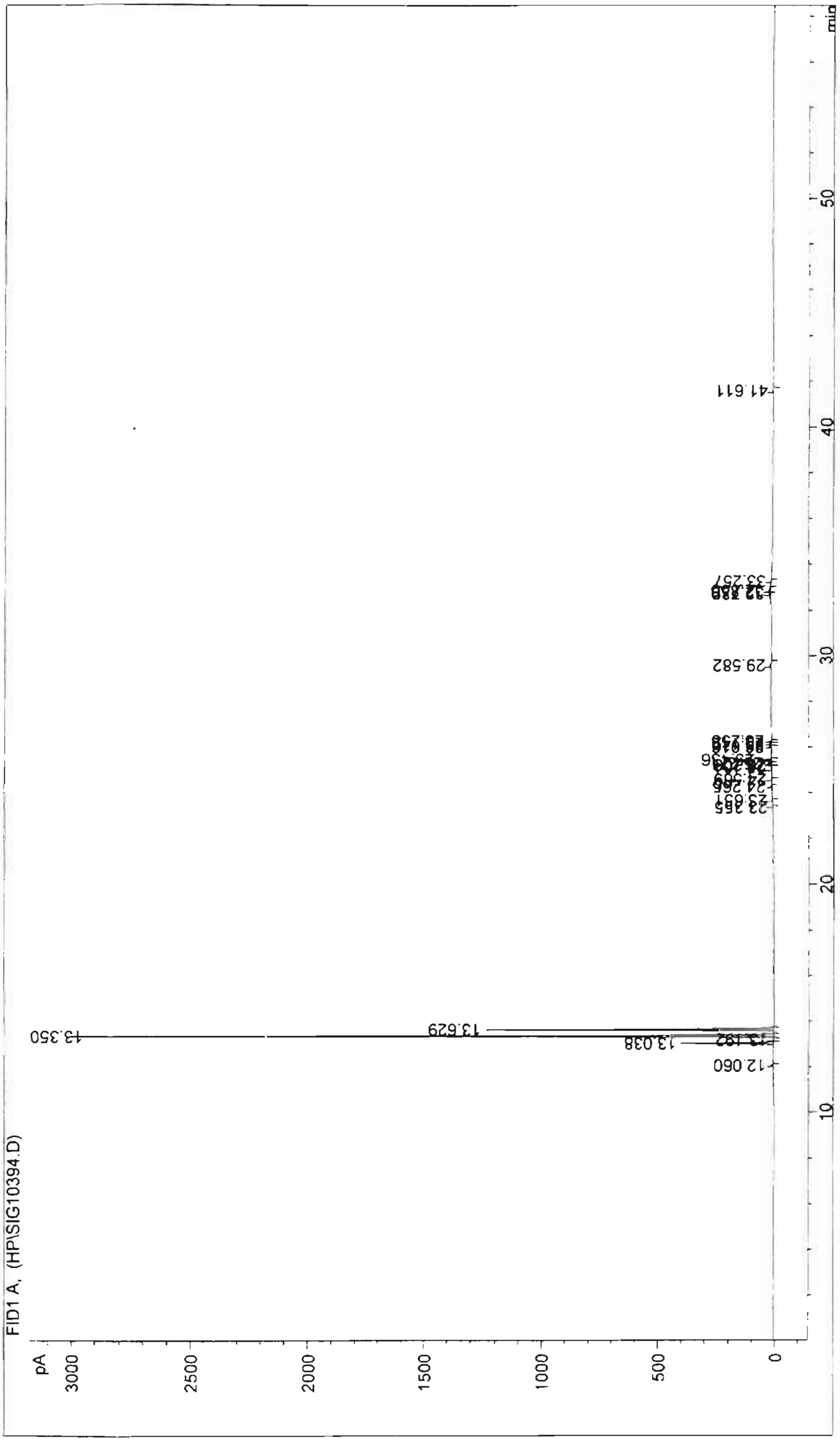
Run #14

```
Data File C:\HPCHEM\2\DATA\HP\SIG10391.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:25:08 PM MSH

======================================================================
Injection Date  : 7/9/00 7:25:52 PM
Sample Name     : 1-butene/NAFION                     Vial :   -
Acq. Operator   : MSH                                  Inj :   1
                                               Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 7/7/00 12:35:42 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

======================================================================
                         Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  12.078 BB    0.0445   33.26461   11.58035  0.22010
   2  13.052 BB    0.0454 7137.33057 2489.40991 47.22458
   3  13.213 BP    0.0471   11.53277    3.72292  0.07631
   4  13.376 VB    0.0457 4336.42676 1502.45691 28.69223
   5  13.651 BB    0.0452 3467.40063 1181.48706 22.94226
   6  25.289 BB    0.0430    8.79750    3.21202  0.05821
   7  25.455 BP    0.0421   29.38958   11.01703  0.19446
   8  26.033 PB    0.0527    8.39304    2.35000  0.05553
   9  26.156 BP    0.0416    6.15097    2.26938  0.04070
  10  32.595 BP    0.0458    5.46646    1.94255  0.03617
  11  32.677 VB    0.0538   11.81328    3.07389  0.07816
  12  32.981 BB    0.0746   12.70780    2.48754  0.08408
  13  41.599 PP    0.0565   11.79350    3.31311  0.07803
  14  58.276 BB    0.0847   33.12616    4.78823  0.21918
Totals :                  1.51136e4  5223.11090

======================================================================
                          *** End of Report ***
```


FID1 A, (HP\SIG10391.D)
pA
2500
2000
1500
1000
500
0
10
20
30
40
50
min
12.078
13.052
13.213
13.376
13.651
25.289
26.058
32.981
41.599
58.276

Run #15

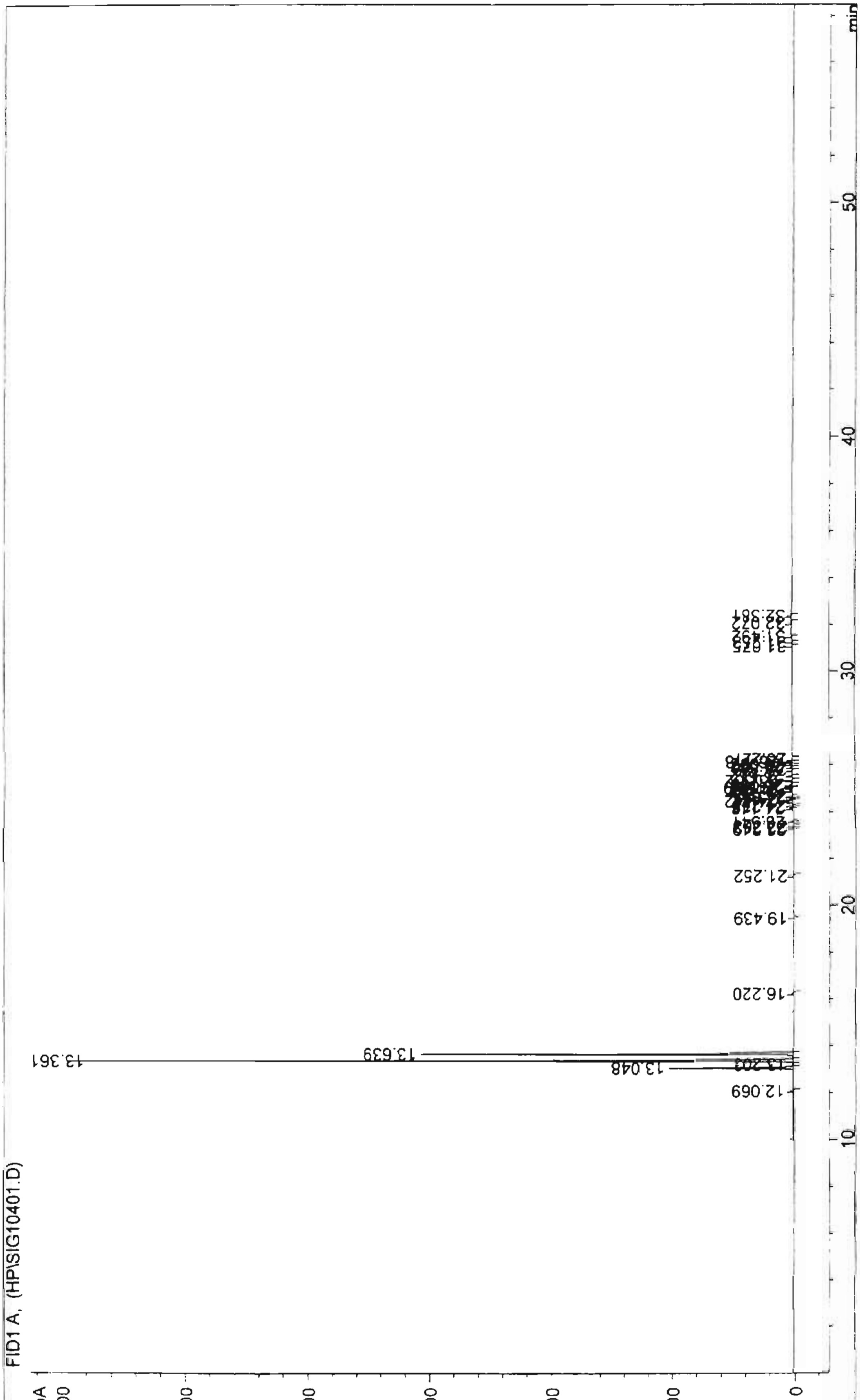
```
Data File C:\HPCHEM\2\DATA\HP\SIG10394.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:27:03 PM MSH

=====================================================================
Injection Date  : 7/10/00 5:24:51 PM
Sample Name     : 1-butene/NAFION                     Vial :   -
Acq. Operator   : MSH                                  Inj :   1
                                               Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 7/10/00 5:12:01 PM by MSH
                  (modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [pA*s]       [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  12.060 BP    0.0454   31.87386   11.13252  0.22771
   2  13.038 BB    0.0441 1116.08215  393.37912  7.97339
   3  13.192 BP    0.0434    9.62773    3.46536  0.06878
   4  13.350 BB    0.0447 8706.60352 3011.95972 62.20073
   5  13.629 BB    0.0461 3588.28271 1227.96155 25.63500
   6  23.355 BB    0.0415    5.57904    2.00437  0.03986
   7  23.651 PB    0.0416    7.81331    2.98264  0.05582
   8  24.265 BB    0.0437   24.68124    8.81642  0.17632
   9  24.569 BP    0.0558   14.02367    3.49799  0.10019
  10  25.131 BV    0.0891   25.81810    3.76237  0.18445
  11  25.206 VV    0.0401    9.86176    3.81930  0.07045
  12  25.271 VV    0.0466   52.94215   16.89529  0.37822
  13  25.436 VP    0.0430  149.58798   52.92804  1.06867
  14  26.016 BV    0.0483   36.14718   11.62358  0.25824
  15  26.142 VV    0.0402   24.91682    9.61804  0.17801
  16  26.255 VP    0.0404   29.51375   11.34077  0.21085
  17  29.582 BP    0.0775   28.88913    4.64936  0.20639
  18  32.739 BV    0.0949   45.39424    6.98003  0.32430
  19  32.855 VB    0.1149   67.47219    8.29296  0.48203
  20  33.257 PP    0.0441    7.53348    2.82676  0.05382
  21  41.611 BB    0.0636   14.94590    3.82016  0.10677
Totals :                  1.39976e4  4801.75635

=====================================================================
                          *** End of Report ***
```


FID1 A, (HP\SIG10394.D)
pA
3000
2500
2000
1500
1000
500
0
10
20
30
40
50
min
12.060
13.038
13.192
13.350
13.629
23.365
23.631
24.266
24.509
29.582
33.257
41.611

Run #16

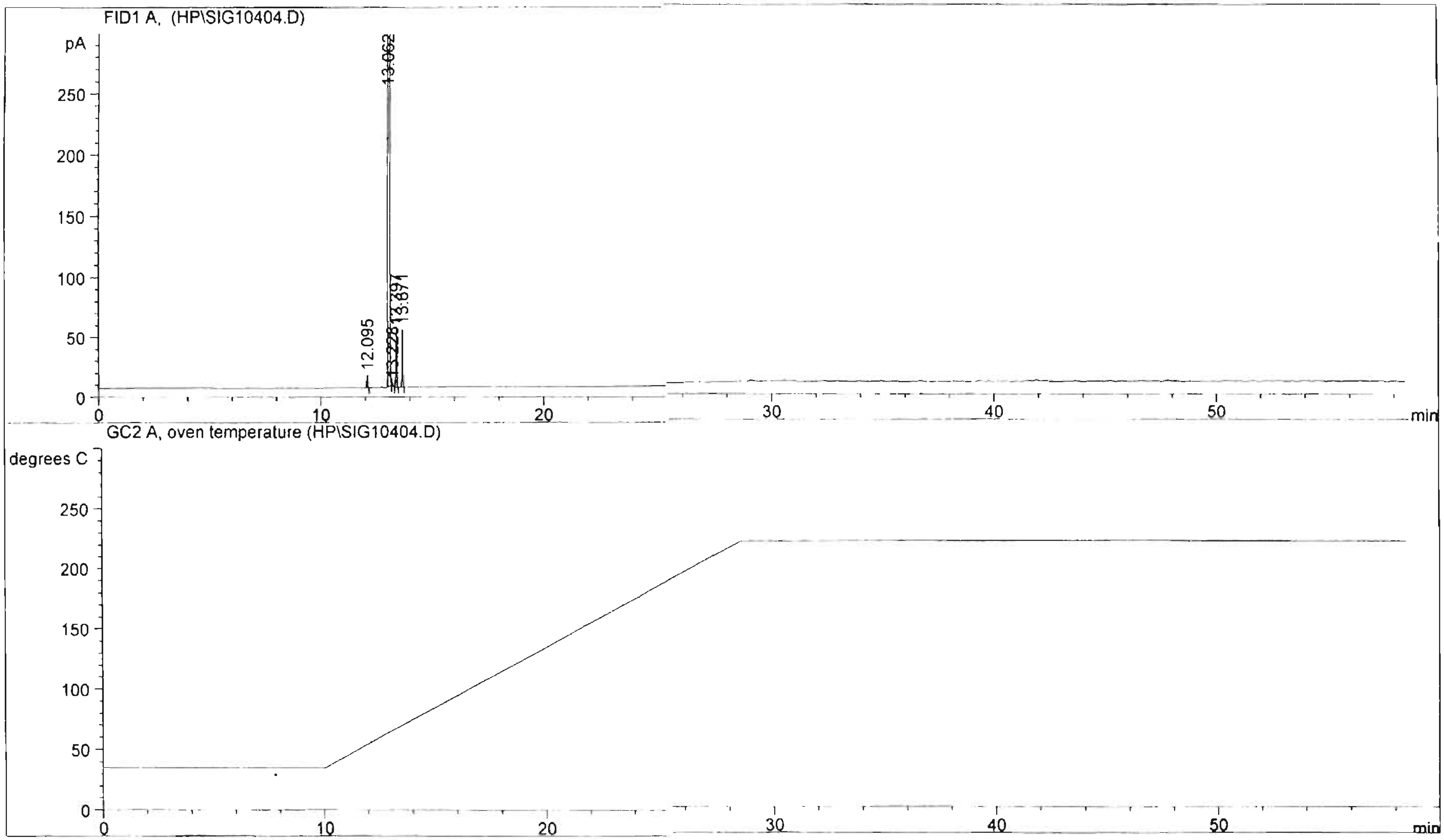
```
Data File C:\HPCHEM\2\DATA\HP\SIG10401.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:28:24 PM MSH

=====================================================================
Injection Date   : 8/12/00 7:38:38 AM
Sample Name      : 1-butene/NAFION                        Vial :   -
Acq. Operator    : MSH                                     Inj :   1
                                                   Inj Volume : Manually
Acq. Method      : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 7/7/00 12:35:42 PM by MSH
Analysis Method  : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 8/30/00 3:11:58 PM by MSH
                   (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                        Area Percent Report
=====================================================================

Sorted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.069 BP    0.0458   34.32468   11.83247  0.22240
   2  13.048 BB    0.0444 1445.59656  504.91733  9.36661
   3  13.203 BP    0.0453   11.94190    4.18717  0.07738
   4  13.361 VB    0.0447 8568.52930 2969.33545 55.51897
   5  13.639 BB    0.0461 4456.46631 1523.50830 28.87525
   6  16.220 BB    0.0443   18.07186    6.32703  0.11709
   7  19.439 BP    0.0412    4.86053    1.81462  0.03149
   8  21.252 BB    0.0402    4.56054    1.75924  0.02955
   9  23.249 PV    0.0420   16.27431    6.12464  0.10545
  10  23.363 VB    0.0602   14.22477    3.44144  0.09217
  11  23.541 BP    0.0388   22.17505    8.97576  0.14368
  12  24.148 PV    0.0617   40.80972   10.65902  0.26442
  13  24.238 VP    0.0401   17.83289    6.90191  0.11555
  14  24.442 BV    0.0523  139.52609   38.44908  0.90405
  15  24.561 VV    0.0405   14.74958    5.65101  0.09557
  16  24.645 VB    0.0479   17.67464    5.73869  0.11452
  17  24.957 BV    0.0426   78.11088   25.62704  0.50611
  18  24.999 VV    0.0400  103.67876   39.01593  0.67178
  19  25.074 VV    0.0372   29.51801   12.22383  0.19126
  20  25.139 VP    0.0464   35.68886   11.13269  0.23124
  21  25.302 VP    0.0392   89.47749   35.70673  0.57976
  22  25.512 BP    0.0369   32.16047   13.93337  0.20838
  23  25.789 PV    0.0507    9.60048    2.62056  0.06221
  24  25.880 VV    0.0588   44.76301   11.41360  0.29004
  25  26.003 VV    0.0459   36.93531   12.69494  0.23932
```

```
  26  26.113 VP    0.0394   88.45250   35.10811  0.57312
  27  26.227 BB    0.0375    8.95080    3.79347  0.05800
  28  31.075 PP    0.0418    4.77865    1.81263  0.03096
  29  31.253 BP    0.0343    3.30299    1.58391  0.02140
  30  31.492 PB    0.0469   11.80084    3.83112  0.07646
  31  32.072 PB    0.0753   22.49819    4.35155  0.14577
  32  32.381 PB    0.0491    6.18025    2.05275  0.04004
Totals :                  1.54335e4  5326.52539

=====================================================================
                       *** End of Report ***
```


FID1 A, (HP\SIG10401.D)
pA
3000
2500
2000
1500
1000
500
0
10
20
30
40
50
min
12.069
13.048
13.203
13.361
13.639
16.220
19.439
21.252
23.349
26.278
31.825
31.492
32.072
32.381

Run #17

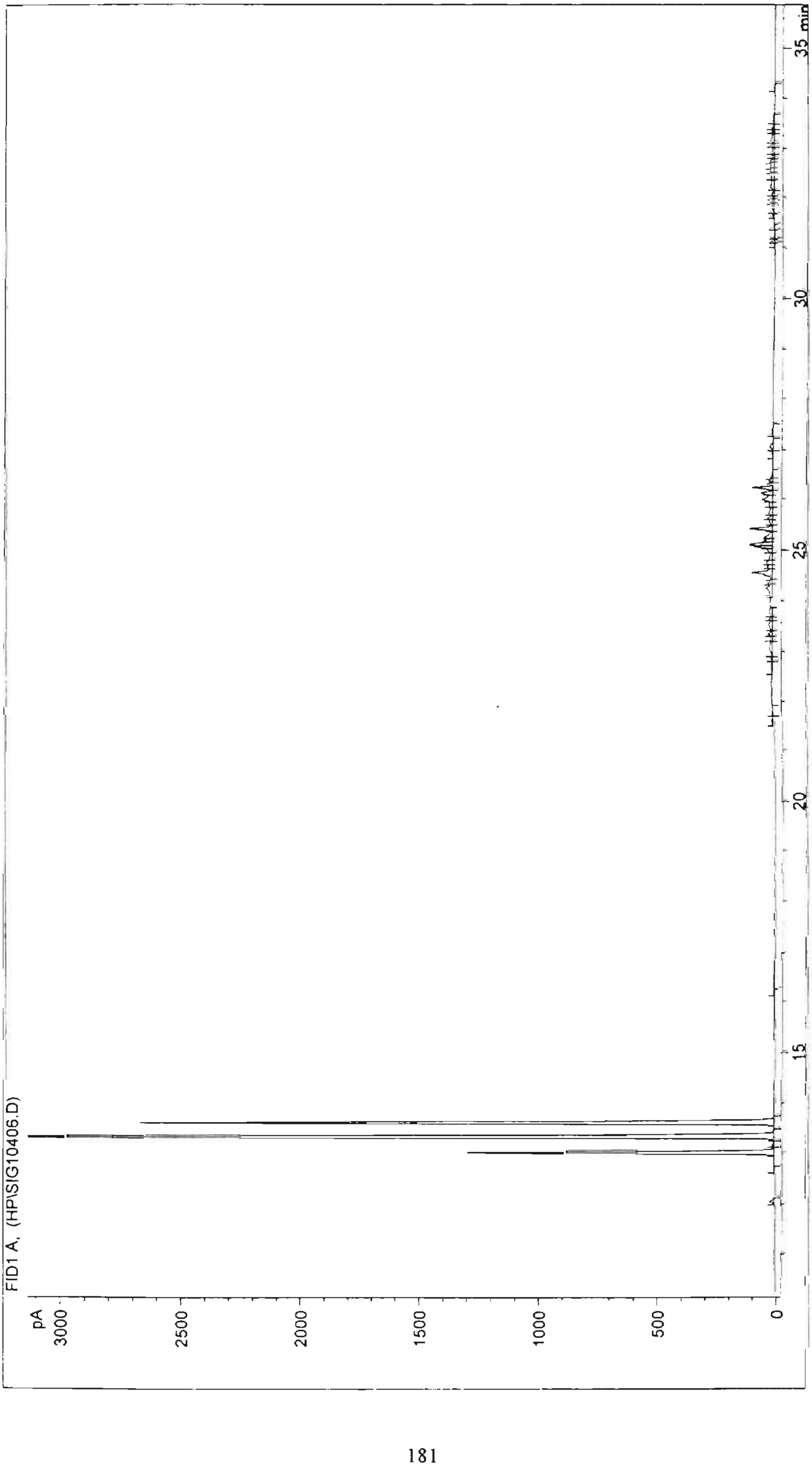
```
Data File C:\HPCHEM\2\DATA\HP\SIG10404.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:30:21 PM MSH

=====================================================================
Injection Date  : 8/14/00 12:25:04 AM
Sample Name     : 1-butene/NAFION                       Vial :   -
Acq. Operator   : MSH                                    Inj :   1
                                                Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 7/7/00 12:35:42 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.095 BB    0.0446   30.76315   10.67442  0.22334
   2  13.062 BB S  0.0460 1.34579e4  4623.51221 97.70633
   3  13.228 BP    0.0363    4.84062    2.32468  0.03514
   4  13.397 BB    0.0457  137.91704   47.73459  1.00129
   5  13.671 BB    0.0451  142.40636   48.66957  1.03389
Totals :                  1.37739e4  4732.91547

=====================================================================
                          *** End of Report ***
```


FID1 A, (HP\SIG10404.D)
pA
250
200
150
100
50
0
13.062
12.095
13.228
13.391
13.871
0
10
20
30
40
50
min
GC2 A, oven temperature (HP\SIG10404.D)
degrees C
250
200
150
100
50
0
0
10
20
30
40
50
min

Run #18

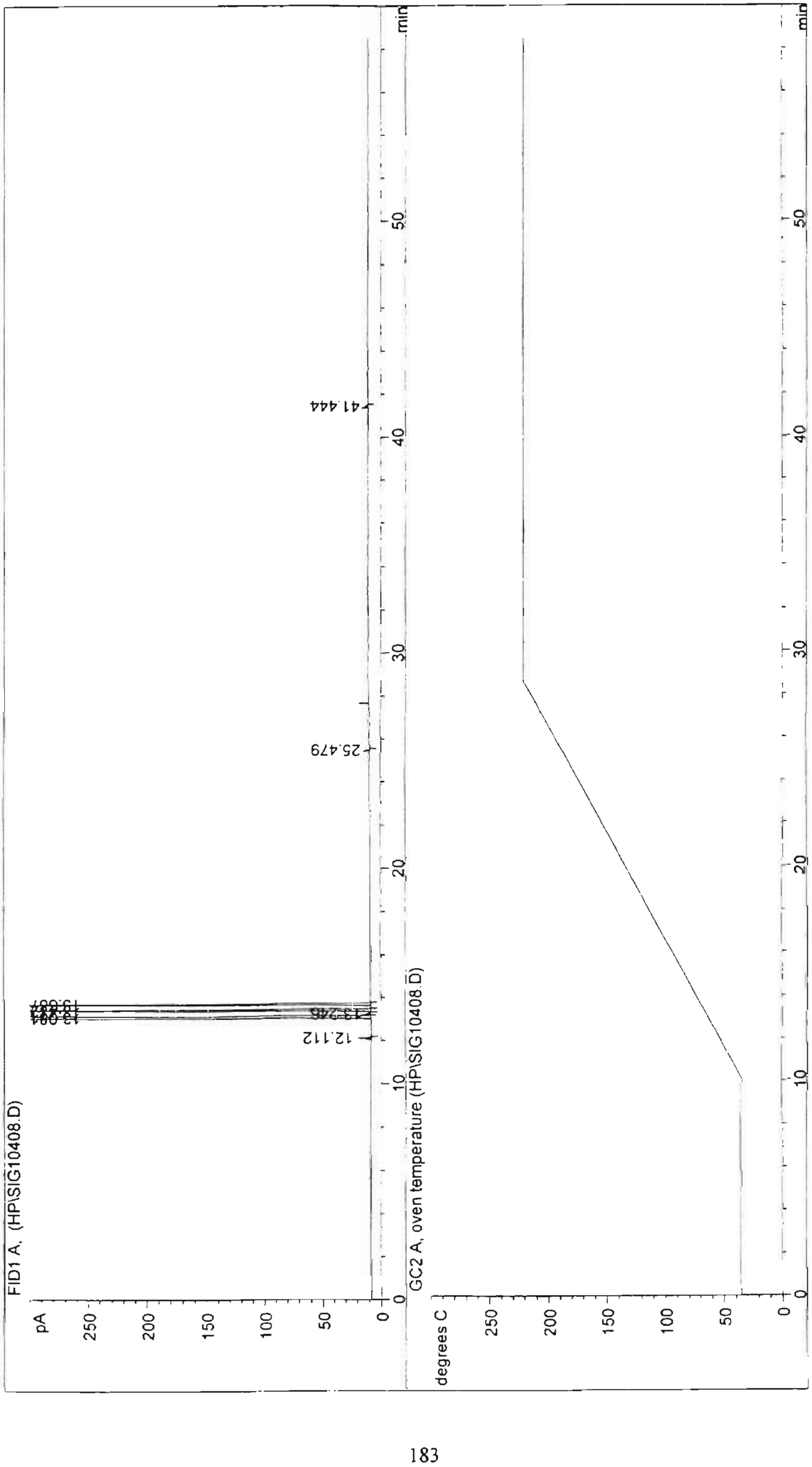
```
Data File C:\HPCHEM\2\DATA\HP\SIG10406.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:33:51 PM MSH

=====================================================================
Injection Date  : 8/15/00 11:08:47 PM
Sample Name     : 1-butene/NAFION                      Vial :   -
Acq. Operator   : MSH                                   Inj :   1
                                                Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 7/7/00 12:35:42 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.045 BB    0.0452   54.18343   18.50647  0.18396
   2  12.671 BB    0.0430    5.16847    1.88327  0.01755
   3  13.020 BB    0.0445 3698.77026 1288.11731 12.55805
   4  13.177 BP    0.0452   19.82180    6.76244  0.06730
   5  13.331 VB S  0.0460 1.28900e4  4424.52490 43.76404
   6  13.610 BB    0.0464 7833.59619 2653.93384 26.59660
   7  16.198 BP    0.0440   11.12190    3.92940  0.03776
   8  21.617 BP    0.0874   30.60888    5.29921  0.10392
   9  21.778 VP    0.0432    7.54477    3.79250  0.02562
  10  22.645 PP    0.1060   29.81433    3.51234  0.10123
  11  22.849 VV    0.0531   15.28072    4.45098  0.05188
  12  23.057 VV    0.1310  133.05334   12.52058  0.45174
  13  23.251 VV    0.0704   52.66493   10.89123  0.17881
  14  23.347 VV    0.0551   68.39395   18.50501  0.23221
  15  23.534 VV    0.1125  128.38219   16.18477  0.43588
  16  23.644 VV    0.0466   46.04044   14.66903  0.15632
  17  23.813 VV    0.1143  113.67049   12.84172  0.38593
  18  24.256 BV    0.1044  223.90205   27.97468  0.76019
  19  24.351 VV    0.0485   68.19924   20.68240  0.23155
  20  24.562 VV    0.0621  398.21136   89.11944  1.35201
  21  24.678 VV    0.0518   86.75493   24.78052  0.29455
  22  24.762 VV    0.0627  114.32135   27.97606  0.38814
  23  24.846 VV    0.0923   97.50473   14.71335  0.33105
  24  25.015 VV    0.0544   87.62077   23.04576  0.29749
  25  25.083 VV    0.0405  213.29091   78.91396  0.72416
  26  25.125 VV    0.0418  272.29358   96.97783  0.92449
```

```
   27   25.200 VV     0.0419  105.38956    37.39520  0.35782
   28   25.267 VV     0.0612  159.89807    36.45401  0.54289
   29   25.433 VV     0.0453  295.22003   100.50661  1.00233
   30   25.577 VV     0.0638   67.98056    15.31717  0.23081
   31   25.644 VV     0.0515   76.74773    22.12240  0.26057
   32   25.746 VV     0.0831  112.01936    18.36929  0.38033
   33   25.927 VV     0.0674   82.50648    16.19160  0.28013
   34   26.015 VV     0.0706  226.38206    45.83917  0.76861
   35   26.142 VV     0.0493  163.40758    51.05592  0.55480
   36   26.251 VV     0.0419  229.68289    86.62046  0.77982
   37   26.367 VV     0.0405   50.94881    19.48764  0.17298
   38   26.437 VP     0.0605   25.05822     5.79055  0.08508
   39   26.932 PV     0.0807   15.16908     3.12396  0.05150
   40   27.069 VP     0.0869   74.03027    13.51095  0.25135
   41   27.376 PP     0.0944   33.66786     5.20838  0.11431
   42   31.067 BP     0.0397    4.65177     1.82597  0.01579
   43   31.139 VP     0.0337    3.17334     1.50168  0.01077
   44   31.237 VP     0.0234    1.53892     1.90266  0.00522
   45   31.414 BP     0.0298    3.36863     1.98215  0.01144
   46   31.655 PV     0.0481   19.85893     6.24230  0.06742
   47   31.838 VV     0.0969   60.77060     8.34618  0.20633
   48   31.920 VV     0.0615   42.20926    10.36237  0.14331
   49   32.031 VV     0.0490   21.16966     5.88512  0.07188
   50   32.090 VV     0.0607   40.62963     9.53597  0.13795
   51   32.233 VB     0.1192  138.10101    16.07429  0.46888
   52   32.425 BV     0.0782   81.00040    14.06862  0.27501
   53   32.540 VV     0.0637   76.39581    17.92198  0.25938
   54   32.660 VV     0.0831   98.33924    15.48843  0.33388
   55   32.736 VV     0.0708   74.02937    15.75282  0.25134
   56   32.840 VV     0.0608   37.15392     9.07749  0.12614
   57   32.918 VV     0.0928   69.58653     9.80808  0.23626
   58   33.073 VV     0.0679   43.01667     9.67340  0.14605
   59   33.161 VV     0.1143  104.04653    12.10669  0.35326
   60   33.343 VV     0.0511   34.15841     9.70139  0.11597
   61   33.410 VB     0.0578   41.09323    10.23356  0.13952
   62   33.551 BB     0.0882   30.39394     4.47597  0.10319
   63   34.205 BB     0.0522   10.37756     3.08596  0.03523
Totals :                      2.94534e4  9576.55537

=====================================================================
                          *** End of Report ***
```


FID1 A, (HP\SIG10406.D)
pA
3000
2500
2000
1500
1000
500
0
15
20
25
30
35 min

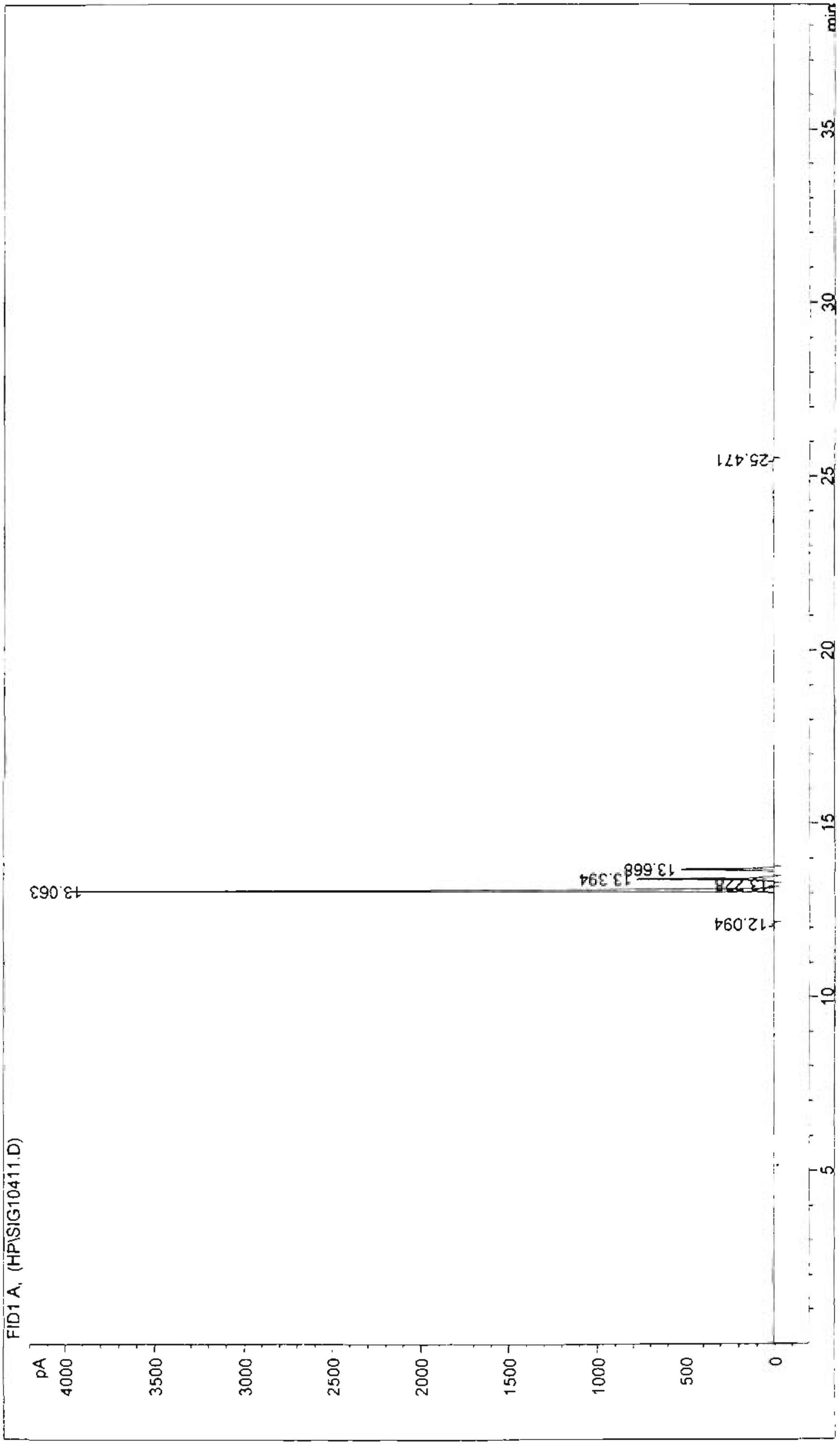
Run #19

```
Data File C:\HPCHEM\2\DATA\HP\SIG10408.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:35:52 PM MSH

=====================================================================
Injection Date  : 8/16/00 9:59:26 PM
Sample Name     : 1-butene/NAFION                        Vial :   -
Acq. Operator   : MSH                                     Inj :   1
                                                  Inj Volume : Manually
Acq. Method     : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 7/7/00 12:35:42 PM by MSH
Analysis Method : C:\HPCHEM\2\METHODS\NEW.M
Last changed    : 8/30/00 3:11:58 PM by MSH
                  (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [pA*s]       [pA]         %
----|-------|----|-------|----------|----------|--------|
   1  12.112 BB    0.0445   33.55912   11.67183  0.22314
   2  13.081 BB S  0.0448 1.15340e4  3983.75098 76.69044
   3  13.246 BP    0.0383    6.60826    2.81926  0.04394
   4  13.412 BB    0.0447 2043.81494  707.92834 13.58954
   5  13.687 BB    0.0461 1402.34558  479.24615  9.32434
   6  25.479 PP    0.0416    9.10425    3.46765  0.06054
   7  41.444 PB    0.0584   10.23819    2.68784  0.06807
Totals :                  1.50396e4  5191.57206

=====================================================================
                        *** End of Report ***
```


FID1 A, (HP\SIG10408.D)
pA
250
200
150
100
50
0
12.112
13.084
13.246
25.479
41.444
0
10
20
30
40
50
min
GC2 A, oven temperature (HP\SIG10408.D)
degrees C
250
200
150
100
50
0
0
10
20
30
40
50
min

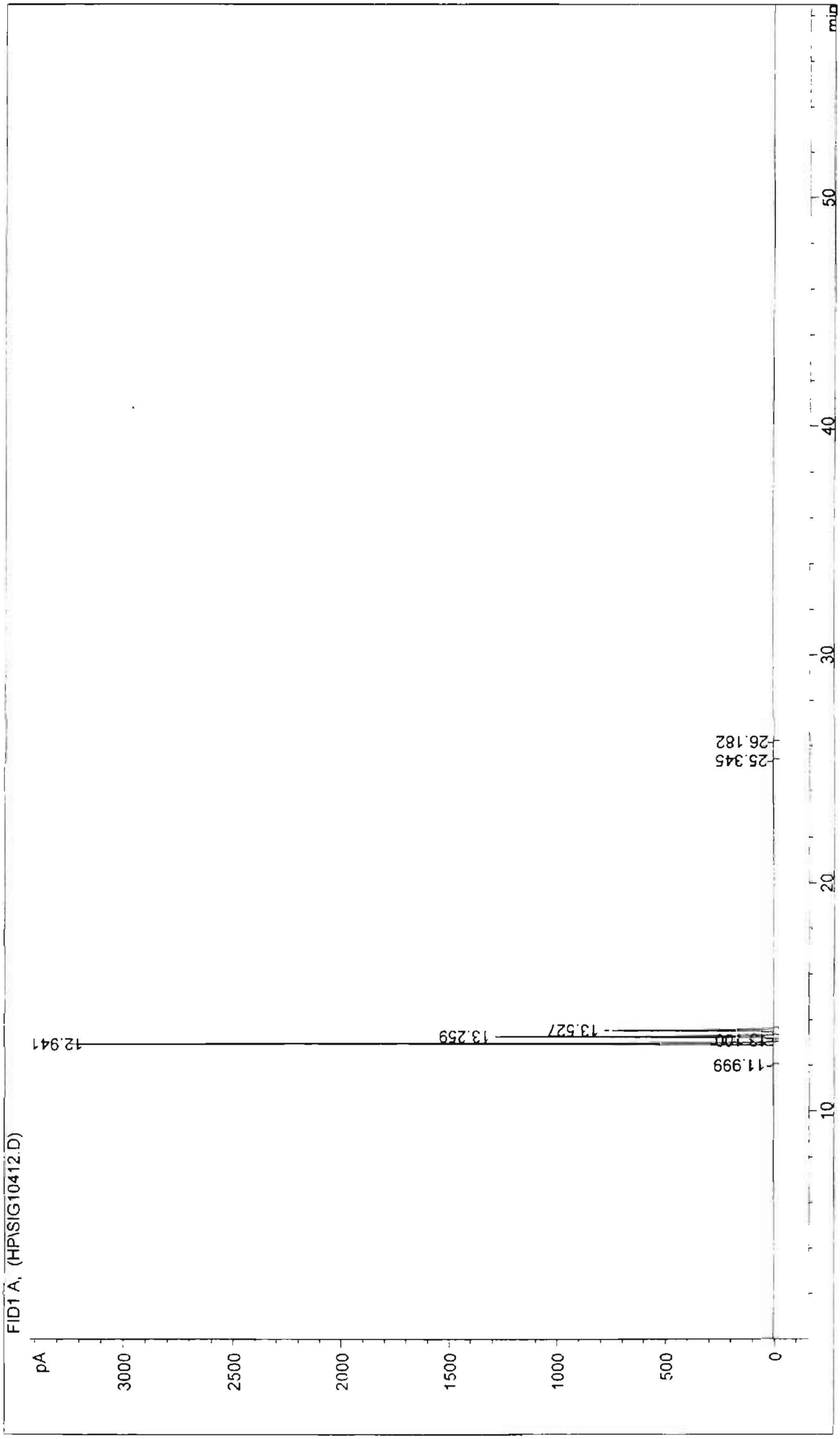
Run #20a

```
Data File C:\HPCHEM\2\DATA\HP\SIG10411.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:37:55 PM MSH

=====================================================================
Injection Date   : 8/17/00 3:28:22 PM
Sample Name      : 1-butene/NAFION                     Vial :   -
Acq. Operator    : MSH                                  Inj :   1
                                                Inj Volume : Manually
Acq. Method      : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 7/7/00 12:35:42 PM by MSH
Analysis Method  : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 8/30/00 3:11:58 PM by MSH
                   (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                        Area Percent Report
=====================================================================

Sorted By              :      Signal
Multiplier             :      1.0000
Dilution               :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.094 BB    0.0445   34.33142   11.95832  0.22387
   2  13.063 BB S  0.0448 1.15330e4  3986.04443 75.20493
   3  13.228 BP    0.0383    6.61914    2.83254  0.04316
   4  13.394 BB    0.0457 2228.51880  772.20343 14.53180
   5  13.668 BB    0.0461 1526.29724  522.06073  9.95273
   6  25.471 PB    0.0417    6.67214    2.53683  0.04351
Totals :                  1.53355e4  5297.63628

=====================================================================
                        *** End of Report ***
```


FID1 A, (HP\SIG10411.D)
pA
4000
3500
3000
2500
2000
1500
1000
500
0
13.063
12.094
13.394
13.668
25.471
5
10
15
20
25
30
35
min

Run #20b

```
Data File C:\HPCHEM\2\DATA\HP\SIG10412.D Sample Name: 1-butene/NAFION
HP 6890 GC 8/30/00 4:39:36 PM MSH

=====================================================================
Injection Date   : 8/17/00 4:12:43 PM
Sample Name      : 1-butene/NAFION                        Vial :   -
Acq. Operator    : MSH                                     Inj :   1
                                                Inj Volume : Manually
Acq. Method      : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 7/7/00 12:35:42 PM by MSH
Analysis Method  : C:\HPCHEM\2\METHODS\NEW.M
Last changed     : 8/30/00 3:11:58 PM by MSH
                   (modified after loading)
new method after pp and column trouble:  flow rate 1.2 ml/min; oven temp
= 35;
ramp 10/min; finish temp 220; inlet t = 150; fid 43 makeup; air flow =
450;
hydrogen flow = 40; FID temp = 250

=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  11.999 BB    0.0445   34.22844   11.92201  0.22258
   2  12.941 BB    0.0446 9345.87891 3247.35034 60.77373
   3  13.100 BP    0.0479   11.64709    3.78378  0.07574
   4  13.259 VB    0.0448 3694.01978 1276.70715 24.02122
   5  13.527 BB    0.0462 2275.89355  775.72577 14.79952
   6  25.345 PP    0.0409   12.05828    4.55718  0.07841
   7  26.182 PP    0.0391    4.42898    1.77376  0.02880
Totals :                  1.53782e4  5321.82000

=====================================================================
                         *** End of Report ***
```


FID1 A, (HP\SIG10412.D)
pA
3000
2500
2000
1500
1000
500
0
10
20
30
40
50
min
11.999
12.941
13.100
13.259
13.527
25.345
26.182

APPENDIX C

University of Kansas
Department of Chemical Engineering
Adsorption Isotherm Analysis
Nafion™Resin/
Silica Nanocomposite

StarDriver V2.01 Gemini 2360 V4.01 Serial # 601

Filename: C:/STARDRVR/SAC2501.MGD
Sample ID: SAC25_Sample 1 50C
Setup Group: Dave's

Started:	Sat. Pressure:	747.36 mmHg	
Completed:	Meas. Freespace:	-0.4312 cm^3	
Report time:	03/08/00 16:57:18	Sample Weight:	0.1203 g
Evac. Rate:	100.0 mmHg/min	Evac. Time:	3.000000 minutes
Analysis Mode:	Equilibration	Equil. Interval:	12 secs

Summary Report

Area

Single Point Surface Area at P/P_o 0.27689468 :	67.5161 m^2/g
BET Surface Area:	69.8569 m^2/g
BJH Adsorption Cumulative Surface Area of Pores Between 17.000000 and 300.000000 A Diameter:	73.7664 m^2/g

Volume

BJH Adsorption Cumulative Pore Volume of pores Between 17.000000 and 300.000000 A Diameter	0.282214 cm^2/g

Pore Size

BJH Adsorption Average Pore Diameter (4V/A):	153.0312 Å

APPENDIX D

Material Specifications

Product Purity Specifications of Gases and Catalyst Used in This Research Effort

Product	Use	Details	Purchased from
Butane	GC analysis	BIC™ Lighter; gc indicates an inert material in lighter fluid	OSU Chemstore
Pentane	GC analysis	99.91% purity	OSU Chemstore
Ultra-Purity Helium	GC analysis	99.999% Helium; 1 PPM O_2, H_2O<1PPM; Hydrocarbons<0.5PPM; CO and CO_2 < 1PPM	Sooner Airgas, Stillwater
H_2 prepurified	GC analysis	99.99% Purity	Sooner Airgas, Stillwater
Standard Grade Helium	Process Gas (diluent)	99.9% Pure Helium	Sooner Airgas, Stillwater
Air, Zero Grade	GC analysis	Hydrocarbons < 1 PPM	Sooner Airgas, Stillwater
1-butene	Process gas	CP Grade 99% Purity	Sooner Airgas, Stillwater
Nafion™ SAC 25 Solid Acid Catalyst	Catalyst	25% Nafion catalyst, Surface area 200m2/g, granular 0.5-3 mm; Pore volume > 0.6 ml/g; Pore Diameter >10nm; Density 0.45 g/ml.	DuPont, Inc.
Nafion™ SAC 25 Solid Acid Catalyst	Catalyst	See Attachement	Engelhard Corp.
Nafion™ SAC 25 Solid Acid Catalyst	Catalyst	See Attachment	Engelhard Corp.

SAC-13 General Information

Revised, 5 September 2000

Currently Engelhard is manufacturing and marketing three versions of SAC-13 solid acid catalyst, all of which have a nominal composition of 13% Nafion(R) sold acid and 87% Silica. This composition and general manufacturing method was first invented by Dar. Mark Harmer @ DuPont. DuPont did not wish to commercialize this product and thus DuPont & Engelhard have entered into an agreement wherein DuPont supplies Engelhard with specific raw material Nafion(R) and we manufacture & sell the catalyst. All three of the SAC-13 catalyst versions are currently in the physical form of 1mm extruded particles with a quadralobe cross sectional area. We find that this size and shape is optimal for may reactions. Previous DuPont work showed that 13% of Nafion(R) is about optimum for most reactions. Higher contents of Nafion(r) are possible but not commercial at this time.

The three versions of SAC-13 catalyst differ mainly in pore volume and surface area with some corresponding differences in physical strength / crush / attrition resistance. All are commercially acceptable and have been used in commercial sized reactors. We are currently selling commercial quantities of SAC-13 catalyst around the following properties:

* Size/ Shape :	1mm diameter cylinders (but can make anything up to 3/16") with either circular or quadralobe cross section shape
* % Nafion:	Nominal 13%
* Acidity:	0.12 to 0.16 milliequivalents / gram (titratable by NaOH) NOTE: the acid strength of Nafion(R) has been stated by DuPont at about same as 95-99% H2SO4 , perhaps even higher. The acid strength of the Silica-Nafion(R) composite is expected to be same as the value for NR-50 resin, however, we have not measured this.
* Type of acidity	100% Bronsted [from sulfonic acid groups in the Nafion(R)]
* Surface area:	150-250 sq. Meters / gram
* Hg Pore volume range :	About 0.55 to about 1.1 cc / gram
SAC-13 version 22-11,	pore volume = 0.55- 0.58 cc/g
SAC-13 version 22-11A ,	pore volume = about 0.7-0.79 cc/gm
SAC-13 version 531,	pore volume = 1.0-1.2 cc/gm
* Bulk Crush:	< 3% to about 12% (this test measures % fines < 20 mesh produced during crushing 50 cc @ 300 lbs.)
* Ion exchange capacity:	Same as acidity, 0.12 to 0.16 meq/gm
* Moisture:	typically 1% - 3%
* Temperature limits:	Same as Nafion(R) NR-50 resin, about 250 C in air or 275C in inert. However, "official" continuous duty working temperature recommendation is to keep below about 225C. It is possible to operate at higher temperatures under some circumstances, especially in absence of air and / or Oxygen.
* Solvent resistance:	Very good, very similar to Teflon(R), however SAC-13 is not stable in aqueous caustic or bases due to slight solubility of Silica in aqueous basic solutions.
* Applications:	same as applied to Nafion(R) NR-50 resin and other solid acid catalysts.
* Activation technique:	Basically designed to remove last traces of residual moisture,

	that is, vacuum dry for several hours at 120C or dry in flowing dry air, N_2 or He at 120-140C for 4-8 hours.
* Known catalyst poisons:	These include water & protic solvents which have the same effect on "leveling" the acidity as they do with acids like H_2SO_4. Also materials containing cations which will ion exchange the H+ and neutralize or diminish the acidity. Obviously all amines & other basic compounds can act as catalyst poisons under most circumstances.
* Storage:	Sealed drum, away from heat and moisture.
* TSCA listed :	Yes
* Handling hazards:	Minimal, same as for non-crystalline silica and NR-50 resin
* Flammable:	No, however, may evolve oxides of sulfur and / or HF on strong heating above 300C
* Availability:	Commercial as acid (H+) or sodium (Na+) form
* Samples:	Yes, contact Jim White (jim.white@engelhard.com, phone = 216-360-5046) or Jeffrey Ramler (jeffrey.ramler@engelhard.com, phone = 216-360-5044)

VITA

Talee K Redcorn

Candidate for the Degree of

Master of Science

Thesis: EXPERIMENTAL ANALYSIS OF 1-BUTENE ISOMERIZATION OVER NAFION™ RESIN/SILICA NANOCOMPOSITE CATALYST

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Tahlequah, Oklahoma, on April 3, 1964, the son of James Lacy (Jim) and Jo Beryl (Joby) Henry Redcorn

Education: Received Associates of Technology in Building Construction at Oklahoma State University School of Technical Training, Okmulgee, Oklahoma in 1984. Received Bachelors of Science in Chemical Engineering at the University of Oklahoma in 1994. Completed the requirements for Masters of Science degree in Chemical Engineering at Oklahoma State University in December 2000.

Experience: Worked in the construction industry from 1982 to 1986 as a frame and finish carpenter, roofer and concrete construction worker. Honorably Discharged from the United States Army; was an infantryman for the 1/52nd, 177th Armor Brigade, Fort Irwin California from 1988 to 1991. Worked in various environmental engineering and management positions for tribal and United States governmental agencies from 1994 to 1998. Employed as a Process Engineer for Conoco, Inc., in Ponca City, Oklahoma in the Refining Technology division, Process Technology and Optimization.