“Reactions under Supercritical Phase: Heterogeneous Dehydrogenation of n-Decane over Pt-Sn/γ-Al_2O_3 catalyst”

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(ENVIRONMENTAL PROCESS DESIGN)

By
Patel Bhavinkumar M.
(04MCH010)

Department of Chemical Engineering
INSTITUTE OF TECHNOLOGY
NIRMA UNIVERSITY OF SCIENCE & TECHNOLOGY
AHMEDABAD 382 481
MAY 2006

CERTIFICATE

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Guide:

(Prof. (Dr.) N. Subrahmanyam)
Visiting Professor,
Chemical Engineering Department,
Institute of Technology,
Nirma University.

(Prof. Amish P. Vyas)
Professor,
Chemical Engineering Department,
Institute of Technology,
Nirma University.

(Prof. Amish P. Vyas)
Head, Chemical Engineering Department,
Institute Of Technology,
Nirma University.

(Dr. H.V. Trivedi)
Director,
Institute of Technology,
Nirma University.

Examiners: i.
(Name and Signature)

ii.
(Name and Signature)

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This is to certify that the work which is being presented by **Mr. Patel Bhavinkumar Maganlal**, a student of M.Tech. (Environmental Process Design), in the dissertation entitled **"Reactions under Supercritical Phase: Heterogeneous dehydrogenation of n-decane over Pt-Sn/γ-Al_2O_3 catalyst"**, has been carried out under our supervision at the Research Centre, Indian Petrochemicals Corporation Limited, Baroda.

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Dr. K.R. Krishnamurthy,
VP (R&D),
IPCL – Baroda.

Dr. D. Rajeshwer,
GM (R&D),
IPCL – Baroda.

Dr. G.S. Rao
GM (R&D),
IPCL – Baroda.

Dedicated to my parents, being the preceptor and the living goddess for me

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PREFACE

Perhaps the most challenging field in environmental engineering practice is the treatment and disposal of industrial and hazardous waters, since the growth and revolution in industrial sector. And at the present time it is going to be crucial both in economic as well as environmental aspect. But now more and more awareness has been immerging in the industry to consider **waste** as **wa$te**, that is why people are of more concern about reduction in waste, and hence getting improved environment and enhancement in economic benefit. This has brought revolutionary change in thinking habits. Instead of 'end of pipe' treatment people are now thinking of reduction at source. In this support Dr. Paul Anastas had released a new concept of Green chemistry with his twelve principles. Green chemistry can be explained as any process which is able to eliminated hazardous reactants or solvents reduce the material and energy usage in the process, reduction in the waste generation and hence improving the atom economy. In the present work, effort has been made to study the dehydrogenation reaction of n-Decane over Pt-Sn/γ-Al_2O_3 catalyst with elimination of hydrogen in the process.

Detergent industry is among the widest area of industry in the world. LAB (Linear Alkyl Benzene) and LAS (Linear Alkyl Sulphone) are most important intermediates used in detergent industry as biodegradable surfactants. LAB can be manufactured in two steps; first step is dehydrogenation of linear long chain normal paraffins (C_{10}-C_{13}) to its mono olefins conversion. And the second step is alkylation reaction of the mono olefin and benzene. This work is mainly focused on the first step. Commercial process is mainly done in presence of hydrogen. As the catalyst used (Pt-Sn on alumina support) in this reaction is highly susceptible to deactivation. This is mainly due to coke formation on the surface of catalyst. So generally hydrogen to hydrocarbon ratio in the rage of 5-8 molar ratio is used to prevent coke formation on the surface. During the dehydrogenation reaction other undesired by products like aromatics leads to coking on the catalyst surface. But the usage of hydrogen may allow to swipe out this coke forming precursor form the surface and this maintaining the activity. But this process consumes lots of hydrogen which is highly hazardous and potential energy source too. So, effort has been made to study this reaction under supercritical phase, with total elimination of hydrogen usage. And it was concluded at the end of the research work that reaction under supercritical phase gives sustained activity with significant conversion and selectivity. And thus this area has good potential to expand green chemistry principles for environmental benefit.

This research thesis has been presented in seven chapters. **Chapter 1** consists of the introductory part and theoretical aspects of the heterogeneous catalytic supercritical phase reaction. This chapter has been divided in two parts, first part covers, the supercritical fluids, properties and benefits for the reactions. Some of the physical phenomena have also been mentioned in this section, for instance activation volume, solubility parameter and effects, dielectric constant etc. While in the second part, catalysis and its components, along with the supported metal catalyst for various processes in petrochemical industry is given. Commercial PACOL^{TM} process for dehydrogenation of C_{10}-C_{13} fraction has also been descried in this section. Undesired by product have also discussed in this portion. And at the end of the chapter main deactivation problem of catalyst for the industrial process is given in a short description.

In **Chapter 2**, research work done by the scientist in various petrochemical reactions is discussed. **Chapter 3** contains the objective of this research work and scope of doing dehydrogenation reaction in the super critical phase. There are three parameters in this reaction; these are temperature, pressure, and Liquid Hour Space Velocity (LHSV). Box Wilson design for experiments is used to study the effects of each parameter at different level. Details are discussed in **Chapter 4**. In **Chapter 5**, experimental methodologies are discussed in detail. This includes the reactor design, setup design, and analysis procedure for reactant and product fraction. While whole experimental analysis, is therein the **Chapter 6**. Various parameter effects on conversion and selectivity of desired product are discussed. In this chapter rate kinetics and reaction mechanism based on LHHW model and Rideal Eley is also derived. In the same chapter modeling, model discrepancy, and parameter estimation is done for the Power low model, LHHW model, R-A model, with different steps like adsorption, surface reaction, desorption as controlling step. And at the last, out come of the research work is presented summarily in **Chapter 7**.

NOMENCLATURE

C(A)	Concentration of A, mole/lit
κ	Transmission coefficient,
k_B	Boltzmann constant,
h	Planck's constant,
T	Absolute temperature,
K_c*	Concentration-based equilibrium constant for the reaction involving the reactants and transition state
$K_\gamma*$	$\Pi\gamma_i^{\nu_i}$
ν_i	Stoichiometric coefficient
γ_i	Activity coefficient
ρ	Molar density of reacting mixture
$\Delta G*$	Gibb's free energy, between the activated complex and the reactants
$\Delta v*$	Activation volume, difference between the partial molar volumes of the activated complex and reactants
v_A, v_B	Partial molar volume of reactants A and B
v_m*	Partial molar volume of activated complex
$\Delta\varphi*$	Volume change due to the variation of atomic distances during transition state formation
$\Delta\Pi*$	As a measure of the interaction of the reacting species with the surrounding solvent e.g. the reaction mixture
δ_i	Solubility parameter of component i
δs	Solubility parameter of solvent
μ	Dipole moment
ε	Dielectric constant
k'	Rate constant in a medium with unit dielectric constant
u	Internal energy
v	Molar volume
h	Enthalpy
ig	Ideal gas
N_{av}	Avogadro's number
L	Bed length

d_P	Catalyst particle diameter
D	Bed diameter
f_y	Permissible Yield Stress
f_t	Permissible Tensile Stress
P	Design Pressure
f	Design Stress
t	Thickness of reactor
J	Joint Efficiency Factor
f_{cir}	Circumferential stress
f_l	Longitudinal stress
f_{we}	Stress due to weight
f_w	Stress due to wind
f_t	Stress due to tubing
f_R	Resultant Stress of all type of stresses
x_1, x_2, x_3	Box Wilson model constants
P	Paraffin
O	Olefin
A	Aromatics
LE	Light Ends
RMSD	Root Mean Square Difference
LHSV	Liquid Hour Space Velocity (h^{-1})
pP, pO, pLE, pA, pH2	Partial pressure of paraffin, olefin, lighters, hydrogen, at
X_P X_O X_{LE} X_A, X_{H2}	Moles of paraffin, olefin, lighters, aromatics, hydrogen
TM	Total mole
r_1, r_2, r_3, r_4	rate of formation of olefin, aromatic, lighters, hydrogen gmole/gm/hr
$k_1, k_2,$	rate equation constant for forward direction
$k_{-1,}k_{-2}$	rate equation constant for reverse direction
K_p, K_o, K_A, K_H	Adsorption constant for the paraffin, olefin, aromatic, hydrogen
L	Active cite on the catalyst surface
Ct	Total concentration of active cite on the catalyst surface
$C_{PL}, C_{OL}, C_{AL}, C_{HL}$	Concentration of components attached with the active site on the catalyst surface

W	Weight of Catalyst, gm
F	Molar flow rate of feed, mole/hr
K_{11}, K_{22}, K_{33}, K_{44}, K_{55}, K_{66}, K'_{O}, K_{OA}	LHHW model rate equation constants
SCFs	Supercritical Fluids

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TABLES AND FIGURES

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1. Introduction

This introductory chapter is subdivided in to two parts. The first one deals mainly with fundamental aspects of supercritical phase reaction its effect on kinetics and equilibrium. The second part discusses about catalysis and its component.

Part-1 Supercritical Phase Reaction

1.1Definition:

Fluid phase above critical temperature and critical pressure is called supercritical phase. At temperature above the critical temperature (*Tc*) a fluid cannot undergo a transition to a liquid phase regardless of the pressure applied. The critical point of a fluid marks the terminus of the vapour-liquid co-existence curve.

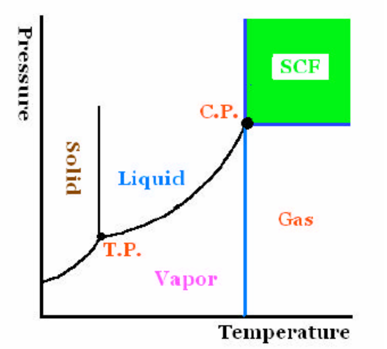


Fig 1.1 Pressure vs Temperature Graph showing critical region

1.2Supercritical Phase as Reaction Media

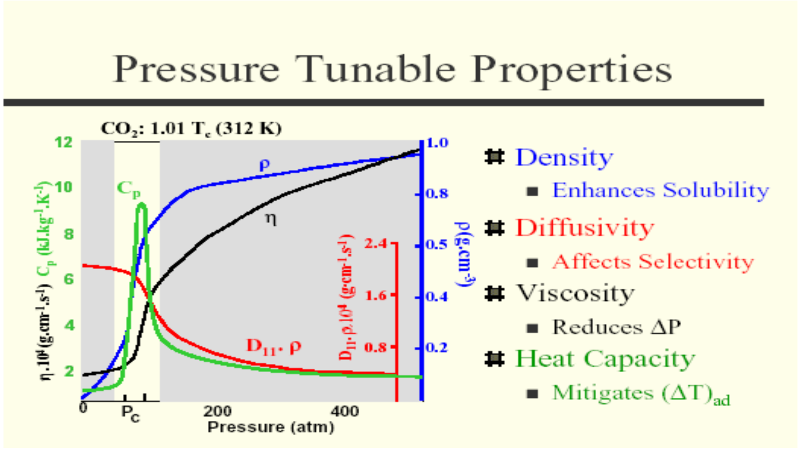
Since 1970, the cost of energy was increasing quite rapidly. Industrial solvents were under increasing scrutiny due to their toxic effects and adverse impact on pollution; while at the same time newer processing techniques were demanding better performance of solvents in terms of selectivity and high solubility. In this scenario, super critical extraction provided a new technology in solvent extraction, having the main advantage of being nontoxic and nonpolluting. It was this situation, which was largely responsible of the great efforts in research and development in supercritical fluid technology, initiated both in industry and academia. In the early 1980s, the emphasis of research and development in supercritical fluid science and technology was on extraction of commodity chemicals and synthetic fluids. Since 1984, attention has shifted towards more complex and valuable substances that undergo much broader range of physical and chemical transformations. A great deal of innovation took place in the studies of extraction of natural food colors, fragrances [1, 2, 3, 4], essence-taste spices and oil separations[5, 6, 7, 8, 9, 10, 11, 12, 13] , foods [14, 15], pharmaceuticals [16, 17] and hazardous wastes[18, 19, 20, 21, 22, 23, 24] etc. In the present work more attention is given to the supercritical phase reaction, more applications of supercritical fluids can be found somewhere else [25, 26, 27, 28, 29, 30].

Table 1.1: Comparison of Magnitudes of Physical Properties of Liquids, Gases and SCFs in the near Critical Region (Phillips et al)

Physical quantity	**Gas (ambient)**	**Supercritical fluid(Tc,Pc)**	**Liquid (ambient)**
Density (kg m^{-2})	0.6-2	200-500	600-1600
Dynamic Viscosity (mPa s)	0.01-0.3	0.01-0.03	0.2-3
Kinematic viscosity (10^6 m^2 s^{-1})	5-500	0.02-0.1	0.1-5
Diffusion coefficient (10^6 m^2 s^{-1})	10-40	0.07	0.0002-0.002

The use of supercritical fluids as reaction media offers the chemical and pharmaceutical industries the opportunity to replace conventional hazardous organic solvents and simultaneously optimize and control more precisely the effect of the solvent on reactions. Supercritical fluids, unlike conventional liquid solvents, can be “pressure tuned” to exhibit gas-like to liquid-like properties. **Table 1.1** shows that fluids at supercritical phase have density as liquid like while viscosity and diffusivity as gas like. Due to this peculiarity, supercritical fluids exhibit following advantages for reaction media particularly heterogeneous catalysis of petrochemical processes.

- **Supercritical fluids exhibit higher compressibility near the critical point** including large changes in density with very small changes in pressure and/or temp which enables separation of the dissolved material easily & completely



Pressure Tunable Properties

- ⌗ Density
  - ■ Enhances Solubility
- ⌗ Diffusivity
  - ■ Affects Selectivity
- ⌗ Viscosity
  - ■ Reduces ΔP
- ⌗ Heat Capacity
  - ■ Mitigates $(\Delta T)_{ad}$

Fig 1.2 Pressure Tunable Properties of Supercritical Fluid

- **As increase in pressure the density occurs as liquid like density** which-enables enhanced extraction of heavy hydrocarbons so this enhanced extraction and maintains wider catalyst pore channels, reduces pore diffusion limitations and increases the availability of reactive sites.
- **Density is comparable to liquid** making it afford substantial dissolution power
- **Diffusivity and viscosity are more gas like** which makes diffusion-controlled reaction in the liquid phase improved
- In this phase **there is only one phase** so it eliminates interphase transport limitation (leads to superior Mass transfer so higher % X)

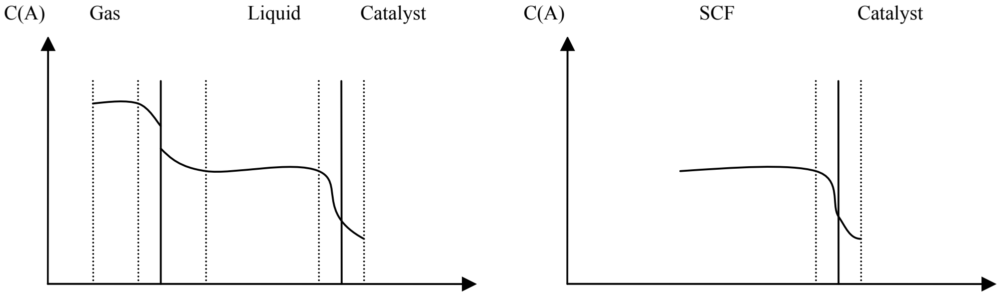


Fig. 1.3 Elimination of interphase mass-transfer in SCF

- **Integrate** reaction and separation
- Low viscosity & higher density results in **superior Mass Transfer**
- **Low surface tension** enabling easy penetration into the pores of catalyst for extraction of nonvolatile materials from within the pores.

1.3 Reaction Kinetics at Supercritical Phase

This section gives a brief introduction to and an overview of transition state theory concept at supercritical phase condition. This theory views a chemical reaction as occurring via a transition-state species (or an activated complex), It means reactant first convert in an intermediate transition-state species M^* and then in to product. The superscript identifies a species or property with the transition state. This is a state with maximum energy along the reaction coordinate, where the reaction coordinate is the minimum energy pathway between the reactants and the products on the potential-energy surface. To develop and illustrate the basic uses of transition state theory we will consider the generic elementary reaction

$$aA + bB + \ldots\ldots.. \leftrightarrow M^{*} \rightarrow \text{Products} \qquad (1.1)$$

The transition-state theory rate constant (k) is given by **[31]**

$$k = \kappa \frac{k_B T}{h} K_c * \qquad (1.2)$$

Where κ = Transimission coefficient,

k_B = Boltzmann constant,

h = Planck’s constant,

T = Absolute temperature,

K_c* = concentration-based equilibrium constant for the reaction involving reactants and transition state

Now the equilibrium constant accessible from classical thermodynamics, K_a* is related to K_c* as **[32]**

$$K_c * = \frac{Ka*}{K\gamma *} \rho^{(1 - a - b - ......)} \qquad (1.3)$$

Where $K_\gamma* = \Pi \gamma_i^{\nu_i}$

v_i = stoichiometric coefficient

γ_i = activitiy coefficient

ρ = molar density of reacting mixture

We can then write the transition-state theory rate constant as

$$k = \kappa \frac{k_B T}{h} \frac{Ka*}{K\gamma *} \rho^{(1 - a - b - ......)} \qquad (1.4)$$

$$k_x = \frac{k}{\rho^{(1 - a - b - .....)}} = \kappa \frac{k_B T}{h} \frac{K_a*}{K_\gamma*} \qquad (1.5)$$

$$k_x = \frac{k}{\rho^{(1 - a - b - .....)}} = \kappa \frac{k_B T}{h} K_x * \qquad (1.6)$$

Where $K_x* = \Pi x_i^{\nu_i}$. Relating this equilibrium constant to the difference in Gibb’s free energy, $\Delta G*$, between the activated complex and the reactants, we can write the rate constant as

$$k_x = \kappa \frac{k_B T}{h} \exp\left(\frac{-\Delta G*}{RT} \right) \qquad (1.7)$$

Thus, the rate constant for an elementary reaction step is a function of the difference in Gibbs' free energies between the reactants and the transition state.

1.4 Pressure effects – Activation volume

From the transition-state theory rate constant in Eq. 1.6 and classical thermodynamics, one can show by taking log (based e) on both side and doing partial differentiation with respect to P with T constant that:

$$\left(\frac{\partial \ln k_x}{\partial P}\right)=\left(\frac{\partial \ln K_x*}{\partial P}\right)+\left(\frac{\partial \ln \kappa}{\partial P}\right)=\left(-\frac{\Delta v*}{RT}\right)+\left(\frac{\partial \ln \kappa}{\partial P}\right) \qquad (1.8)$$

Where $\Delta v*$ = activation volume, difference between the partial molar volumes of the activated complex and the reactants.

$$\Delta v* = v_m* - av_A - bv_B - ..... \qquad (1.9)$$

The second term on the right-hand-side of Eq. 1.8 is neglected in most developments, either because the transmission coefficient is taken to be equal to unity or because there is insufficient information to evaluate the contribution of this term. Note however, that experimental measurements of $(\partial \ln k_x/\partial P)_T$ will include the effect of pressure on the transmission coefficient. More information on this can be found somewhere else **[33]**. $\Delta v*$ has two parts, these parts are: the intrinsic part or van der waals volume, v_1; the salvation part v_2. The intrinsic volume accounts for volume changes arising from changes in bond lengths and angles. While second parts account for the volume changes arising from electrostriction and other solvent effects.

$$\Delta v* = \Delta\varphi* - \Delta\Pi*(\partial v/\partial P) \qquad (1.10)$$

Where $\Delta\varphi*$ = volume change due to the variation of atomic distances during transition state formation

$\Delta\Pi*$ = as a measure of the interaction of the reacting species with the surrounding solvent e.g. the reaction mixture

Integration of Eq. 1.8 with second term neglecting and using Eq. 1.10 gives

$$\ln k(P,T) = \ln k_0(T) - \frac{\Delta\varphi*}{RT}(P-P_0)+\frac{\Delta\Pi*}{RT}(v(P)-v_0) \qquad (1.11)$$

Activation volumes for reactions in the liquid phase are typically between -50 and 30 cm^3/mol **[34]**, where as apparent activation volumes on the order of 1000 cm^3/mol have been reported [35, 36] for reactions in dilute fluids near their critical points. As one moves from critical point, activation volumes approach their liquid-phase values.

1.5 Solubility effect (Reactions in solution)

Solubility are especially important for reactions in SCFs, as in this phase reactant behaves more solvent like. Consider an elementary bimolecular reaction, A+ B → C, but the methods discussed can be readily extended to other types of reactions. Rate constant for this bimolecular reaction in a given solvent can be related to the rate constant in an ideal fluid phase as

$$k = k_0 \left(\frac{\gamma_A \gamma_B}{\gamma_{M^*}} \right) \qquad (1.12)$$

But according to regular solution theory, activity coefficient can be related to solubility parameter as given below:

$$\mathrm{RT}\ \ln\gamma_i = v_i\ (\delta_i - \delta s)^2 \qquad (1.13)$$

Where v_i = molar volume of component i

δ_i = solubility parameter of component i

δs = solubility parameter of solvent

Now using activity coefficient value from Eq. 1.13 in Eq. 1.12 we get

$$\ln\left(\frac{k}{k_0} \right) = \frac{v_A(\delta_A - \delta_s)^2 + v_B(\delta_A - \delta_s)^2 - v_{M^*}(\delta_A - \delta_s)^2}{RT} \qquad (1.14)$$

This expression allows one to correlate or predict the effect of solvents with different solubility parameters on the rate constant.

1.6 Effect of Dielectric Constant

The dielectric constant is another solvent property that has found frequent use in correlating solution-phase reaction kinetics, especially for reactions involving polar molecules and/or transition states. Considering exclusively electro-static, it is showed [37] that the free energy of a point dipole with dipole moment μ and in a cavity of radius r in a medium of dielectric constant ε relative to its free energy in a medium with a dielectric constant of unity is [38]

$$\Delta G = -\left(\frac{\mu^2}{r^3} \right) \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} \qquad (1.15)$$

Combining this expression for the free energy with the transition-state expression for the rate constant leads to

$$\ln k = \ln k' - \left(\frac{N_{av}}{RT}\right)\frac{(\varepsilon - 1)}{(2\varepsilon + 1)}\left[\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{M^*}^2}{r_{M^*}^3}\right] \tag{1.16}$$

Where k' = rate constant with unit dielectric constant

N_{av} = Avogadro's number

Equation shows that rate constant should increase with the dielectric constant of the medium if the transition state is more polar that the reactants. And it should vary linearly with the quantity (ε - 1)/ (2ε + 1) on semi log plot. This expectation has been confirmed for reactions in the liquid phase [31, 38]. Several investigators have correlated rate constants for reactions in SCFs with the solvent dielectric constant [38, 39].

1.7 Thermodynamics Properties

The variation in solvent strength of a supercritical fluid from gas like to liquid like values may be described qualitatively in terms of density; ρ, or the solubility parameter; δ (square root of the cohesive energy density). According to the rigorous thermodynamic definition

$$\delta = \left(\frac{u^{ig} - u}{v_m}\right) = \left(\frac{h^{ig} - RT - h + Pv_m}{v_m}\right)^{1/2} \tag{1.17}$$

Where, u = internal energy

v_m = molar volume

h = enthalpy

Superscript ig = ideal gas

Similar characteristics are observed for the density dependent variables versus pressure, e.g., enthalpy, entropy, viscosity and diffusion coefficient. However, unlike δ some of these properties decrease with density. The δ (solubility parameter) for gaseous carbon dioxide is essentially zero. Where as the value for liquid carbon dioxide is like that of a hydrocarbon. Above the critical temperature, it is possible to tune the solubility parameter continuously over a wide range of either a small isothermal pressure change or a small isobaric temperature change. This ability to tune the solvent strength of supercritical fluid is its unique feature and it can be used for extraction and then recovery of selected products. The density and solubility are more direct measures of the solvent strength of a

SCF than pressure. Density is good indicator of a solvent strength for a single supercritical fluid, but it is not a useful indicator for comparing different fluids. For e.g. CF_3Cl at 40^{o}C and 1300 bar has mass density **[81]** of 1.95 g/cm^3, yet it is a weaker solvent that a much less dense fluid SCF CO_2 or liquid hexane.

A better indicator of the Vander Waals Forces contributed by SCF is obtained by multiplying density by the molecular polarizability; α, which is a constant for a given molecule. The solubility parameter of CO_2 can be misleading. It is larger than ethane's even though ethane has a larger value of $\alpha\rho$. However 20% of δ for CO_2 may be attributed to its large quadrapole moment. For nonpolar solutes, where this quadrapole moments is unimportant, which also have small values of $\alpha\rho$. SCFR water on heating expands by a factor of 3 destroying about 2/3 of the hydrogen bonds, and the dielectric constant drops from 80 to 5. Supercritical water behaves like a nonaqueous solvent and it dissolves many organics and even gases such as O_2. At 400^o C and 350 bars, the density of water is 0.47 g/ml, the electric constant, ε is 10 and the ion product, KW, is 7×10^{-14}compared with 10^{-14} at room temperature. Here water behaves as a dense fluid which can dissolve electrolytes, with high diffusion coefficients and ion nobilities. At 500^o C and the same pressure, the density of water is only 0.144 g/ml, ε is 2 and KW is 2×10^{-2}, at these conditions, water is high temperature gas which does not solvate ions significant.

PART 2: General Catalysis

1.8 Catalyst definition

"A Catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without itself becoming permanently involved in the reaction"

1.9 Classification of catalysis

A catalyst, in simplest terms, is a material, which enhances the rate, and selectivity of a chemical reaction and in the process is cyclically regenerated.

Catalysts are broadly classified into homogeneous, heterogeneous and enzyme catalysts.

In Homogeneous catalysis, the catalyst and the reactants are in the same phase. For instance: hydrolysis of ester by acids (liquid-liquid), oxidation of SO_2 by NO_2 (gas-gas) and decomposition of $KCLO_3$ by MNO_2 (solid-solid). Usually, the liquid phase is the most common, with both the catalyst and the reactant being present in solution.

In heterogeneous catalysis, as the name indicates, the catalyst and the reactant(s) exist in different phases. The primary step, in this case, is the adsorption of reactant(s) onto the surface of the catalyst. Adsorbed reactant molecules, thus activated by interaction with the catalyst surface are rapidly and selectively transformed into adsorbed products. Finally the adsorbed products leave the surface in a desorption step. Once the product is desorbed from its surface the catalyst momentarily returns to its original state until the next set of molecules adsorb, repeating the catalytic cycle. These interactions provide a "chemical shortcut" in which reactants are converted to products more rapidly and in several cases, under much milder conditions than if no interaction occurred.

The second aspect of the definition indicates that the reactants can be directed down a certain a chemical transformation path to generate a specific product. In this respect, the catalyst provides selectivity or specificity. It is these aspects of the definition, " enhancing rate and directing reactants to specific products" that makes catalysis play such a major role in the chemical, petroleum, petrochemical, fertilizer, pharmaceutical and fine chemicals industries and in solving environmental and energy related problems therein.
Automobile emissions control provides an interesting example of how rate enhancement by a catalyst is put to useful practice. The internal combustion engine in automobiles burns gasoline-air mixture to generate heat, which is converted to mechanical work in the engine (piston movement). The combustion process, however, is stoichiometrically less than 100% efficient, that is, undesirable byproducts such as carbon monoxide (CO) and unburnt hydrocarbons (HC) as produced, which pollute the atmosphere.

At moderately high temperatures and high flow rates typical of auto-exhausts there is insufficient time for CO and HC to react further with available oxygen to form CO_2 and water before they exit the tailpipe. However, placing a catalyst in the exhaust manifold allows these reactions to occur within the limited residence time and at the moderate reaction conditions of the catalytic converter. Thus, this catalyst provides an alternative chemical path leading to the destruction of the pollutants.

Another consequence of combustion processes is the generation of nitrogen oxides (NO_X), which can be catalytically, converted to harmless nitrogen, and safely emitted into the atmosphere. Enzymes are protein molecules of colloidal size. They are the driving forces of biochemical reactions. Present in life processes, they are characterized by tremendous efficiencies and selectivity. For instance, an enzyme, catalase, decompose hydrogen peroxide 10^9 times faster than any inorganic catalyst [40].

In this thesis, the emphasis is on heterogeneous catalysis, and especially in supercritical condition for dehydrogenation reaction.

1.10 Catalyst Components

Although some catalytic materials are composed of single substances, most catalysts have three types of easily distinguishable components:

1.10.1 Active components

Active components are responsible for the principal chemical reaction/activation. These could be in the form of metals, metal oxides or metal salts, crystalline or amorphous in nature. Based on the electronic theory of catalysis one can catalogue active components according to the type of electrical conductivity, i.e. metals, semiconductors and insulators. Since charge transfer is common for both electrical conductivity and catalysis, many aspects of catalysis could be explained on the basis of the theories for electrical conductivity of solids and electronic configurations of elements. Depending on their electronic structure, active components could catalyze different reactions as shown below in **Table. 1.2**

Table 1.2 Classification of active components

Class	Conductivity	Property	Reactions	Examples
Metals	Conductors	With metals, overlapping electronic energy bands promote electron transfer with adsorbing molecule [41]	Hydrogenation Hydrogenolysis, Oxidation	Fe, Ni, Pt, Pd, Cu, Ag
Metal oxides	Semiconductors	Electron donor and acceptor levels provide redox type activation but surface configurations are more complex than with metals. Greater geometric complexity leads to more selective redox reactions.	Selective hydrogenation, Hydrogenolysis, Dehydrosulfurization	NiO, ZnO, CuO

1.10.2 Catalytic Support

An important question that looms over a catalyst researcher at this juncture is the choice of appropriate support. This critical choice has to be made of the basis of the properties of the active species, the nature and conditions of the reaction under investigation, mobility of reactants/products. The options are infinite; for they range from naturally, occurring materials such as diatomaceous earth, kieselghur, activated carbon, pumice, kaolin, bentoites, etc to synthetic inorganic supports such as alumina, silica, magnesia, zirconia, titania, alumino-silicates etc.

How does the support contribute to catalysis? It provides a means to prepare a large particle or tablet of catalyst. Active phase, when incorporated on a suitable support gains stability against sintering. The support material, acting as walls between independent active species, helps in achieving this [42]. Thus, a high surface area is an important prerequisite, high surface area leads to increased dispersion and hence high activity. Often the loss of selectivity is an outcome of high activity and hence one should choose and optimum surface area farther than high surface area so as to maintain optimum activity [43, 44]. The selection of pore structure of the support should be such that the transport/mobility of reactants and products through the pore should not be restrained this choice purely depends upon the reactant molecular size. Increased porosity will lead to thin wall formation, thus adversely affecting the mechanical strength. An optimum porosity should be selected, such that the catalyst is suitable for continuous operations during the course of which, it should withstand immense thermal shock, attrition, and tendency for crumbling/powder formation etc.

Another aspect to be considered at this stage is the intrinsic catalytic activity of the support. One, must there for select a support, keeping in mind, whether this inherent activity is desirable or not, with reference to the selected reaction.

In the case of the reforming catalyst (Pt/acidic alumina), while the inherent acidity of alumina is necessary of dehydrocyclisation activity [45], the same is undesirable for the dehydrogenation of paraffin (Pt/neutral alumina), since it promotes side reactions [46]. Apart from this, the support may have some interaction with the active species, which may modify the catalytic action commonly termed as Strong Metal Support Interaction (or simply SMSI). In many a system, SMSI aids in stabilizing the active species and improve the activity [47, 48, 49, 50, 51]. Hence the metal-support system should be chosen in such a way that the optimum level of SMSI exist.

Considering all the afore-discussed factors, alumina is found to be the most compliant support. This is because the predation variables can be modified in such a way that the desired surface area, pore size distribution, pore volume acidity can be achieved [52].

As discussed earlier, the most important function of support/ carries is to provide a high surface area required for the active component. This is best illustrated with platinum, an important active component used widely for catalytic reforming [53]. For high activity, platinum crystallites must have the highest surface area possible, ideally, Pt crystallites should be as small as possible in the 0.5-5.0 nm range, but when platinum crystallites of this size are used directly as catalyst at very high temperatures, rapid agglomeration occurs resulting in sintering.

Supports also function as table surfaces over which the active component is dispersed in such a way that sintering is reduce [54]. The support itself must be secure from thermal growth, which means that it should have a high melting point - at least higher than that of the active component. High melting points are found in oxides materials cannot be utilized as catalytic supports. A good support - the oxide material, must be amenable to preparations yielding high surface area. Examples of such supports are γ – alumina, silica, diatomaceous clay, silica-alumina etc.

The level of active metal loading on the support is an important factor, since crystallites, even though isolated from each other, may sinter via the migration mechanism. Thus, sintering may not only be cause by high temperatures, but also by factors such as crystallite size, concentration, interaction of active metal with support, and atomic mobility [55]. Porosity is necessary for high surface area within the support, and pore shape and pore size distributions are critical when the reaction under consideration is diffusion controlled [56].

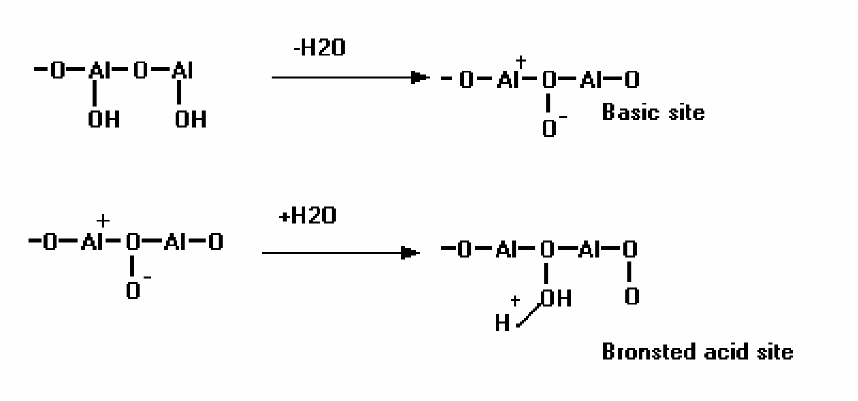


Figure 1.4: Inherent acidity of Alumina

The inherent acidity of the support also plays a vital role. In the case of alumina, the Bronsted site, **(Figure1.4)** that initiate carbonium ion reactions, giving ion radical reactions, coexist. Also though it appears that in practice Bronsted acidity predominates [57]. It is relevant to mention here that when using γ – alumina as support, undesirable side reactions such as cracking and isomerization leading to "coke" formation always occur. This coke formation is one of the principle reasons that lead to the deactivation of the catalyst.

In some cases, support acidity also has a positive influence, by directly controlling the main reaction. The catalytic dual functionality (- the metal function and the acid function) is illustrated in catalytic reforming, wherein the objective is to convert low octane components of naphtha(a mixture of normal paraffins and naphthenes) into high-octane isoparaffins and aromatic, typically, the catalytic system employed here is a low loading of platinum on alumina support. Platinum dehydrogenates naphthenes to aromatics but cannot isomerizes or cyclize normal paraffin's. This is accomplished by the acidic function of the support. This dual functionality becomes an important aspect of catalyst design. Depending upon the nature or our reaction, we can attenuate both or either of these functions to suit our needs.

Metal dispersion on the support is an important factor that affects the catalytic activity directly. But in actual practice there are various factors that contribute to the poor dispersion of active metal on support. Contaminated commercial agents could contain impurities that act as poison, or spillover (a phenomenon, in which a reactive species is generated in a metal site and then migrates over the support to other sites where further reaction occurs) can take place.

1.10.3 Promoters

A promoter is some third agent, which is not a catalyst by itself, but when added, often in small amounts, produces desirable activity, selectivity or stability.

Promoters are designed to assist either the support or the active component. A significant example is that of alumina. Alumina exists in various phases, out of which γ – alumina phase is the most preferred support. This phase being a defect spiral has a high surface area, a certain degree of acidity and forms solid solutions with transition oxides. This transition occurs at about 900^{o}C. This temperature, though not usually encountered during actual reaction, but might become necessary during catalyst regeneration. Addition of promoters such as silica or zirconia in very small amounts would push the transition temperature further beyond 900^{o}C [58]. The Support is then adequately protected against major thermal upsets and long term changes.

Most often, promoters are added to supports in order to inhibit undesirable activity, such as coke formation. Coking originates from cracking on the Bronsted sites followed by acid catalyzed polymerization to give $(CH_x)_n$ species that cover surface sites and ultimately block pores. Removal of coke by burning may itself lead to activity loss due to sintering. Bases neutralize acidic cracking sites, most effectively by alkali elements [59]. Potash, as a promoter, when added to alumina, reduces its coking tendencies.

When dual functionality is needed, as in catalytic reforming, extra acidity is achieved by adding chloride ions to the support [60]. A glance at Table 1.3 gives the effect of promoters in various catalytic processes. Promotion of active components may either by structural or electronic [61]. Addition of Re to Pt in reforming catalysts leads to vastly improved performance, due to decreased hydrogenolysis of the hydrocarbons [53]. Chemically, Re preferentially a bond with low coordination sites on crystal plane corners, edges and steps, since these sites are known to be involved with hydrogenolysis, coke formation reactions are suppressed [60].

In general, any additive, which enhances or inhibits catalytic functions, can be classified as a promoter.

Table 1.3 Examples of promoters in major catalytic process

Catalyst	Promoter	Function
Al_2O_3	SiO_2, ZrO_2, P K_2O HCL MgO	Improves thermal stability Poisons coking sties Increases activity Retards sintering active components
SiO_2 - Al_2O_3	Pt	Increases CO oxidation
Zeolites	Rare earth ions Pd	Increases acidity and thermal stability Increases hydrogenation
Pt/Al_2O_3	Re	Decreases hydrogenolysis and sintering
MoO_3/ Al_2O_3	Ni, Co	Increases hydrogenolysis of C-S and C-N
Cu-ZnO- Al_2O_3	ZnO	Decreases Cu sintering

1.11 Supported metal catalysts

In general, supported catalysts are of two types:

- Supported base metal catalyst
- Supported precious metal catalyst

Both the types are equally important as industrial catalysts in specific applications. In Supported catalysts, irrespective of base or precious metal, the catalytically active material is deposited on an inert or active support in a finely divided from [42]. As stated in the earlier section, the adsorption of reactants that governs the catalytic activity of a material directly depends on the extent of dispersion of the active species on support. Hence the active species have to be present in a finely divided or micro-crystalline form. Since most of the industrial reactions are carried out at high temperatures, these crystallites rapidly sinter and lose the desired high metal surface area, often leading to deactivation of the catalyst. Hence, they are supported on refractory materials like alumina, silica, clay, carbon etc., having adequate surface area to disperse the material. Some supports may have inherent catalytic properties, which may be desired or undesired [45, 46].

Thermal and mechanical stability of the support materials at the operating conditions is as important as the features of the active species for a specific reaction [62].

As mentioned earlier, factors like, state of the active species (metal / oxide / oxide / sulphide / chloride), their location, geometry, etc determine activity, selectivity and specificity of any supported metal catalyst. Two major steps are of great importance at this juncture:

- A suitable mode of incorporating the active phase onto the support in the required form
- Appropriate treatments to generate the necessary active sites and induce interaction between the active phase and support.

In general, the intention of using supported metal catalysts is to achieve a high metal surface area with relatively lesser amount of active material and to maintain it in the active form for the longer duration. In order to achieve this ultimate goal the catalyst should be prepared with:

- Optimum activity and maximum selectivity
- Longer life and easier regenerability
- Appropriate transport, thermal and mechanical properties

1.12Commercial Dehydrogenation Processes and Catalysts

Dehydrogenation reactions find application in production of hydrogen alkenes and oxygenates such as aldehydes and ketones. These alkenes and oxygenates are Important chemical intermediates in the production of polymers, rubbers, detergents, solvents, pharmaceuticals and insecticides. Reactants, products, catalysts, process conditions, and applications for commercially important dehydrogenation processes are summarized in **Table 1.4**.

Dehydrogenation is a class of chemical reaction by means of which unsaturated and more reactive compounds are produced. There are many important conversion processes in which hydrogen is directly or indirectly removed. In principle nay compound containing hydrogen atoms can be dehydrogenated. The large scale of dehydrogenation processes currently in use are the conversion of the benzene to styrene, paraffins, to olefins (propane to propylene), olefins to diolefins (butanes to butadiene), cycloparaffins to aromatics (cyclohexane to benzene) and alcohols to ketones or aldehydes.

Table 1.4 Catalyst used for various dehydrogenation reaction [65]

Reactant/Product	Catalysts	Process Conditions	Applications

Alkanes/alkenes	Cr/Al_2O_3,Cr/ZrO_2, Pt-Sn/Al_2O_3, Mo/Al_2O_3	400-500 C, 1-3 atm, LHSV = 1-3 h^{-1}, process time = 15 min to few hr	Detergents, polymers, rubbers
n- Butane/isobutene	Cr/Al_2O_3, Pt-Sn/Al_2O_3, alkali promoted Pt-Sn/ Al_2O_3	550-600 C, 1-3 atm, LHSV = 13 h^{-1}, process time = 10 - 100 min	MTBE, rubbers
Ethylbenzene/styrene	Fe_2O_3, K_2O,Cr_2O_3	590-600 C, Steam	Polystyrene
Cyclohexane/Benezene	Ag, Cu gauze, Pt/C Pd/C, Ni/Alumina	200-500 C	Fine Chemicals source of H_2
Alcohols/aldehydes, Ketones	Cu, Cu chromite, Cu/K/SiO_2	250-400 C, 1atm, 2-5 h^{-1}	Chemicals, solvents, polymers
Cyclohexanol/cyclohexanone	Cu-ZnO/Al_2O_3, Cu/MgO, Cu/K/SiO_2	325-400 C, 1atm, 0.6-1.25 h^{-1}	Nylon solvents, pharmaceuticals, insecticides

Dehydrogenations of less specific in character occur frequently in refining and petrochemical industries, where many of the processes have names of their own. Some of them in which dehydrogenation plays a large part are pyrolysis, cracking, gasification by partial combustion and reforming.

In general dehydrogenation reactions are difficult reactions. They require high temperatures for favorable equilibrium as well as adequate reaction velocities. Pure dehydrogenation reactions are endothermic by 15-35 Kcal/mole and hence have large heat requirements. Active catalysts are usually necessary. Because of these problems with pure dehydrogenation, efforts have been made to use oxidative dehydrogenation, in which oxygen or another oxidizing agent combines with the hydrogen, which is removed as water.

This expedition has been successful with some reactions where it has served to overcome thermodynamic limitations & coke formation. Conversion of 1-butene to 1, 3-butadiene, methanol to formaldehyde and isopropyl alcohol to acetone in the presence of oxygen is a few examples of oxidative dehydrogenation processes. The oxidative dehydrogenation reactions are exothermic in contrast to normal dehydrogenation, which are endothermic. Dehydrogenation of n-paraffins to yield olefins is one of the major industrial catalytic processes. Dehydrogenation of n-paraffins can be divided into tow main categories.

1.12.1Dehydrogenation of C_3 and C4 alkanes

The production of C_3 and C_4 alkenes via dehydrogenation of the corresponding alkanes is an important technology. In large part, light alkenes are presently produced as by-products of other processes, steam cracking of napththa/ehane/propane/natural gasoline, and fluid catalytic cracking of heavier petroleum fractions. These processes have until recently; met global demand for light alkenes, however, world demand for light alkenes is rapidly increasing, largely due to the accelerating demand for various applications. Several new plants have been built in Asia and Europe for propane and isobutene dehydrogenation using UOP and Houndry technologies for production of propylene and iso-butylene.

1.12.2Dehydrogenation of $C_6 – C_{15}$ alkanes

In detergent industry, the mono olefins obtained by selective dehydrogenation of C_{10} - C_{14} n-paraffins are converted to the corresponding Liner Alkyl Benzene (LAB) by reaction with benzene. Liner Alkyl Benzene (LAB) is the ingredient for the manufacture of biodegradable detergents.

LAB is the most important industrial raw material for surfactants derived from petrochemical sources and is even otherwise the most dominant raw material of the detergent industry. Its level of consumption in any global region is an indicator of the scope for the production of various detergents such as laundry detergent, dishwashing detergents etc. LAB is the raw material for the production of alkyl benzene sulphonic acid and alkyl benzene sulphonate (LAS). Detergent industries make use of both types of these intermediates. Two basic routes employed for the manufacture of LAB are:

- Alkylation of benzene with long chain mono-olefins using HF and other catalysts
- Alkylation of mono chlorinated benzene with n-paraffins using $AlCl_3$ Catalysts

The mono-olefins alkylation process is predominant around the globe. Therefore production of mono-olefins is of greater importance. Many of the manufacturers of LAB adopt the first procedure. In India the major manufacturers of LAB include Indian Petrochemicals Corporation Limited, Baroda (43,500 MTA), Tamil Nadu

Petrochemicals Corporation Limited, Chennai (120,000 MTA) and Reliance Industries Ltd., Pathalganga (100,000 MTA) [66]

Paraffins in the range C_{10} - C_{14}, usually segregated into four carbon fractions, can be dehydrogenated to the corresponding mono olefins at low pressure over non acidic noble metal catalysts. A mixture of n-olefins is obtained since the position of the double bond shifts readily under dehydrogenation conditions.

The multiplicity of the olefins on the right hand side of the chemical equation raises the equilibrium conversion relative to what it would be with only a single olefin formed. An example of such a process is the PACOL process of UOP, which is used to manufacture detergent range olefins from n-paraffins. Conversion levels are about 12-15% and selectivity to mono olefins is about 90%. Di-olefins, cracked products and aromatics are undesired minor by-products, to the extent of 2-4% each. A separation process is necessary to isolate unconverted n-parafifins for recycle to the dehydrogenation step. Selective extraction of olefins or olefin alkylation followed by distillation serves for this separation.

A fixed bed catalyst is used in which the dehydrogenation reaction is carried out in the vapor phase in the presence of excess hydrogen. The lower paraffins can be dehydrogenated over chromia/alumina or alumina supported noble metal catalysts. Since formation of aromatic ring is predominant for dehydrogenation of paraffins with six or more carbon atoms on chromia/alumina catalyst, it is not preferred for such applications.

In general the catalyst for the dehydrogenation of higher normal paraffins to olefins consists of group VIII metal supported on alumina and promoted by various elements like Sn.

1.12.3Pt-Sn/Alumina Bimetallic Catalysts

Platinum-sin supported on γ - alumina is an important candidate in lower as well as higher carbon number paraffins dehydrogenation, as well as naphtha reforming reactions. It is interesting to see the historic development of this important catalytic system.

The bi-functional platinum/alumina catalyst for naphtha reforming, introduced shortly after the end of the World War II, led to a revolution in petroleum processing [67]. While the platinum/alumina catalysts were an outstanding success, they had short lifetime. Therefore they had to be regenerated frequently,. The introduction of platinum-rhenium bimetallic catalyst solved the problem but lengthy procedures are required for the regeneration of platinum-rhenium catalysts. Later on, platinum-tin/alumina appeared to be an attractive catalyst for reforming reactions, especially due to its application for Continuous Catalyst Regeneration (CCR) process, wherein such frequent catalyst regeneration and consequent loss of production as experienced for PT-Re catalysts could be avoided. Besides, the exceptional stability of Pt-Sn catalysts at low pressures resulted in additional benefits in terms of liquid yields (reformat) with higher aromatics/RON. At the same time platinum-tin/alumina was very useful as a catalyst in the dehydrogenation of n-paraffins.

Two main explanations for the increased stability of the bimetallic platinum-tin catalyst compared to the monometallic platinum catalyst have been proposed, though opinions differ widely among the scientists:

- Geometric effect due to the formation of smaller contiguous platinum ensembles by the addition of tin [68, 69]
- Electronic effect due to changes the electronic environment of the platinum atoms caused by tin [69, 70]

Published information on dehydrogenation of lower paraffins dealing with catalyst, process and kinetics [71] are plenty, while for the dehydrogenation of higher paraffins useful in detergent industry, it is not so. Most of the studies are by Soviet authors [72], on monometallic Pt/Al_2O_3 catalysts.

The overall chemical composition of dehydrogenation catalyst resembles that of a typical reforming catalyst except for the presence of alkali metals [73]. In dehydrogenation catalyst the side reactions are suppressed by neutralizing the acidity with alkali metals. Porosity of the alumina support is another distinguishing factor in the case dehydrogenation catalysts.

Temperature is another factor governing the activity, selectivity and stability of dehydrogenation catalysts. The thermodynamics that prevails for dehydrogenation of higher normal paraffins requires the use of relatively higher reaction temperatures in the order of 673-773 K to achieve significant levels of conversion [74]. Though the undesired side reactions can be suppressed by modifying the properties of the support, even the best catalyst uncovered to date tend to catalyze many side reactions can be suppressed by modifying the properties of the support, even the best catalyst uncovered to date tend to catalyze many side reactions and produce excessive coke deposition when operated at higher conversion levels. This makes it necessary to identify other means than temperature, to achieve better activity.

As a general rule, an increased dispersion of the active species improves the catalytic activity. A better dispersion can be achieved by the choice of proper support and appropriate method of preparation and pretreatments. But this method of improving activity is associated with some inherent drawbacks. It is a well-known fact that the more the dispersion, the more the catalyst is prone to sintering and hence growth of crystallites leading to decreased activity [75]. Moreover, the predominantly paraffinic nature of mono olefins in the range of C_{10} to C_{14} permits sequential dehydrogenation to occur readily, leading to the formation of di tri olefins, aromatics and coke. This effect will be more pronounced in the case of catalysts with higher initial activity and they tend to deactivate faster.

Stability and resistance to sintering or a highly dispersed catalyst depends on the extent of interaction between the active species and support, which is usually generated by the pre-treatment. Other than this, as mentioned earlier, addition of other elements which by themselves may be catalytically inactive, were found to have favorable effect on the activity, selectivity and stability of catalysts. The mode of action of these elements, known as promoters, varies significantly form system to system. Some modify the properties of the support [76] or combine with it to form new phases, which stabilize the active species from sintering [77]. In some other systems promoters modify the active species by effects usually referred to as either ensemble effect **[78]** or ligand effect **[79]**. In many of the known systems all these effects are found to be operating simultaneously and to different extents. Considering all these aspects of this reaction and catalyst, it becomes necessary to design the catalyst in such a way that the optimum activity, maximum selectivity and better stability/life are achieved.

1.12.4 Dehydrogenation of C_{10} – C_{13} paraffins

The desired product of C_{10} – C_{13} paraffins dehydrogenation is generally a mixture of C_{10}-C_{13} normal mono-olefins. These olefins are then further processed to get more pure olefins (commercially most reputed process is UOP OLEX^{TM} process unit), or reacted with benzene (commercially UOP HF detergent Alkylation process or UOP/CEPSADETAL^{TM} process unit) to produce linear alkyl benzene (LAB). The LAB is normally sulfonated to produce a biodegradable detergent in a downstream unit. Feed to the PACOL^{TM} unit comes form a normal paraffin separation process (such as the UOP MOLEX^{TM} Process) and must be properly hydro treated and free of potential catalyst poisons, such as sulfur and nitrogen compounds along with fluorides and chlorides.

Reactions involved in the dehydrogenation are summarized in figure1.5 and figure 1.6. Figure 1.5 generalized representation of all the possible reaction paths, while figure 1.6 individually lists a few of the more important reactions. The primary reaction is the dehydrogenation of n-paraffins to form n-mono-olefins (see figure 1.6, reaction A) which is the desired product. However, because of the high severity processing conditions employed (high temperature, low pressure), subsequent dehydrogenation of n-mono-olefins to n-diolefins and aromatics (see reactions B and C) also occurs to a minor extent. Although no appreciable amount of either linear or branched triolefins is produced, the dehydrogenation of diolefins to triolefins is possible. In fact, the small amount of aromatics produced in the dehydrogenation is believed to quickly form via thermal or catalytic cyclization of triolefins. Finally, the entire reactions scheme is indicated in figure 1.6 reaction D. All these by products lead to formation of coke, which retards the activity of catalyst by consuming the active sits. Generally on industrial scale the flow of hydrogen gas is kept some what in higher amount (H_2/HC mole ratio = 5-8) to swipe out all the possible coke forming components. In the reaction system depicted in figure, the conversion of n-paraffins to n-mono olefins is near equilibrium; where as the other reactions are controlled well away from their equilibrium. Therefore, from a practical point of view, the only significant thermodynamic process to be considered is the primary dehydrogenation of n-paraffins to mono-olefins.

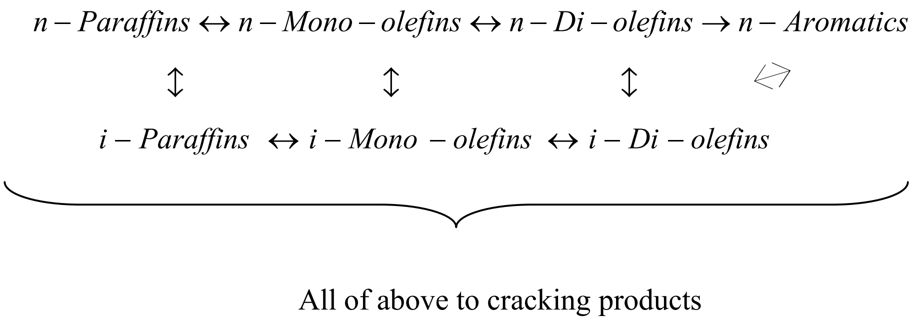


Figure 1.5 Reaction scheme of n-paraffins dehydrogenation process

The dehydrogenation of n-paraffins is an endothermic reaction with heat of reaction of about-30 kcal/mole **[83]**. The equilibrium conversion for this reaction is determined by temperature, pressure, and the molar ratio of hydrogen to n-paraffins. As might be expected, the equilibrium conversion increases with temperature and decreases with rising pressure and hydrogen to hydrocarbon ration.

The dehydrogenation catalyst is generally Platinum/alumina catalysts (UOP DEH-7), which are highly active and capable of achieving a specified conversion at very high space velocity. The conversion is limited by the chemical equilibrium of n-paraffin dehydrogenation rather than by kinetics. The chemical equilibrium affects not only the achievable conversion level, but also the selectivity for n-mono-olefins. At typical processing conditions for a PACOL unit employing A DEH-7 catalyst and operating at a nominal per pass conversion level of 12 to 13%, selectivity of the order 90% towards n-mono-olefins are approached. The balance 10% consists primarily of hydrogen, cracked light ends, diolefins, and some alkyl-aromatics. Minor skeletal isomerization to iso-paraffins and iso-olefins is also detected.

The side reactions of the catalyst are minimized as much as possible to assure good catalyst selectivity to mono-olefins. Reactions B, C, and D, in figure 1.6 are the main secondary reactions that occur across the reactor. The combined paraffin (recycle and fresh) feed to the reaction unit typically contains 3-6% non-normals and these non-normals also react.

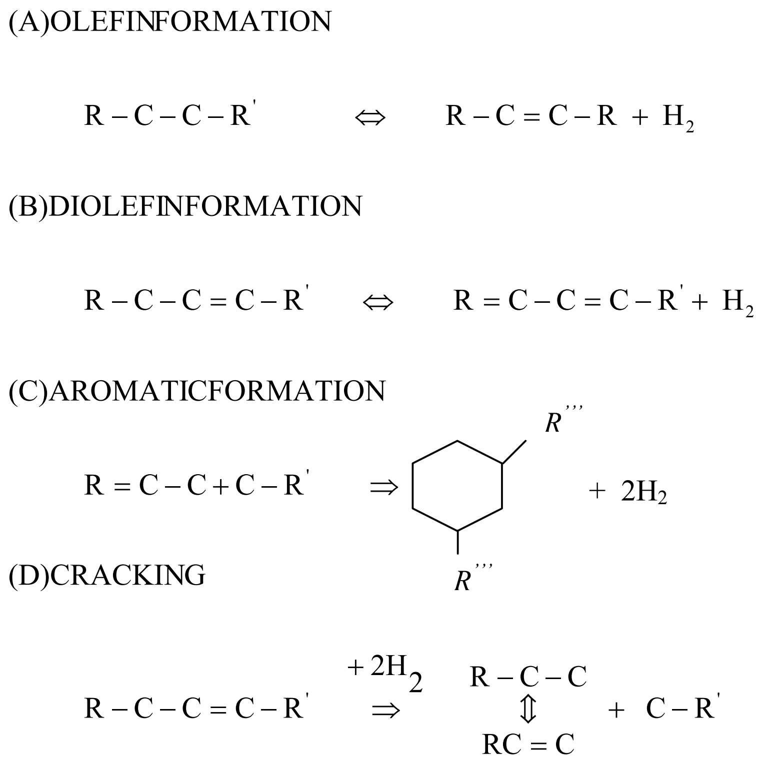


Figure 1.6 Possible reaction schemes for normal paraffins

Excessive sulfur in the linear paraffin feed tends to lower the activity of the catalyst necessitating higher reaction temperatures to maintain linear paraffin conversion. This decreases the range between start-of-run and end-of-run temperatures, thus lowering catalyst life. Because of this, the feedstock sulfur content should be maintained below 5 weight ppm.

When the fresh feed emanates from a UOP MOLEX^{TM} process unit, the sulfur levels are typically well under 1 ppm.

Nitrogen compounds in the feed must be limited as the nitrogen will break down in the reactor and NH_3 will be formed. The ammonia will react with any chloride or fluoride in the system to form a salt which can foul the process equipment. Oxygen and oxygenated compounds will either react with the olefins to produce gum (the gum is a permanent catalyst poison) or decompose to form water.

Potential acidic catalyst poisons such as chloride and fluoride containing compounds must not be allowed to enter the rector. These Compounds could decompose on the catalyst and deposit the chloride or fluoride ions on the catalyst surface. This would produce acidic catalyst sites that would significantly increase cracking reactions, light end production, and n-paraffin isomerization. To prevent fluoride contamination when recycle paraffins enter the PACOL^{TM} unit from a HF Detergent Alkylation unit, the recycle feed I alumina treated to remove any organic fluoride compounds or residual HF. The reactions involved in the alumina treating are shown in the figure 1.8. The fluoride level should be <1 ppm.

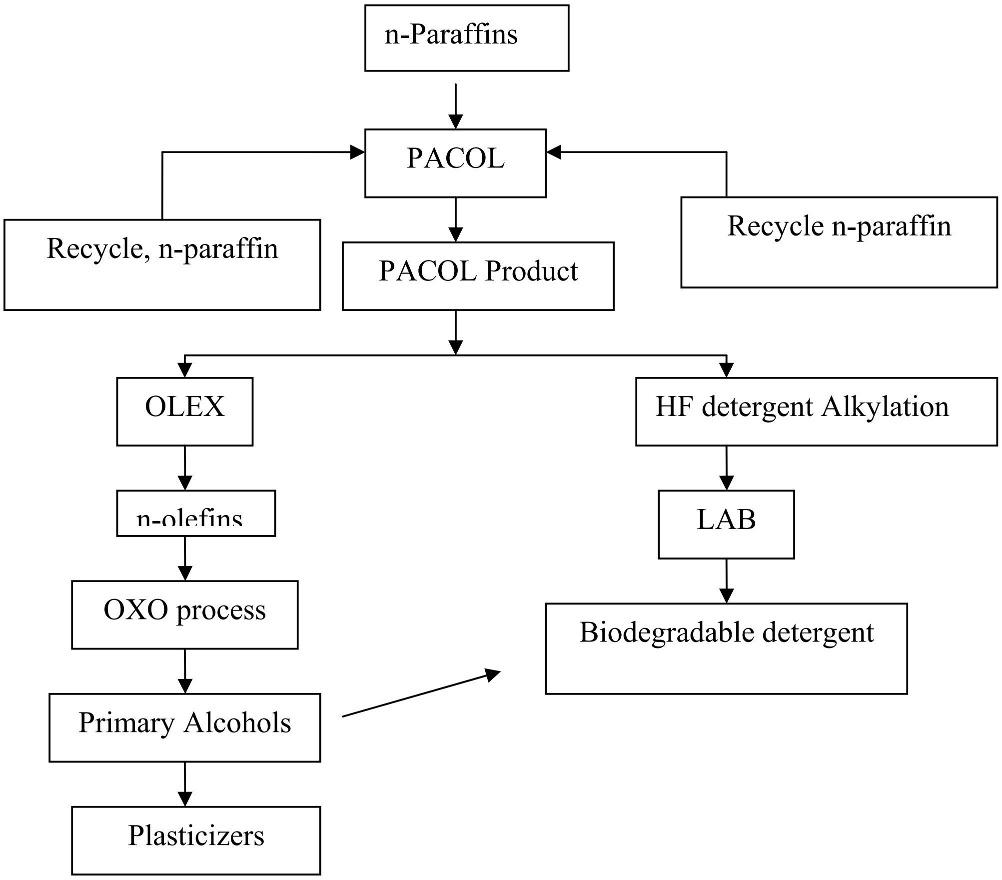


Figure 1.7 Use of PACOL^{TM} Product

Figure 1.7 shows a schematic diagram of some processing routes based on n-paraffin dehydrogenation using the UOP PACOL^{TM} dehydrogenation process. And the **Figure 1.8** shows the detail schematic diagram of the typical PACOL process. The OLEX^{TM} unit shown in the **Figure 1.7** is a liquid-phase unit for the adsorptive separation of olefins from paraffins employing UOP SORBEX^{TM} separation technology.

Choice of n-paraffin conversion is dictated by process economics [79]. A variety of other undesired reactions are also feasible in the process as depicted in figure bellow. Although the catalyst is tailored to maximize the desired reaction, process variables affect each of these reactions in different ways & to different extents. The scheme given below was also supported by the studies by Kylova et al [80] wherein dehydrogenation of decane on Pt/Al_2O_3 promoted by W and Li involved slowly desorption of olefins and dienes and formation of decatriene. Aromatic products were desorbed rapidly. Consecutive mechanism was proposed.

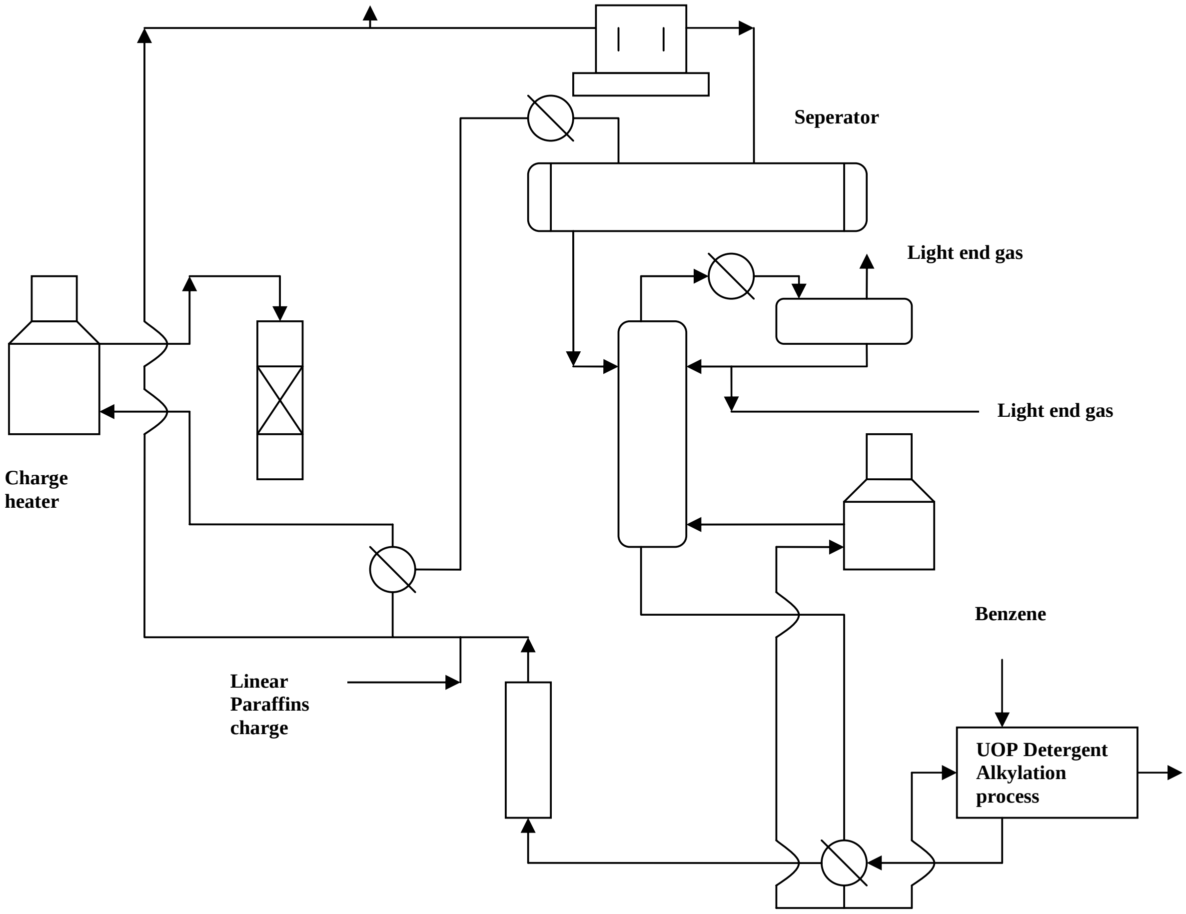


Figure 1.8 Schematic diagram PACOL^{TM} Process [82]

In petroleum and petrochemical industry, virtually all the catalysts deactivate during the use and need to be regenerated and /or even replaced by fresh catalyst. The deactivation i.e. decline in activity and selectivity as a function of life time is due to poisoning/fouling (feed stream impurities like sulphur, metals etc.), sintering (change in catalyst structure), and the most important is the coke formation. Operating variables would determine the extent and nature of coke on the catalyst. Generally, the microstructure of a typical supported metal catalyst can be depicted as shown in figure 1.9.

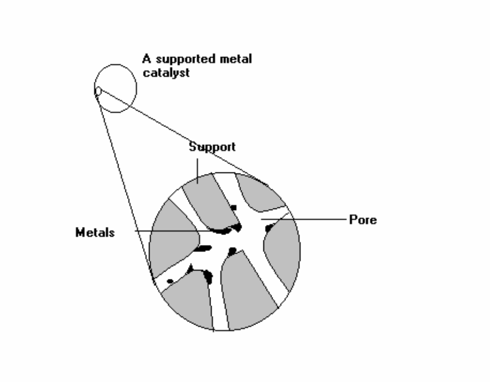


Figure 1.9 Micro structure of a typical supported metal catalyst

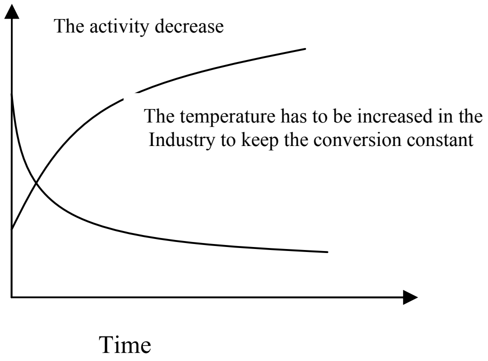


Figure 1.10 Temperature, activity profile in commercial plat

Commercial plats are operated in constant conversion mode by increasing the temperature as represented in **Figure 1.10**.

The deactivation can take several years, but can also occur in parts of a second. There could be several modes of deactivation as described in the **Table 1.5**. Four basic types of deactivation are represented in **figure 1.11** [65].

Table 1.5 Typical catalyst lifetime and modes of deactivation

Reaction	**Lifetime, Years**	**Deactivation mechanism**
Ammonia synthesis	5-10	Sintering
Semi regenerative reforming	1	Coking, sintering
Ammonia oxidation	0.1-0.5	Loss of Pt, poisons
Acetylene hydrogenation	0.1-0.5	Coking
Propane dehydrogenation	0.001-0.02	Coking
Higher paraffin dehydrogenation	0.082-0.12	Coking, sintering
Catalytic cracking	0.000002	coking

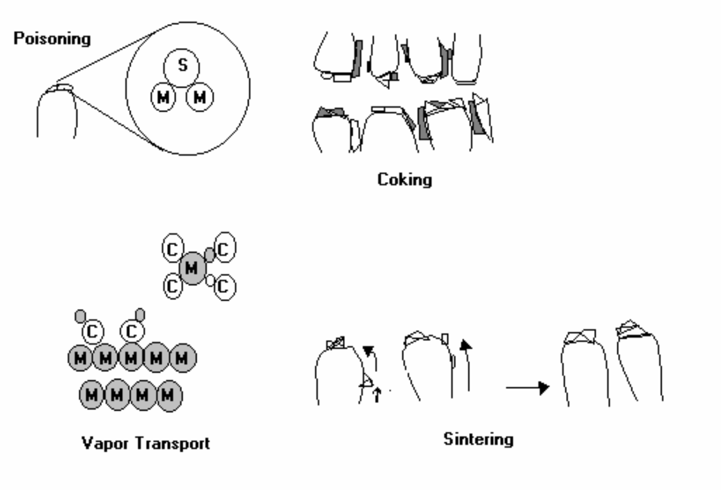


Figure 1.11 Basic types of catalyst deactivation

The most common mode of deactivation in the case of supported metal catalysts is coke deposition, which is illustrated in **Figure 1.11** establishing the mode of deactivation analyzing the cause and control of deactivation by suitable methods in the preparation stage as well as during its use forms and integral part of catalyst development

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2. Literature Review on Supercritical Phase Reaction

Supercritical phase of fluids for extraction has been proved to be immense use in chemical industries, but here in this section, work done by various scientists on supercritical phase reaction, is presented. Supercritical phase mainly useful when there is coking formation and so deactivation of catalyst which lowers the conversion as well as affects the yield and selectivity.

Tiltscher et al **[1, 2, 3]** (1987) showed that catalyst deactivation can be prevented while isomerization of 1-hexene. Thus one advantage of conducting heterogeneous catalytic reactions at SC condition is the possibility of doing in-situ extraction of coke precursors. Subramaniam and coworkers **[4, 5, 6, 7, 8, 9]** greatly extended this work on 1-hexene isomerization by industrial Pt/γ-Al_2O_3 catalyst and using CO_2 as a diluents in the reactor. They studied this on batch scale and continuous scale. The conversion achieved in batch scale confirmed the authors' equilibrium analysis. The continuous runs were used to study deactivation. At a sub critical pressure, the activity of the catalyst, decreased (presumably due to coking), whereas at a nearly identical temperature but supercritical pressure no loss of catalyst activity was observed. Saim et al. (1989) **[6]** attributed this catalyst activity maintenance to the solvent power of the dense SCF, which presumably prevented the deposition of higher molecular weight oligomers within the catalyst pores.

Fischer-Tropsch synthesis provides a means to produce higher hydrocarbons in the liquid-fuel range from synthesis gas (CO and H_2). Yokota, Fujimoto **[10, 11, 12, 13, 14]** and coworkers used n-hexane as the reaction medium, and they compared fischer-Tropsch synthesis in a gas-phase, in liquid n-hexene, and in SC n-hexane. They found that although the conversion of CO for the SCF phase synthesis fell between the conversion in the gas and liquid phase reactions, the total amount of products from the SCF phase reactions was greater than that from the gas phase reaction because of reduced coking and plugging of catalyst pores and reduced production of CO_2.

n-Butane isomerization was investigated **[15]** at the supercritical state in a flow type reactor. Sulfated zirconia (SZ), heteropolyacids (HPA) of the Keggin type H3PW12O40 (HPWO), H4SiW12O40 (HSiWO) supported on titania, H-mordenite (HM) were studied as catalysts at 488, 533 and 573K and 6.1, 11.0 and

13.8MPa, respectively. Gas-phase isomerization was carried out on the same catalysts for comparison. Rapid deactivation of the studied catalysts was observed in the latter conditions. Conducting the reaction of *n*-butane isomerization in the supercritical phase resulted in the stable activity. No poisoning of catalysts was observed. It was shown that even the catalyst aged in the gas-phase isomerization can be reactivated by the supercritical media and the catalyst performance can attain the initial value of 20–25% conversion, when the *n*-butane density is in the vicinity of its critical value or higher. The selectivity for *i*- butane reached 80% on SZ and supported HSiWO/TiO2 catalysts in supercritical *n*-butane. At the same time, i-butane selectivity on HM zeolite did not exceed 40% at 25% conversion. Cracking side reactions predominated at an elevated temperature (573 K) on the zeolite catalyst yielding the following by-products: propane, *n*-pentane, *i*-pentane and traces of ethane and hexane.

Off-line, in-situ alkylation **[16]** activity recovery from a completely deactivated solid acid catalyst was examined in a continuous-flow reaction system employing supercritical fluids (SCF). A USY zeolite catalyst was initially deactivated during the liquid phase alkylation of butane with isobutane in a single-pass reactor and then varying amounts of alkylation activity were recovered by passing supercritical fluids over the catalyst bed. A comparison of reactivation fluids on catalyst activity recovery is reported. Fluids examined included helium, propane, *n*-butane, isobutane, *n*-pentane, and isopentane. Phases studied included gas, liquid, and supercritical. As much as 82% of the fresh catalyst activity was recovered when employing supercritical isobutane. The ability of the fluid to facilitate a hydride reaction with the adsorbed deactivating high-molecular weight carbonations was indicated as an important property necessary to attain high levels of catalyst activity recovery. Activity recovery utilizing supercritical fluids that enhance reactivation by both reacting with and desorbing fouling compounds appears to be a promising technique to advance solid catalyst alkylation.

A comparative analysis of the reactions between maleic anhydride and furan derivatives is presented **[17]** in near and supercritical carbon dioxide and traditional organic solvents. Reaction kinetic was monitored by UV-vis absorbance spectroscopy in conjunction with an optimization technique which greatly simplified the experimental approach. In all of the reactions studied, supercritical carbon dioxide proved to facilitate a rate enhancement over conventional organic solvents. The reaction between maleic anhydride and furfuryl alcohol at 69 bars and 35°C was found to proceed 10 times faster in CO2 compared to reactions carried out in diethyl ether. All kinetic results were obtained from reactions undertaken in true homogeneous one phase fluid systems. The results achieved further indicate the potential of using carbon dioxide as a medium to carry out such chemical transformations through more environmentally acceptable processes.

The kinetic studies on the hydrogenation of 1-octene and cyclohexene using a fluoroacrylate copolymer grafted rhodium catalyst in supercritical carbon dioxide (scCO2) are reported **[18]**. The reactions were investigated at temperatures between 50 and 120 °C, and pressures ranging from 172 to 241 bars. The catalyst also deactivated at these reaction conditions. For the case of 1-octene, isomerization to (*E*) 2-octene and (*Z*) 2-octene also occurred as side reactions. To represent the experimental data, a kinetic model was developed on the basis of reported studies about hydrogenation and isomerization of olefins in conventional solvents. It was proposed that two hydride catalytic species are formed during the kinetic cycle. Monohydride species promoted the isomerization, and dihydride species catalyzed the hydrogenation. Deactivation of the catalyst was attributed to the formation of an unsaturated olefin complex. Statistical methods were applied to discriminate among rival models. It was found that the rate-determining steps for hydrogenation and isomerization were the formation of the alkylrhodium hydride complex and the coordination of the olefin in the monohydride catalytic species, respectively.

M.M. Sharma and coworkers **[19]** examine the kinetics of isobutane oxidation in the liquid phase and under supercritical conditions. Isobutane oxidation has gained importance because of the applications of the oxidation products such as tert-butyl hydroperoxide and tert-butyl alcohol in the manufacture of the important chemicals like propylene oxide and MTBE. An interesting aspect of this reaction is that, the reaction conditions can be conveniently manipulated in such a way that isobutane exists in supercritical state. The influence of supercritical conditions on the rate and selectivity of the reaction is investigated and this permits a comparison of liquid phase and supercritical phase oxidation. The reactions were also performed in a glass-lined continuous reactor. This mode of operation allows kinetic studies without an intervention of gas-liquid mass transfer and in addition eliminates the catalytic effect, if any, of the stainless-steel walls. The reaction is autocatalytic and the selectivity towards the hydroperoxide decreases with an increase in overall conversion. Under supercritical conditions, the rates and selectivity were significantly high compared to those obtained in liquid phase oxidation. In both, subcritical and supercritical oxidations, temperature has an adverse effect on selectivity towards tert-butyl hydroperoxide. A proposed kinetic model successfully explains the kinetic data and allows the rate constants and the activation energy to be determined. It is shown that the supercritical-phase oxidation shows all features present in the liquid-phase oxidation. Thus, this work provides a unified treatment for the supercritical- and the liquid-phase oxidation of isobutane.

The alkylation of toluene with ethylene over micro porous USY zeolite and mesoporous sulfated zirconia (S/ZrO2) catalysts was explored at liquid, near-critical liquid, and supercritical conditions using propane as the supercritical co solvent by Ginosar et al [20]. Liquid, near-critical liquid and supercritical conditions were examined for their effects on product selectivity and catalyst activity maintenance. The S/ZrO2 catalyst demonstrated alkylation activity almost exclusively, whereas the USY catalyst demonstrated both alkylation and cracking/disproportionation activities. Near critical and supercritical reaction conditions improved product selectivity with the USY catalyst through the suppression of disproportionation reactions and enhanced ortho- and paraethyltoluene selectivity. However, the addition of the supercritical co solvent resulted in increased deactivation for both the S/ZrO2 and USY catalysts, with deactivation increasing with propane mole fraction.

Wei et al [21] has also found increased conversion and selectivity at critical region for the dehydrogenation reaction. They used C_{10}-C_{14} n-paraffin mixture as the row material and create reactant itself in supercritical condition. Industrial dehydrogenation process gives near 12% conversion and 92% selectivity. But in supercritical phase of reactants they found 25-30% conversion without loosing the selectivity. This is also without the use of hydrogen which is very hazardous chemical and necessary in normal condition to prevent deactivation of catalyst.

In detergent industry, the mono olefins obtained by selective dehydrogenation of C_{10}-C_{14} n-paraffins, are converted to the corresponding Liner Alkyl Benzene (LAB) by reaction with benzene. LAB is the ingredient for the manufacture of bio-degradable detergents. Many of the manufacturers of LAB adopt this procedure. Commercial dehydrogenation processes use a promoted Pt/Al_2O_3 catalyst. Typical process conditions for dehydrogenation of higher paraffins are:

Temperature (T)	460-490^oC
Pressure (P)	20-25 psig
LHSV (L)	20-30 h^{-1}
H_2/HC (mol/mol)	6
Typical n-paraffin conversion	10-13 wt%

The work presented here is motivated by the potential removal of hydrogen use in this dehydrogenation process with targeting the improvement of conversion in Supercritical phase of reactants itself.

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3. Objective and Scope of the Study

The present work is based on highly Selective Catalytic Dehydrogenation of the n-paraffin to desirable Mono-Olefins in presence of Pt-Sn/ γ-Al_2O_3 Catalyst under Supercritical condition. This selective dehydrogenation of n-paraffins to mono-olefins is first step for the LAB production followed by the second step that is alkylation of benzene. Coking is crucial problem in this reaction. Mono olefins continue to dehydrogenate giving diens and consequently aromatic and other high molecular cracked product, this all leads to olegomerzation and form the precursor which retards the active sites of the catalyst. Under supercritical phase, reaction significantly improves the overall efficiency and catalyst activity of the dehydrogenation reaction. The present work is proposed to:

- To study the Selective Catalytic Dehydrogenation n-paraffin in supercritical condition or near supercritical condition under different parameter, viz. temperature, pressure, LHSV without using Hydrogen flow.
- To evolve a suitable experimental design for studying the effect of these parameters.
- To study the parametric sensitivity of conversion of n-paraffin & selectivity to olefins.
- To generate response surface models to describe the system and to optimize the process parameters to maximize the conversion & selectivity.
- To arrive at the rate equations/constants for individual steps in reactions scheme and establish equations for prediction of kinetic parameters and to check their use in supercritical condition.

4. Design of experiments

Experimental methods are widely used in research as well as in industrial settings, however, sometimes for very different purposes. The primary goal in scientific research is usually to show the statistical significance of an effect that a particular factor exerts on the dependent variable of interest. The design of experiments (*DOE*) thus becomes very useful in industries as the industrial researcher/engineer is always under constant pressure to produce product with exact specifications with the fewest resources. To adhere to rigours product requirements, the industrial scientist/engineer must employ those design and analysis methods that allow the most information to be squeezed from the least effort.

Formal experiments design has several advantages over the classic, one-step approach that has been favored by academia. These advantages include performance characteristics and reduced cost. Formal experimental design examines the changes in output for any combination of input variables. By isolating and better understanding those factors that most affect the output, one can devote fewer resources to investigating the less important factors, design strategies and trouble shooting of the established ongoing processes. The experimental process may be used to gain additional knowledge about the relationship among output variable. Formal design also allows to mathematically optimizing the process response.

The goal is to fill a design space with the least number of points that fully characterize the system. Well-defined design types that are available in the literature can accomplish this [1]. The main objective in design of experiments for a process development laboratory is the search for “optimal reaction conditions to maximize the yield and selectivity from the reactor, because the process costs normally are predominantly raw materials costs. Secondary aims are to know the behavior of the reaction in the region of optimum performance and to understand the reaction well enough to be able to scale-up with confidence [2].

The first experiment is screening run. The run isolates input factors that are most important. The second step is exclusion of factors that are of minor significance. The third step is generation of a response surface model to predict the response as a function of input factors. The last experiment is a verification run; whereby the outputs are checked with the predicted response form the response surfaces model obtained [3, 4].

The levels of the any design indicate the increment to be given to any factor (parameter). The levels are selected such that they are far enough apart for resulting differences to be significantly greater than experimental errors. A two level design gives linear response at minimum and maximum of the factors. The limitation is what may happen at the center of the design space, perhaps a bend over the area where no data have been taken. A center point design is similar, but uses the midpoint value (between the maximum and minimum limits) for all selected inputs thus eliminating the draw back of strictly linear design. These are the most popular designs. The axial design includes center points, and points at the minimum and maximum of each input while other inputs to their nominal values **[4]**.

4.1 Factorial Designs

Factorial design is of two types, full factorial and fractional factorial. Full factorial design is used to estimate all possible effects, including interactions of the input variables. Significant interactive effects i.e. the change would only occur only when two or more variables are moved simultaneously; can be detected by a complete set of all combinations of the two levels. This is called a complete two level (full factorial) experimental design planned and it is planned simply, by combining all possibilities in the systematic way. These ‘full’ factorial experimental designs would cover all possible interactions, which are first order with respect to each variable. A full factorial design requires L^k, where L is number of levels and k is number of factors [1]. The difficulty in full factorial is that the number of combinations increases with the number of variables and it is impractical.

A fractional design reduces the number of experiments at the expense of the number of high order interactions. Experimental plans involving incomplete interaction information are called partial factorial designs and these designs are useful because they can quickly give an indication of major effects with the minimum of experimentation. As compared to full factorial design which are overdone for a set of variables for all order of interaction, here the interactions can be identified which has main effects on the system to reduce the design. Experimentalists do not readily accept partial factorial designs because they go against the old rule “never change two variables at once” when carrying out experiments.

4.2 Box-Wilson Design

Box-Wilson design employs two-level partial factorial experimental designs to locate significant parameter and these parameters are then used to choose the direction in which to move the experimental conditions. A series of experiments is then made in the chosen direction until an optimum has been achieved. Because the model used does not represent the whole system, but only a linearized fit about the experimental point, this new "optimum'" point will have a completely new set of linear parameters which describe the surface local to it. It is therefore necessary to repeat the partial factorial design at this new point to determine the new significant parameters, and the new direction in which to move. Experiments are carried out in this direction until a new optimum is found, and this whole procedure is then repeated.

Box-Wilson designs are also known as central composite design **[1]**. These symmetrical, space-filling designs are fairly efficient. The Box-Wilson design includes the center point, and axial points and corner points distributed by the input minima and maxima. This requires $2^k + (2k+1)$ experiments, where k is number of factors. The Box-Wilson design always results in an improvement, even though it might not find the best operating conditions. It is a systematic algorithm, which is of great value in a complex situation. The only draw back in this design is total number of required for larger designs become very large.

4.3 Experimental Design by Box-Wilson Method

Four important reaction parameters such as reaction temperature, pressure and LHSV were considered as main factors for the experimental study. The full factorial design for three factors with five levels requires 125 experiments, which are not feasible. Hence Box-Wilson's central composite design was used. The number of experiments required is 15. This included full factorial design at two levels(2^3), 8 experiments, 1 experiment at centre point, plus (3x2=6) 6 experiments at axial points and the total amounts to 15 experiments that allows us to vary each variable at 5 (centre point, minimum and maximum of intermediate level, and minimum and maximum of axial level) [1]. And with this 6 more experiments were done to know the effect of the parameters. The advantage of this method is estimation of second order effects and sequential experimentation with minimum number of experiments. Since one of our objectives of this experimental design is fine-tuning of the commercial operating conditions, central point conditions were kept closer to commercial operating conditions with pressure as critical pressure. The Box-Wilson design with the codes for the experimentation and the corresponding operating conditions are given in the following **Table 4.1**.

Table 4.1: Reaction parameters and factorial levels

PARAMETER/ FACTOR			LEVEL		
	-k	-1	0	1	k
x_1, Temperature, °C	445	460	475	490	505
x_2, Pressure, atm	17	19	21	23	25
x_3, LHSV, hr^{-1}	15	20	25	30	35

The relation between the actual values and coded values of the independent variables from –2 to +2 levels are given by the following equations:

$$x_1 = (T - 475/15$$

$$x_2 = (P - 21)/2$$

$$x_3 = (LHSV - 25)/5$$

The terms in the denominator are step length i.e. difference between two levels. The designed 15 experimental allow us to know the effect of each factor at three levels while the other three factors are kept constant. Hence, to enable to get information on the effect of each factor at five levels while the rest three factors are kept constant. The complete experimental plan carried out in the present work is presented in **Table 4.2** in terms of level code and their corresponding operating conditions.

The conversion of Paraffins and selectivity of olefins are the main products of this reaction system. Olefin is the desired product, while the conversion of olefins to aromatics and that to lighters are the undesired reactions.

Table 4.2: Experimental design according to Box-Wilson method

Exp. No.	x_1 T, °C	x_2 P, atm	x_3 LHSV, hr-1	x_1 T, °C	x_2 P, atm	x_3 LHSV, hr-1
1	-1	-1	1	460	19	30
2	-1	1	-1	460	23	20
3	1	-1	-1	490	19	20
4	-1	1	1	460	23	30
5	1	-1	1	490	19	30
6	1	1	-1	490	23	20
7	-1	-1	-1	460	19	20
8	1	1	1	490	23	30
9	0	0	0	475	21	25
10	-2	0	0	445	21	25
11	0	-2	0	475	17	25
12	0	0	-2	475	21	15
13	2	0	0	505	21	25
14	0	2	0	475	25	25
15	0	0	2	475	21	35
16	-1	0	0	460	21	25
17	1	0	0	490	21	25
18	0	-1	0	475	19	25
19	0	1	0	475	23	25
20	0	0	0.5	475	21	22
21	0	0	1	475	21	30

Where, x_1, x_2, & x_3 are the process parameters or factors, which are varied for four levels.

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5. Experimental Methodology

In this section catalyst selection, reactor design, experimental set up design and all physical setup preparations are describe. Dummy reactions are to be done prior to the exact required reaction runs to eliminate internal (pore resistance) as well as external mass transfer effects. This may give intrinsic rate mechanism on the catalyst surface.

5.1 Catalyst Selection

In present study industrial Pt-Sn/ γ-alumina, having bulk density 0.4 ml/gm, is used. It is manufactured in the R&D center IPCL, Baroda. Catalyst size was reduced to 0.5 mm size by crushing it to avoid channeling; more detail is explained in the presiding heading under reactor aspect ratio.

Table 5.1 Pt-Sn/ γ-Al_2O_3 catalyst specification

Test	Units	Specifications		Test Method
		Min	Max	
Appearance		**Grayish black spheres**		
Granule diameter	**mm**	**1.2**	**2.0**	**SOP/QA/DHC-1902**
Composition		**Al2O3**		
Moisture	**% (w/w**	**NA**	**5**	
Surface area	**m2/gm**	**140**		**SOP/QA/DHC-1924**
Attrition loss	**% (w/w)**	**NA**	**0.15**	**SOP/QA/DHC-1929**
Av. Crush strength	**Kg**	**0.6**		**SOP/QA/DHC-1928**
Bulk Density	**gm/cc**	**0.34**	**0.40**	**SOP/QA/DHC-1927**
Water Pore Volume,	**cc/gm**	**1**	**1.4**	**SOP/QA/DHC-1926**
Platinum	**% (w/w)**	**0.38**	**0.42**	**SOP/QA/DHC-1910**
Tin	**% (w/w)**	**-**	**0.50**	

5.2 Catalyst Bed and Diluents Concentration

Dehydrogenation of n-paraffin reaction is endothermic in nature; hence there would be temperature variation in the catalyst bed. Without any diluents the reactor in-let and outlet temperature difference across the catalyst bed is found to be 16^oC. To provide a heat sink without scarifying on uniform feed contact with catalyst particle, optimization of diluents concentration is required.

The diluents should not contribute itself towards any enhancement or retardation of reaction (inert). To serve this purpose, low surface area neutral explored. In our study glass bids with average particle size of 1-1.5 mm have been used. It was experimentally verified that no reactant conversion resulted with diluents only as catalyst bed.

Experiments were conducted with various catalysts to diluents volume ratios, starting from 1:1, 1:2, 1:3 and all other experimental conditions were kept constant. At lower dilution the conversion decreased due to no isothermal condition and temperature gradient across the bed. Based on the above experiments catalysts to diluents ratio was fixed at 1:3. Initially it has been used as sandwich of catalyst bed between two layers of diluents bed. But this way was not able to overcome the endothermic nature of the reaction so diluents were mixed to gather with catalyst. More details are given in the preceding chapter under the reactor aspect ration heading.

5.3 Reactor Design

Fixed bed reactor finds number of applications in liquid phase as well as gas phase reactions. Its importance in the chemical industries stimulated further research, and new process of various hydrogenations, selective hydrogenation, oxidation of organic compounds in waste waters, treatment of effluent gases, production of hydrogen peroxide, deuterium exchange reactions, reactions of immobilized enzymes etc. The advantages as well as the drawbacks of fixed-bed reactors versus slurry reactors have also been reviewed [2, 3].

Advantages

- The flow in fixed bed reactors is close to the plug flow, which is very convenient if high degrees of conversions are to be achieved. In case of slurry reactor the flow is quiet complex and not well known, but certainly far from plug flow, and with considerable by passing. This behavior is unsatisfactory from the standpoint of effective contacting and requires much more catalyst for high conversion.
- Liquid flows as a film over the catalyst, thus offer very small resistance to the diffusion of the gaseous reactant to the catalyst surface while in the case of the slurry reactor the liquid holdup is high near the catalyst surface which provides high resistance to the gaseous reactant.
- Flooding is not a problem and separation of the product mixture from the catalyst is not a problem.

- Less pressure drop in the fixed bed will allow an essentially uniform partial pressure of reactant across the length of the reactor.
- The need for the separation of the deactivated catalyst and higher installation costs of slurry reactors means that fixed bed reactors are preferred.
- In the commercial fixed bed reactors, uniform distribution of gas and liquid are achieved as well as the catalyst is uniformly and effectively wetted by the liquid.

Disadvantages

- The effectiveness factor of the catalyst pellets in packed beds is usually low due to their large size, which would result into more resistance to the diffusion of the reactants and products.
- The mechanical strength of the pellets must be also greater to avoid erosion by the liquid reaction mixture.

Thus, based on the above comparison; a **fixed-bed reactor** system was chosen.

5.3.1 Reactor Aspect Ratio

To approximate plug flow residence time distribution behavior, suitable axial and radial aspect ratios were adhered to, according to the guidelines of Denbigh and Tarhan [3, 4].

If axial mixing proves to be detrimental and/or selectivity, the design must be such as to increase the Pecklet number as large as possible. If we view a packed bed as consisting of an array of voids into which fluid flows at a high velocity from small area ports created by reason of close particle – particle contact, it can be visualized that as a result of acceleration in the ports and deceleration up to entering the voids, mixing occurs. In the limit if perfect mixing occurs in each void, the bed may be viewed as a series of perfectly mixed vessels interconnected by ports consisting of closely packed regions [7]. A fixed bed is generally characterized by *L/dp* values of the order of at least 30 to several hundreds [5, 6].

$$\text{The axial aspect ratio} = \frac{L}{d_P}$$

= Bed length / catalyst particle diameter

≥ 30 [1, 5] (5.1)

Radial mixing is always desirable as to avoid variation in conversion and selectivity, which results if molecules at the centerline of the reactor enjoy a different retention time from those of at the wall. Radial dispersion can be viewed to occur as a result of stream splitting and sidestepping. A stream of fluid at a particular radial position strikes a piece of packing in its axial journey and is split into two by the collision, and on the average, one half the stream moves laterally to the right, the other to the left. This event occurs repeatedly with the result that the original (tagged) single stream is laterally dispersed, or fans out forwards the wall.

The radial aspect ratio $= \frac{D}{d_P}$ = Bed diameter / catalyst particle diameter

≥ 15 [5, 6] (5.2)

The overall reactor aspect ratio $= \frac{L}{D}$ = Bed length / Bed diameter

≥ 1.5 (5.3)

Based on the above discussions at first we arrived to the following data for the reactor:

Let d_P= diameter of particle = 0.5 mm

Axial aspect ratio = 50

Radial aspect ration = 25

So, $\frac{L}{d_P} = 50 \Rightarrow \frac{L}{0.5} = 50 \Rightarrow$ **$L = 25$ mm**

$\frac{D}{d_P} = 25 \Rightarrow \frac{D}{0.5} = 25 \Rightarrow$ **$D = 12.5$ mm**

Volume of catalyst $= \frac{1}{3}\left(\frac{\pi}{4}D^2 L\right) = \frac{1}{3}\left(\frac{\pi}{4}12.5^2 25\right) = 1.055\ \text{mm}^3 \approx$ **1 ml**

The overall reactor aspect ratio $= \frac{L}{D}$

= Bed length / Bed diameter

= 25 / 12.5 = 2 $\geq$ **1.5**

But, it had found temperature variation in the cyclic manner while the experiments were done keeping the over all reactor aspect ratio of 2. So as per the discussion with Dr. K.K. Choudhari, CEPD, R&D center IPCL, the overall reactor aspect ratio was increased to 4.4 by adding diluents. This works as heat source and by which it can be overcome the endothermic nature of the reactions. So the overall height of the bed as 40 mm to gather with diluents (mixed with catalyst) is used. The reactor was also change with the one supplied by Dr. S. Gnanpragasam, Group Manufacturing Services, Relene Petrochemicals Pvt. Ltd., having the inside diameter of 9mm (SS-316).

5.3.2 Reactor thickness

Reactor thickness should be design in such a way that it can sustain the required pressure induced in the system.

Material selected is SS 316 and the detail required to design for the reactor is as given below [8, 9, 10]:

Permissible Yield Stress (f_y) = 21.14 kg/mm^2

Permissible Tensile Stress (f_t) = 59.89 kg/mm^2

Factor of safety = 2

Design Stress f = minimum of two permissible stress (f_y)/ 2 (5.4)

= 21.14/2 = 10.568 kg/mm^2

Design Pressure P = 10 % of Max. Pressure

= 1.1(50 kg/cm^2) = 0.55 kg/mm^2

$$\text{Thickness of reactor } t = \frac{PD}{(2fJ - P)} \tag{5.5}$$

$$= \frac{(0.55)(12.5)}{(2(10.568)(1) - 0.55)} \text{ (for seamless pipe } J\text{=1)}$$

$$= 0.339 \text{ mm}$$

Now we can check weather the reactor with this thickness will sustain the induced stress as describe below, total five type of stress will be there on the reactor

- Circumferential stress (f_{cir})
- Longitudinal stress (f_l)
- Stress due to weight (f_{we})
- Stress due to wind (f_w)
- Stress due to tubing (f_t)

But out of this stresses, stresses due to weight wind and tubing is neglected and so the stress induced can be find as given bellow

$$f_{cir} = \frac{P(D+t)}{2t} = \frac{0.55(12.7+0.34)}{2(0.34)} = 10.56 \text{ kg/mm}^2 \qquad (5.6)$$

$$f_l = \frac{PD}{4t} = \frac{0.55(0.34)}{4(0.34)} = 5.136 \text{ kg/mm}^2 \qquad (5.7)$$

Now overall stress experienced by the system can be found out as the resultant of this stress as bellow

$$f_R = (f^2_{\text{cir}} - (f_{cir} f_l) + f^2_{l})^{0.5} \qquad (5.8)$$

$$= (10.552 - (10.55)(5.136) + 5.136^2)^{0.5}$$

$$= 9.1376 \text{ kg/mm}^2 < \text{Permissible Yield Stress}$$

Thus thickness **t = 0.33 mm** is safe for the pressure up to 50 kg/mm^2 but here the design thickness is selected as **t = 1mm** for all the tubing as well as condenser and separator too. And the reactor used was also having the thickness 3 mm.

5.4Thermal Homogeneity of Reactor Furnace

By measuring the temperature profile of the furnace under process conditions, it has been ensured that, the catalyst bed is in isothermal region, which extends well below and above it. In the set up thermocouple was kept under the thermo well to know the temperature profile and the isothermal zone. Insulation with the help of glass wool and asbestos thread were kept at the starting and end point of the furnace.

5.5Reaction With Empty Reactor

Without catalyst in the reactor, the reaction was conducted at very high severity conditions to know the contribution of inner walls of the reactor. No substantial conversion was observed.

5.6Mass Transfer Effects

External mass transfer resistance can be minimized by operating at a high velocity at a high velocity of gases and the pore diffusion resistance can be minimized by proper sizing of the catalyst.

Internal Mass Transfer: To eliminate internal mass transfer effects preliminary runs were carried out to find out the particle size that allows neglecting internal transport limitation. Experiments were carried out by varying particle size and keeping W/F ratio constant. The results did not show any significant deviation in conversion, which indicates the absence of intra particle diffusion.

External Mass Transfer: Absence of external mass transfer resistance was ensured by carrying out experiments at different mass flow rates and keeping W/F ratio constant. The conversion at two different liquid feed flow rate having same W/F ration remains almost constant which indicates that the mass transfer effect on conversion in the given range of feed flow rate is negligible. The feed flow rate used in all experimental runs is in the range of 10-50 ml/h.

5.7 Feed and product analysis method

n -Decane specification:

n-Decane was supplied by M/s S.D. Fine chemicals, India. Having the purity as mentioned bellow. The same feed was used for all the experiments carried out:

Table 5.2 Typical analysis of feed

Paraffins	Aromatics	m-olefins	di-olefins	Lighter	Total
Wt%	**Wt%**	**Wt%**	**Wt%**	**Wt%**	**Wt%**
99.2236	0.7689	0.0000	0.0000	0.0075	100

The reaction products were analyzed in a Shimadzu gas chromatograph GC-17A attached to a Shimadzu CBM-101 and a Shimadzu auto injector AOC-17A. The separation of the products was achieved by Innowax^{TM} capillary column and products were detected by using a flame ionization detector (FID).

The conditions used for the separation of products and properties of the GC components are given bellow:

Table 5.3 Conditions of GC and other components

Column	Supplied by Agilent Technologies, Part no: 19091N-205
Column specifications	Packing material: Cross linked Polyethylene Glycol 50m x 0.2mm x 0.4 μm Film Thickness
	Length x I.D = 300 x 3.9 mm
Sample Injector	Injection Method: Microsyringe, 10 μl Injection Speeds: 0.5-1 sec/μl
Constant Carrier gas flow of hydrogen	1.7 ml/min through column.
Oven programming	40°C for 10 min 40 to 100°C @ 1.6 °C/min
First dwell time	Nil
Second temperature ramp	100 to 200 °C @ 5 °C/min

Second dwell time	10min
Preconditioning of column	220 °C for 1min.: flow conditions are same as above
Splite ratio	1:100
Sample injected 1	1μl
Analysis method	UOP 689

Identity of the products was established with mass spectroscopy (52). A typical feed and product chromatographs are given in **Appendix-1**. Total conversion was obtained from the disappearance of n-Decane and the selectivity towards each of the products namely, olefins, aromatics and lighters (cracked products), were obtained from their appearance in the product.

General Operation of GC

The underlying principle of operation of GC is based on the recording Flame ionized detector for continuously and quantitatively monitoring the ion current of the hydrocarbon present in the sample. Any components when it is in saturated state, it shows the neutral potential. So Hydrocarbons are ionized in presence of hydrogen-air flame. They become positively charged and so when they come near detector which is already having negative charge get attracted. And this shows as a peak on the display. Components of the sample, which are weakly adsorbed to the stationary phase (column adsorbent), will travel along with the mobile phase down the column faster than components strongly adsorbed to the stationary phase. And thus at different time interval we can get peak of different component which can be further quantitatively analyzed and converted to mass fraction

GC basically consists of

1. Vial Sample Holder – To keep the vial of different sample.
2. Injector Unit – To introduce fix volume of sample into the system.
3. Column – It is the heart of the system and usually consists of an SS tube packed with adsorbent. The column separates the components in the sample.
4. Detector – Measures the Ion current of the component and sends the signal to the processor proportionate to the component concentration.
5. Data Processor – Collects the signal and converts it into area counts proportional to the amplitude of the signal.

Coke content of the spent catalyst was measure using the DTA TGA of TA Instruments, modle: SDT 2960.

Prior to do chromatographic analysis the rough idea of the product composition was also made by doing bromine no test with the instrument Titralab 90. The magnitude of bromine number is an indication of the quantity of bromine reactive constituents, not an identification of constituents.

Bromine Number:

The **bromine Number** which gives a measure of unsaturation (mono and di-Olefins) is expressed as the number of grams of bromine consumed by 100 g of the sample when reacted under given conditions [12].

Reagents Needed:

a) Carbon Tetrachloride

b) Acetic acid-glacial

c) Sodium Thiosulphate Solution (Approximately 0.1 N accurately standardized)

Dissolve 25 g of $Na_2S_2O_3.5H_2O$ in water and add 0.01 g of Na2CO3 to stabilize the solution. Dilute t 1 liter and mix thoroughly by shaking

d) Potassium Iodide Solution – 150 g per liter

e) Starch Solution – Mix 5 g of soluble starch and 5-10 mg of HgI_2 with 3 to 5 ml of water. Add the suspension to 2 liters of boiling water and boil for 5 – 10 minutes. Allow cooling and then decant the clear, supernatant liquid into glass-stopper bottles.

f) Porassium Bromide-Bromate Solution - (Standard 0.5N) Weigh out exactly 51 g of potassium bromide and 13.92 g of potassium bromate, dissolve in distilled water, and dilute the solution to 1 liter.

In addition to above reagents, the following titration mixture is also needed: Every liter of the BNS solution must constitute:

Glacial Acetic Acid (AR Grade)	714 ml
Carbon Tetrachlorid (AR Grade)	268 ml
Methanol (AR Grade)	268 ml
1:5 Sulphuric Acid (AR Grade)	36 ml

Normality of $Na_2S_2O_3$ = (0.1) (25) / Burette reading

Standardization of above reagents can be done as describe bellow:

1. Standardization of Sodium Thiosulphate Solution:

In a clean dry beaker, weigh out 0.1226 g of pure $K_2Cr_2O_7$ and dissolve I 50 ml DM water. In a flask, weigh 3.0 g of Potassium Iodide (KI) and 2 g $NaHCO_3$. Add

100 ml distilled water and 6 ml conc. Hydrochloric acid to the flask. Carefully add the contents of the beaker to the flask. Rinse the beaker with 50 ml DM water. Keep the flask in the dark for 10 minutes. Titrate with $Na_2S_2O_3$ solution till color changes to pale yellow. Add 2 ml starch and continue titration till the yellow color turns blue. Note the volume on the burette.

2. Standardization of $KBr-KBrO_3$ Solution:

Take 50 ml Acetic acid and 1 ml conc. Hydrochloric acid in an iodine flask, stopper it and put in ice bath for 10 minutes. Then add 5 ml $KBr-KBrO_3$ solution to it drop wise. Stopper it cool in ice bath for another 5 minutes and put 5 ml KI in lip of flask. Let it stand for 5 min in ice bath and shake vigorously for 1 min, add KI and approx. 100 ml DM water. Titrate it with the standardized $Na_2S_2O_3$ solution. Color will change Reddish Brown to Yellowish here add 2 ml Starch indicator color will change to colorless and it will be end point.

Normality of $KBr – KbrO_3$ = (Reading) (Normality of $Na_2S_2O_3$) / 5

This is an amperometric titration and done by the electronic instrument to find out bromine no. The Pt – Pt electrode directly measures the current in the olefin solution and current baseline remains steady remains steady as long as the Br species are consumed by the olefin sample. When the latter longer take up any more of Br, the current in the solution shoots up, indicating the completion of titration.

Method: Accurately weight out between 0.6 – 0.8 g of the sample. Add 70 ml of BNS to it. Titrate it with the standardized $KBr – KbrO_3$ solution from the burette.

Bromine number = 7.99 (N V) / W

Where **V** Volume of $KBr – KbrO_3$ solution to the sample, ml

N Normality of the $KBr – KbrO_3$ solution

W Weight of sample in g.

5.8 Experiment set up and experiment procedure

The reactor used was tubular reactor with 9 mm internal diameter and length of 46 mm made of SS 316. The catalyst bed was supported in the reactor on a metal grid. The overall reactor aspect ratio of L/D = 4.4 was maintained. 1 ml of catalyst (Pt-Sn/ γ-Al_2O_3) volume (bulk density of 0.4 gm/cc) mixed with 3 ml of diluents was charged over the grid. The catalyst bed of 40 mm deep was obtained. This bed was adjusted in the isothermal zone of furnace by filling the bottom portion with diluents only. The catalyst was in the size to 0.5 mm in diameter, which essentially consists of spherical alumina coated with Pt and Sn. The volume of the reactor that was not utilized for the catalyst loading is filled with inert over the catalyst bed, which reduces the dead volume as well as keeps the catalyst intact in its position. The reaction mixture is heated up to the reaction temperature through a heating furnace attached with a programmable temperature controller (Yokogawa – UP 25 S) to maintain the temperature of the furnace with an accuracy of ±1°C. n-Decane is pumped by HPLC pump (K-120, 0.001-9.999 ml/min, pump head is stable up to 400 bar) supplied by KNAUER, Germany through the NRV so as to avoid the backpressure of the reactor system. The reaction products pass through a condenser kept at 10°C with the help of Julabo F-30 thermostat water circulator. The liquid product is collected from the bottom out let of the reactor after separating the hydrogen gas in the Gas-Liquid separator. The schematic diagram of the experimental setup is shown in **Figure 5.1** which was made at R&D workshop of IPCL.

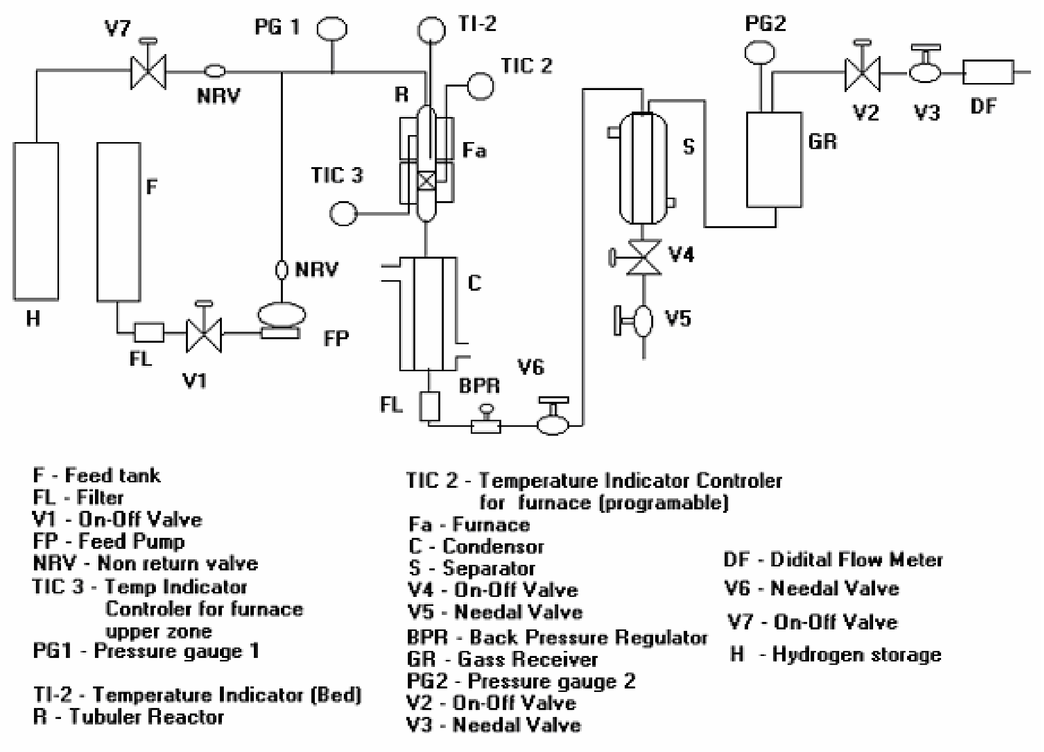

Fig. 5.1 Experimental set up

The Pt-Sn/γ-Al_2O_3 catalyst can not be used as it is directly, because the active phase is there in its oxide form. Therefore, the catalyst has already undergone a surface stabilization step during the open air exposure. Hence, some mild oxidation may have occurred. Therefore, the catalyst is subjected to an in-situ reduction step.

In-situ Reduction

Initiate a flow of hydrogen into the reactor and raised gradually the temperature of the catalyst bed of 150 °C within 60 min and maintain 150^0C temperature up to 2 hr to drive out adsorbed moisture. Start heating such that to reach 480 °C @ of 1.78 °C/min to get this temperature in 4.5 hrs and held the system at 480 °C for 4 hrs. Stop heating and allow the system to cool up to the $150\,^{o}$C temperature.

Start up

1. Pressurize the system with fresh feed to the desired pressure by throttling the outlet BPR (Back Pressure Regulator) close.
2. Adjust the BPR as at the required pressure then introduce n-paraffin fresh feed as per the required flow rate.
3. Heat the system up to the desired temperature.
4. Discard first half hour sample
5. Carry out the sample from the bottom of the separator at 1 hr intervals and do the analysis by bromine no test and if the satisfactory bromine no is there then analyze the product using Gas Chromatograph

The definitions of the performance variables used in the present work are as follows:

$$\text{Conversion} = \frac{(\text{Wt.of n - paraffin in the feed - Wt of n - paraffin in the product})}{\text{Wt. of n - paraffin in the feed}}$$

$$\text{Selectivity} = \frac{(\text{Wt. of mono Olefin in the product})}{(\text{Wt. of n - paraffin in the feed - Wt. of n - paraffin in the product})}$$

$$\text{Yield} = \frac{\text{Wt. of mono Olefin in the product}}{\text{Wt. of n - paraffin in the feed}}$$

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6. Result and Discussion

6.1 Results of Experimental Design

The analysis of the product was carried out using Gas Chromatography. The results of experimental runs as per experimental design (as shown in **Table 4.2**) are as indicated in **Table 6.1.**

Table 6.1: Results of experimental design

		Selectivity, wt%			Yield, wt%		
Exp. Run.	**Conv. of Paraffin**	**O**	**A**	**LE**	**O**	**A**	**LE**
1	6.383	68.422	25.491	6.188	4.368	2.403	0.395
2	11.238	53.815	35.848	6.405	6.048	4.805	0.720
3	15.476	25.453	38.556	32.453	3.939	6.743	5.023
4	7.752	59.514	20.909	19.663	4.614	1.621	1.524
5	16.666	47.497	39.671	12.873	7.916	6.612	2.145
6	18.645	39.563	37.199	23.277	7.377	6.936	4.340
7	8.471	55.729	23.978	20.371	4.721	2.031	1.726
8	5.534	45.507	17.636	27.992	2.519	0.976	1.549
9	12.359	54.253	37.421	8.379	6.705	4.625	1.036
10	5.416	69.895	22.083	8.143	3.785	1.196	0.441
11	3.581	35.055	15.117	43.192	1.255	0.541	1.547
12	8.846	49.449	31.018	19.608	4.374	2.744	1.734
13	25.242	35.486	52.622	11.918	8.957	13.283	3.008
14	10.958	54.818	33.479	11.762	6.007	3.669	1.289
15	12.337	57.248	36.011	6.796	7.063	4.443	0.838
16	6.990	68.017	24.422	7.656	4.754	1.707	0.535
17	13.581	50.560	36.178	13.318	6.867	4.913	1.809
18	13.805	44.523	27.704	8.621	6.147	3.825	1.190
19	9.272	57.128	28.301	14.644	5.297	2.624	1.358
20	11.287	54.394	32.375	13.294	6.139	3.654	1.500
21	8.965	56.173	29.334	6.188	5.036	2.630	1.315

Where, **O -** olefin; **A** - Aromatic; **LE -** Lighter

6.2 Response Surface Model

A reactor is a highly non-linear system, which has a yield, selectivity, or profit function which will be non-flat, and which will contain an optimum. Generally, optimum yield is a good first estimate of a profitable operating point for an industrial reactor, or, if an inexpensive recycle system is involved, the optimum selectivity may be preferred. The problem is thus to find the location of the position of the optimum on an unknown surface [1], when the responses that define the surface are subject to experimental error. The presence of this random component causes numerical optimization algorithms to fail, since such algorithms are based on the assumption that all responses are accurate. What are necessary, are optimization procedures, which handle random errors in the responses. To do this methods are developed based on statistics and linear regression to determine which effects are significantly greater than the experimental errors, and then only these effects are used in the optimization search.

6.2.1 Improving the Linear Model

More important than the prediction of variances and correlation for a model is the analysis to see whether the form of the equations of the model agrees with the experimental results. When these variances are significantly different, this means that predictions of the model will probably have errors at least as large as the largest residual, and the regression analysis to determine the confidence limits of parameters and predicted points is worthless, because the basis of the analysis is that systematic error is not significant. When a model is "inadequate", the equations should be altered to give a better fit. This normally involves fitting more terms to the simple linear model to provide interaction and curvature in a series of stages i.e. simple linear model, linear plus interactive term, general quadratic model & quadratic plus full interactive terms and so on. In this way it is possible to systematically create more complex models linear in the parameters as a way of improving the model [1]. It is also worth looking at the results and the theory of the process under discussion to try to detect any special characteristics e.g. exponential terms.

The results of such model-improvement techniques are progressively more complex models with many parameters. Complex models should be avoided and models with many parameters (in comparison with the number of experiments) achieve good fits because the degrees of freedom are reduced, and not because the model is good. In the extreme case, a model with as many parameters as experimental results will fit exactly. It is useful, therefore, to be able to reduce the number of parameters by excluding those, which do not contribute to the regression. For linear regression, both model improvement and determining the significance of the individual parameter are based on the systematic inclusion (or exclusion) of more terms in the regression. This procedure can be easily programmed and so some linear regression programs have the ability to automatically include terms to improve the model, or exclude terms to determine the significance of the parameters.

6.2.2Quadratic Response Surface Model

For the Three inputs (x_1, x_2, x_3) the equation of quadratic response surface is given as

$$\mathbf{Y = (b_0 + b_1x_1 + b_2x_2 + b_3x_3) + (b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3) + (b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2)} \qquad \mathbf{(6.1)}$$

$$= \text{(linear terms)} + \text{(interactive terms)} + \text{(quadratic terms)}$$

Based on the above model equations, quadratic surface models were developed for Paraffin conversion; P, olefin selectivity; O, aromatic selectivity; A, and lighter selectivity, L based on the experimental results indicated in **Table 6.1**. These models were obtained using the regression analysis of Polymath software & are as given by the equations **6.2, 6.3, 6.4** and **6.5** respectively. While doing the regression the effects of each parameter (x_1 – x_3) were studied for a system with linear terms, linear with interactive terms and finally quadratic with linear & interactive terms. The regression statistics indicated by the quadratic response model were giving better results then compared to the linear and linear with interactive terms models as indicated for conversion of selectivity; O, in the **Table 6.2**. Similarly, compared with linear terms & linear with interactive terms the regression fit was better for quadratic with interactive & linear terms.

Table 6.2: Comparison of the regression statistics for various models for computing selectivity of olefin

STATISTICAL PRECISION PARAMETER	Quadratic with Linear & Interactive terms	Linear & Interactive terms	Linear terms
R^2	0.9	0.81	0.76
Adjusted R^2	0.8	0.73	0.71
RMSD	0.78	1.04	1.19
Variance	24.82	34.34	36.74

The quadratic response model was generated for the main responses of the system for the conversion of Paraffin, P; selectivity of olefins, O; selectivity of Aromatics, A and selectivity of Lighters, LE are as given below:

$$P = (76.87 - 2.68x_1 + 37.58x_2 + 9.21x_3) + (-0.05x_1x_2 - 0.01x_1x_3 - 0.196x_2x_3) + (0.004x_1^2 + 0.20x_2^2 + 0.004x_3^2) \quad \textbf{(6.2)}$$

$$O = (157.14 + 0.2142x_1 - 4.28x_2 + 1.07x_3) + (0.09x_1x_2 + 0.016x_1x_3 - 0.29x_2x_3) + (-0.003x_1^2 - 0.77x_2^2 - 0.037x_3^2) \quad \textbf{(6.3)}$$

$$A = (-716.19 - 2.029x_1 + 93.42x_2 + 12.64x_3) + (-0.13x_1x_2 - 0.008x_1x_3 - 0.46x_2x_3) + (0.006x_1^2 - 0.49x_2^2 + 0.016x_3^2) \quad \textbf{(6.4)}$$

$$L = (1096.43 - 0.99x_1 - 77.17x_2 - 5.56x_3) + (0.027x_1x_2 - 0.0268x_1x_3 - 0.646x_2x_3) + (0.0013x_1^2 - 1.1154x_2^2 - 0.0516x_3^2) \quad \textbf{(6.5)}$$

The comparison of the predicted responses with the actual experimental conversion of paraffin and selectivity of olefin, aromatic and Lighters is shown in **Figures 6.1, 6.2**, **6.3** and **6.4**. The correlations were tested for the prediction of validation experiments, which are not included in the development of the correlations. The predicted responses matched nearly well with that of actual experimental responses.

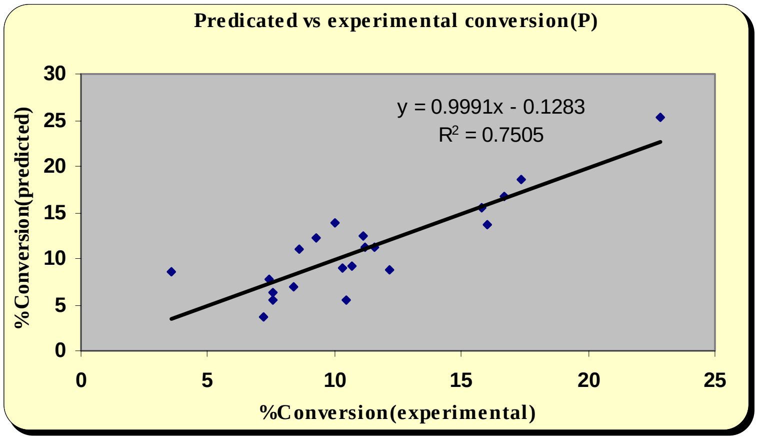

Figure 6.1 Predicted v/s Experimental paraffin conversion

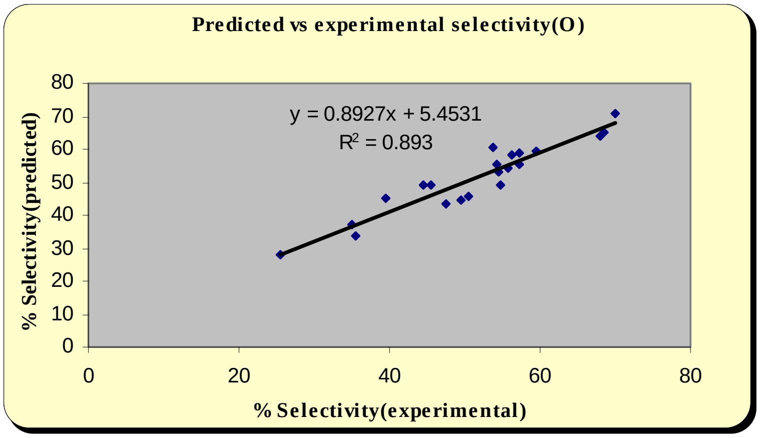

Figure 6.2 Predicted v/s Experimental olefins selectivity

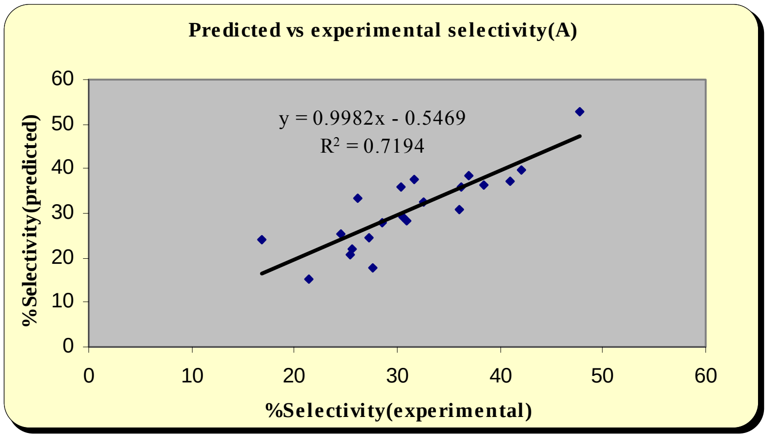

Figure 6.3 Predicted v/s Experimental aromatic selectivity

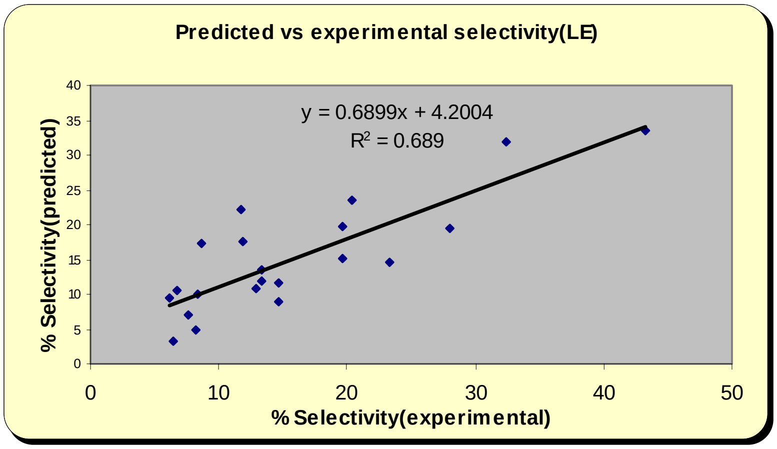

Figure 6.4 Predicted v/s Experimental Lighters selectivity

6.3 Effect of various factors

6.3.1 Effect of time on stream

The results on conversion and selectivity of various products are presented as a function of time in **Figure 6.5** to check the activity of catalyst. The dehydrogenation catalyst gets deactivated with time on stream and that's why H_2/HC molar ratio in the range of 5-8 is used industrially, while in this work the system is in supercritical state and without use of hydrogen and hence it can be observed that the rate of deactivation is not abruptly.

It is assumed that as n-paraffin attached to the active site of catalyst; it gets converted to mono-olefin. Due to supercritical phase of the reactant, reactant fluid serves as solvent with high density and hence high dissolution of coke precursors and also increases diffusivity of the phase. This property desorbs the olefin from the active sites of catalyst and thus not allowing further dehydrogenation of the product to aromatics and that to cracked product which finally form to coke deposition on the catalyst. Although the deactivation observed in the reaction might be due to non extractable coke under experimental conditions. In the present work hydrogen was totally avoided to study the reaction, this leads to formation of undesirable products like aromatics light ends instead of olefin.

Figure 6.5a shows the effect of time on the paraffin conversion product selectivity at atmospheric pressures. When the reaction run has been carried out at atmospheric pressure, abrupt decrease in the olefin selectivity was observed. This might be due to decreased activity of catalyst. This deactivation is mainly due to coking there is lots of aromatics formation, and coke is mainly this aromatic and cracked product only. This also supports the decrease in the aromatic contents after some time. It is observed that as we move towards sub critical to supercritical phase the selectivity get improved with time but when the reaction was carried out at 25atm pressure, more then the critical pressure value (Pc=21atm), drop in selectivity of olefin observed. Experiment is carried out for five hours and care is taken to isolate fresh catalyst kinetics with deactivation. The data considered in the present investigation for estimation of kinetic parameters corresponds to 1st hour data when the catalyst is fresh and there is no deactivation.

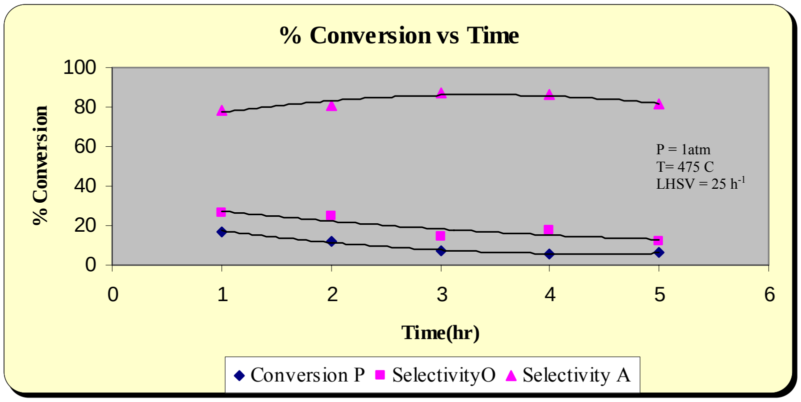

Figure 6.5a Effect of time on conversion and selectivity at Pressure = 1atm, Temp = 475 C, LHSV = 25 h^{-1}

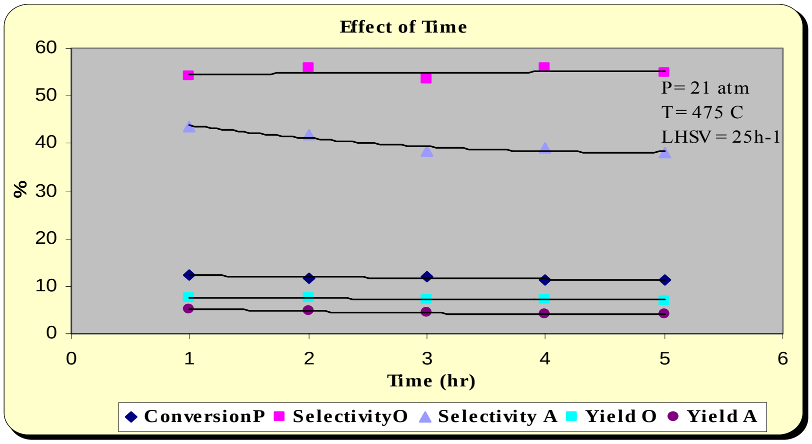

Figure 6.5 Effect of time on conversion and selectivity at 475^{o} C temperature, 21atm pressure, 25 h^{-1} LHSV

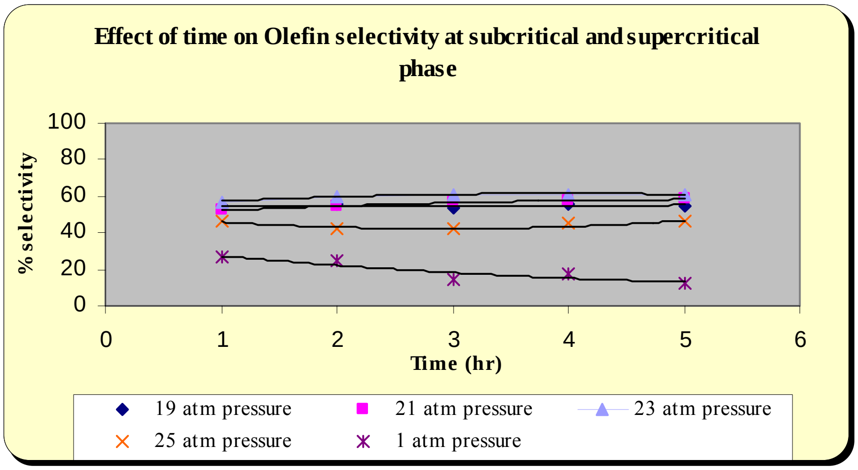

Figure 6.6 Effect of time at 475^{o} C temperature, 25 h^{-1} LHSV and pressure in the rage of 17-25atm on the selectivity of olefins

6.3.2 Effect of Temperature

Experiments were carried out to study the effect of temperature on product distribution in the temperature range between 445°C and 505°C at; LHSV = 25 hr-1 and pressure = 21atm. The conversion, selectivity and yields of all products at different temperatures are included in **Table 6.3. Figure 6.7** shows the variation of olefin selectivity with conversion and **Figure 6.8** shows the effect of temperature on paraffin conversion and selectivity of the various products.

Table 6.3 Effect of Temperature on conversion, selectivity and yields (Pressure = 21atm, LHSV = 25h^{-1})

	Conv. wt%	**Selectivity, wt%**			**Yields, wt%**		
T, °C	P	**O**	**A**	**LE**	**O**	**A**	**LE**
445	5.41	69.895	22.083	8.143	3.785	1.196	0.441
460	6.99	68.017	24.422	7.656	4.754	1.707	0.535
475	12.35	54.253	37.421	8.379	6.705	4.625	1.086
490	13.58	50.560	36.178	13.318	6.867	4.913	1.809
505	25.24	35.486	52.622	11.918	8.957	13.283	3.008

As can be seen from the results, paraffin conversion increased with increase in reaction temperature. The selectivity of olefin decreased with increase in temperature. The loss of olefin selectivity is due to successive dehydrogenation reactions such as secondary dehydrogenation to aromatics and, they also get cracked to light products. The selectivity of aromatics and lighters increases with increase in temperature.

Temperature is essentially the only variable which is used to control the conversion rate in the reactor. The temperature is generally adjusted as necessary to maintain the desired concentration of total olefins in the reaction product. Since the dehydrogenation to olefins is a reversible, endothermic reaction, equilibrium conversion of the linear paraffins to mono-olefins is favored at higher temperatures. The temperature is fixed at 475°C for all the other experiments for checking the effect of other factors.

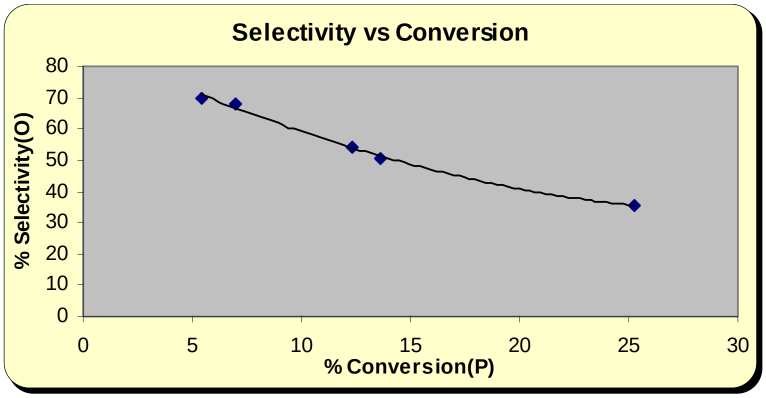

Figure 6.7 Variation of olefin selectivity with paraffin conversion

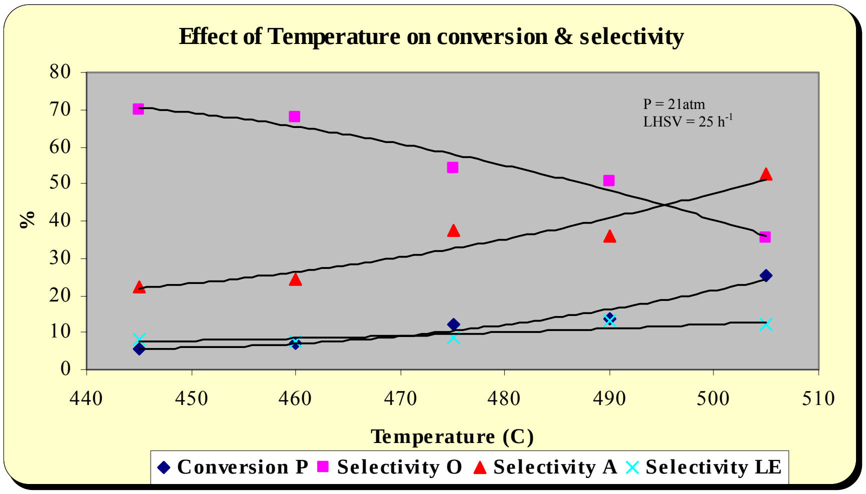

Figure 6.8 Effect of temperature on conversion and selectivity of products

6.3.3 Effect of pressure

Experiments are conducted at constant temperature = 475°C, LHSV =25 h^{-1} and varying pressure from 17atm to 25atm. The results on effect of pressure on conversion, selectivity of all the products and yields are presented in **Table 6.4.** The effect of pressure on conversion and selectivity of all products is shown in **Figure 6.9** and **Figure 6.10** respectively. The conversion as well as the selectivity is lower in the region of sub critical zone as shown in figure but at supercritical pressure it increases drastically and also corresponding olefins selectivity increases with increase in pressure. It has also observed that further increase in the pressure resulted in lower conversion, thus it is only a critical composition and combination of process conditions (critical band) at which the changes occur dramatically. As discussed earlier that increased diffusivity at supercritical phase allows the reactant components and product for easy diffusion into the catalyst pores. More over the increased density and dissolution power extract the olefin molecules form the active site of catalyst thus interrupting the successive dehydrogenation of olefin to the coke forming precursors. This leads to increase in selectivity of mono-olefin. The results show an increasing trend in selectivity of aromatics with pressure. The selectivity of Lighters decreases with increase in pressure. This result shows very much nearer to the reaction done for n-Dodecane over Pt-Sn/γ-alumina at very low pressure (1-2.5 kg/cm^2) but with H_2/HC mole ratio in the range of 5-7 by K.K. Chaudhari at al [2].

Table 6.4 Effect of pressure on conversion, selectivity and yields
Temperature = 475°C, LHSV = 25 h^{-1}

Pressure	Conversion, wt%	Selectivity, wt%			Yields , wt%		
atm	**P**	**O**	**A**	**LE**	**O**	**A**	**LE**
17	3.581	35.054	36.788	43.192	1.255	0.541	1.547
19	13.805	44.523	33.325	8.610	6.146	3.824	1.190
21	12.360	54.253	43.700	8.379	6.705	4.624	1.036
23	9.272	57.128	36.670	14.644	5.296	2.623	1.358
25	10.958	54.818	40.561	11.762	6.007	3.668	1.289

Catalyst stability is improved by increased pressure, but this leads to decrease in the equilibrium conversion. Operating pressure is fixed based on optimization between olefin selectivity and catalyst stability. Hence for all the other experiments for checking the effect of other variables the operating pressure is fixed at 21atm.

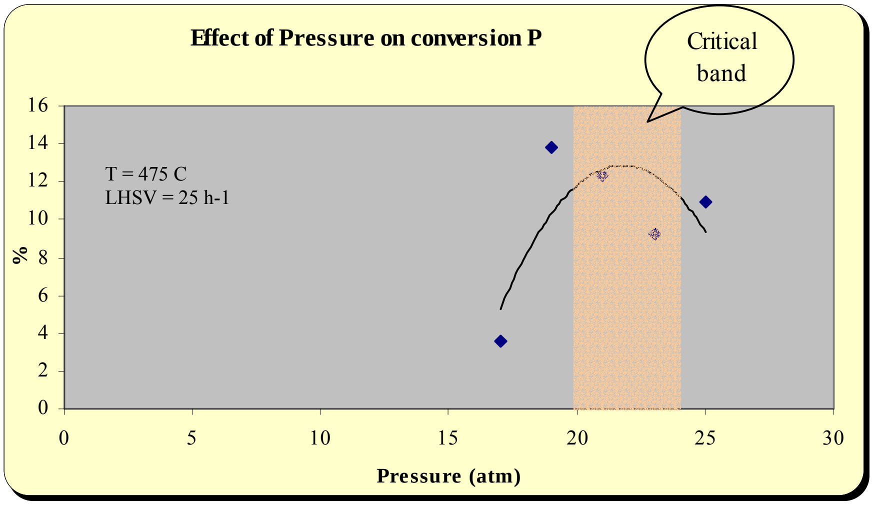

Figure 6.9 Effect of pressure on conversion

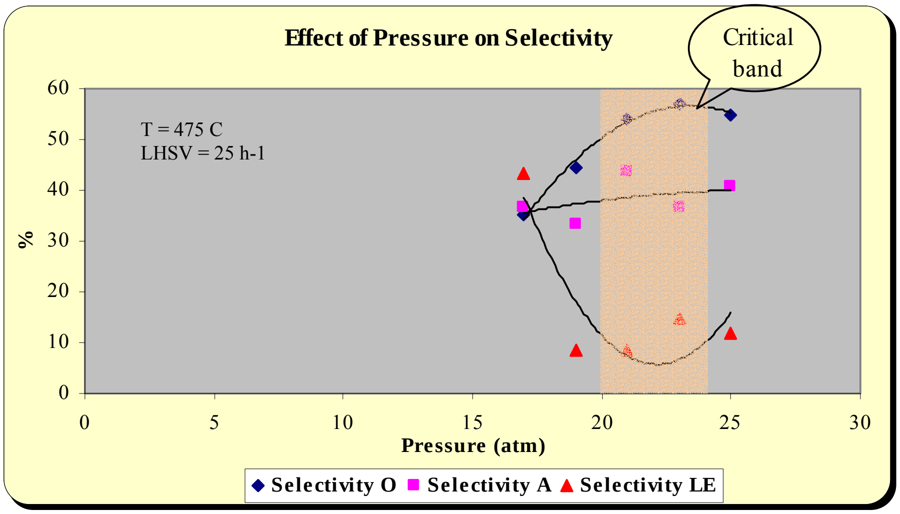

Figure 6.10 Effect of pressure on Selectivity

6.3.4 Effect of LHSV

Liquid hourly space velocity (LHSV) indicates the volume of feedstock charged to the reactor per volume of catalyst in an hour. Experiments were carried out by varying LHSV between 18.28 h^{-1} and 30 h^{-1} at constant conditions of temperature = 475°C; and pressure = 21atm. The LHSV was varied by both catalyst concentration and flow rate and also by varying flow rate at constant catalyst concentration. The effect of LHSV on paraffin conversion, selectivity of all products and yields are presented in **Table 6.5.**

Table 6.5 Effect of LHSV on conversion, selectivity and yields
Temperature = 475 °C, Pressure = 21 kg/cm^2

LHSV	Conversion, wt%	Selectivity, wt%			Yields, wt%		
h^{-1}	P	O	A	LE	O	A	LE
18.28	14.165	46.821	46.312	12.390	6.632	5.784	1.755
22	11.287	54.393	39.250	13.294	6.139	3.654	1.500
25	12.359	54.253	43.700	8.379	6.705	4.624	1.036
30	8.964	56.172	37.990	14.663	5.035	2.629	1.315

The effect of LHSV on conversion and selectivity of the entire product is shown in **Figure 6.11** and **Figure 6.12** respectively. Conversion decreases with increase in LHSV. Selectivity of olefins increases with increase in LHSV where as the selectivity of aromatics and light ends decrease. As seen from the results (**Figure 6.11)** though conversion can be controlled by varying LHSV, it is inconvenient to change the unit throughput. Better selectivity can be obtained by varying the temperature at constant LHSV. In all the experiments we have kept LHSV constant at 25 h^{-1}, which is in the range of commercial operating conditions.

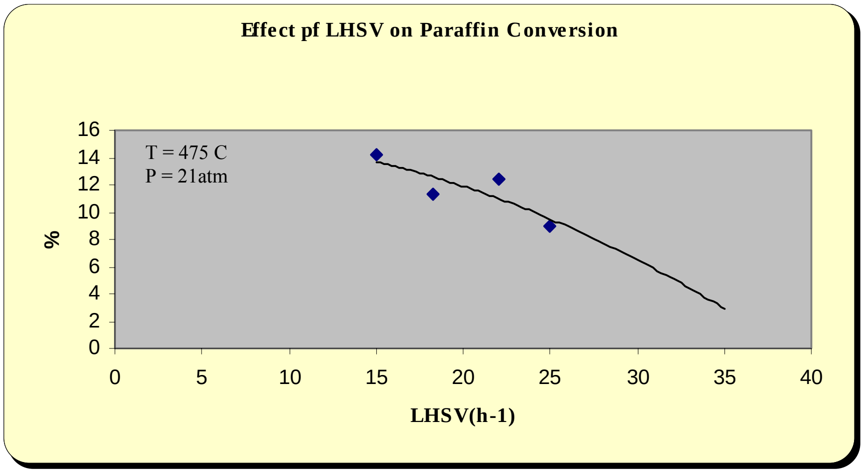

Figure 6.11 Effect of LHSV on conversion

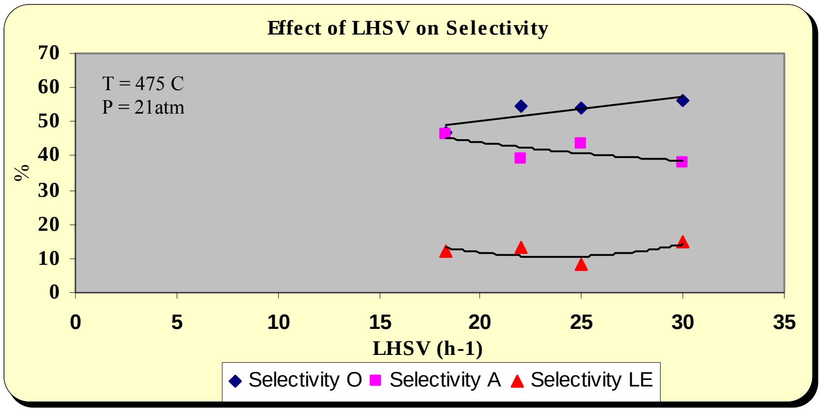

Figure 6.12 Effect of LHSV on selectivity

6.4 Kinetic study

Kinetic runs were carried out using different W/F ratio, at a constant pressure and at the temperature of 475^{0}C.

The inner diameter of the reactor used for the experimental run was 9.0 mm. Space above and below the catalyst in the reactor was filled in with inert glass bids. The total bed height including catalyst with an average particle size of 0.5 mm and inert glass bids amounts to around 4 cm. Since the larger fraction of the reactor length contained only inert material, the question of axial dispersion does not arise [3]. The radial aspect ratio Dt/d_p (diameter of reactor tube/diameter of particles) was kept 18 (Dt = 9 mm, dp = 0.5 mm, ideally it should be >15 [4]) by using dp in the range of 0.5 mm. The difference in temperature is hardly observed between the center and the wall of the reactor. Thus there was no radial temperature gradient. The isothermal zone in the furnace was around 5.5 cm. the catalyst bed is adjusted to come in the middle of the uniform zone. The temperature was maintained constant throughout the run. The reactor was considered to be an integral one and the data were analyzed following integral method of analysis [5].

6.4.1Estimation of diffusion effects

It is very essential to evaluate the contribution of mass transfer resistance on the rate of reaction as well as the kinetic studies of catalytic vapor phase reaction. In general, either it should be shown experimentally that the pore diffusion and bulk mass transfer is not rate controlling or the rate equations must be corrected for any positive influence of diffusion. In a system, where a study of the kinetics is desired, it is generally preferable to eliminate diffusion as rate controlling process by adjusting system parameters rather than including their influence in the rate equations. Film resistance can be minimized by operating at a high velocity of gases and the resistance due to pore diffusion by proper sizing of the catalyst.

By carrying out experiments at different mass flow rates maintaining the constant W/F ratio, we can ensure absence of external film resistance. Results show that the conversion at two different liquid feed flow rate having same W/F ratio remains almost constant which indicates that the mass transfer effect on conversion in the given range of feed flow rate is negligible. In all experimental runs above range of feed flow rate is used. The feed flow rate used in all experimental runs is in the range of 10-50 ml/h.

To test the intra particle diffusion limitation, experiments were carried out by varying particles size and keeping W/F ratio constant. Smaller particle size is obtained by crushing the spherical catalyst particles. The results did not show any significant deviation in conversion as shown in the **Figure 6.13** which indicates the absence of intra particle diffusion [2, 6]. So finally the catalyst size was taken as 0.5 mm range

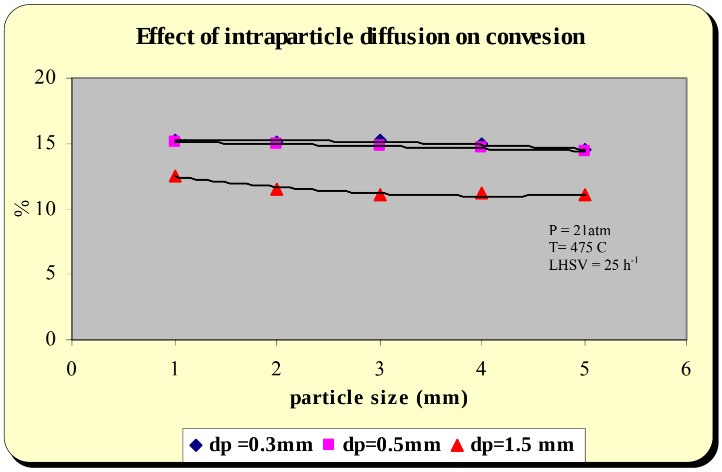

Figure 6.13 effect of particle size on internal mass transfer for paraffin conversion (Temperature = 475C, Pressure = 21atm, LHSV = 25 h-1)

6.4.2Effect of W/F

Figures 6.14 describe the effect of W/F on conversion and selectivity of all the products. The conversion, selectivity and yields of all the products as a function of

W/F at the temperature value 475° C is presented in **Table 6.6**. The rate of reaction was calculated from the W/F vs conversion data. The conversion of each reaction was calculated by material balance. The W/F vs conversions (X_1 to X_3) of the three reactions assumed are presented in **Table 6.7**. The rate of each reaction was then calculated from W/F vs conversion data. The data were fitted in to a smooth 3rd order polynomial curve of the type $X = a\,(W/F)^3 + b\,(W/F)^2 + c$. Then the equation is differentiated $dX/d(W/F)$ to obtain rate as a function of W/F. The calculated W/F vs rate of all the three reactions ($r_1 - r_3$) and partial pressures of all the components in the products are presented in **Table 6.8**.

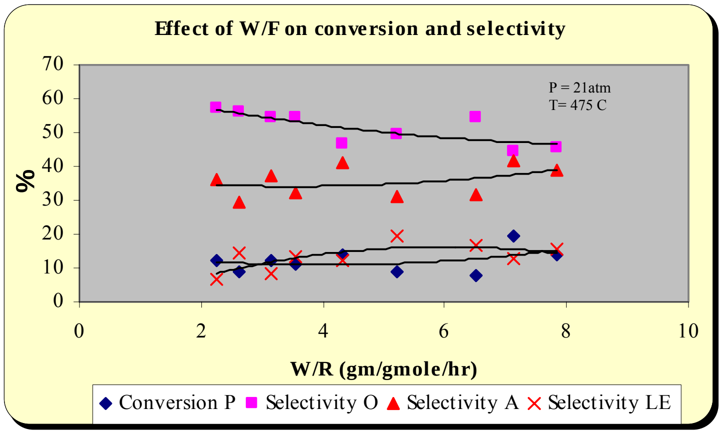

Figure 6.14 Effect of W/F on conversion and selectivity

Table 6.6 Conversion, selectivity and yields of n-decane dehydrogenation products

	Selectivity, wt%				Yields, wt %		
W/F, gm h/ gmole	**X_1**	**O**	**A**	**LE**	**O**	**A**	**LE**
P = 21 atm T = 475°C							
2.2384	12.337	57.248	36.011	6.734	7.063	5.219	0.838
2.6105	8.965	56.173	29.334	14.578	5.036	3.406	1.315
3.1348	12.359	54.253	37.421	8.318	6.705	5.401	1.036
3.5615	11.287	54.394	32.375	13.227	6.139	4.430	1.500
4.313	14.166	46.822	40.834	12.337	6.633	6.560	1.755
5.2219	8.846	49.449	31.018	19.523	4.374	3.520	1.734
6.5274	7.957	54.669	31.897	16.736	4.350	3.314	1.339
7.12	19.458	44.364	41.489	12.589	8.632	8.849	2.457
7.83	13.978	45.446	38.880	15.667	6.353	6.211	2.198

Table 6.7 W/F vs conversion

W/F, gm h/ gmole	X_1	X_2	X_3
P = 21atm T = 475°C			
2.2384	12.337	5.219	0.838
2.6105	8.965	3.406	1.315
3.1348	12.359	5.401	1.036
3.5615	11.287	4.430	1.500
4.313	14.166	6.560	1.755
5.2219	8.846	3.520	1.734
6.5274	7.957	3.314	1.339
7.12	19.458	8.849	2.457
7.83	13.978	6.211	2.198

Table 6.8 Reaction rates and partial pressures of n-decane dehydrogenation

W/F gm h /mole	r_1	r_2	r_3	pLE atm	pP atm	pO atm	pA atm	pH atm
P = 21 atm T = 475°C								
2.2384	0.1226	0.0153	0.0018	0.193	5.005	0.316	0.409	15.077
2.6105	0.1376	0.0043	0.0032	0.167	2.875	0.114	0.161	17.683
3.1348	0.1548	0.0082	0.0046	0.236	4.947	0.323	0.384	15.111
3.5615	0.1653	0.0158	0.0055	0.068	0.995	0.053	0.070	19.815
4.313	0.1765	0.0236	0.0062	0.697	8.455	0.685	0.663	10.500
5.2219	0.1773	0.0235	0.0056	0.226	2.939	0.120	0.143	17.572
6.5274	0.1542	0.0052	0.0023	0.170	2.905	0.111	0.139	17.675
7.12	0.1343	0.0102	0.0003	0.394	3.198	0.372	0.348	16.688
7.83	0.1026	0.0344	0.0041	0.285	2.767	0.212	0.207	17.529

6.5 Reaction Scheme and modeling

Based on the product distribution obtained from the analysis of liquid product streams, it is obvious that decene is the desired product in decane dehydrogenation. The experimental results indicated that the liquid product is more than 98% and rest is gas product. Mono-olefins and Di-olefins are not separated in this scheme and considered as olefins to gather. All the products of decane dehydrogenation such as, decene, decadiene and decane itself can crack to form light. Isomerization reaction was ignored.

In according with the product distribution and above observations the system can be described with the following reactions.

Dehydrogenation

Olefins formation

$$C_{10}H_{22} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} C_{10}H_{20} + H_2$$

Secondary Dehydrogenation

Aromatic formation

$$C_{10}H_{20} \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} C_{10}H_{14} + 3H_2$$

Lighter formation

$$C_{10}H_{20} + 2H_2 \overset{k_3}{\rightarrow} < C7 \text{ hydrocarbons}$$

In this work various rate equation based on power low, LHHW model, Rideal Eley model, was proposed and the model with the best fitting of the experimental data is consider as final model.

The reactor is operated in integral mode. The moles of different components present at any point when conversion of paraffin is X_p

Moles of paraffin = $1 - X_P$

Moles of olefins = X_O

Moles of Lighters = X_{LE}

Moles of aromatics = X_A

Moles of H_2 = X_{H2}

Partial pressure of each species can be expressed as

$pP = 1 - X_P * p_t / TM$

$pO = X_O * p_t/TM$

$pLE = X_{LE} * p_t/TM$

$pA = X_A * p_t/TM$

$pH2 = X_{H2} * p_t/TM$

Where TM = total moles

6.5.1Power Low model

The rate of each reaction based on power law can be given by the following material balance

Material Balance

The rate of formation of each component can be expressed as:

Rate of formation of olefins (Decene)

$$\frac{dX_O}{d\theta} = r_1 = k_1\,pP - k_{-1}\,pOpH - k_2 pO + k_{-2} pApH^3 - k_3 pO$$

Rate of formation of aromatic

$$\frac{dX_D}{d\theta} = r_2 = k_2\,pO - k_{-2}\,pApH^3$$

Rate of formation of lighter

$$\frac{dX_A}{d\theta} = r_3 = k_3\,pO$$

Rate of formation of H_2

$$\frac{dX_H}{d\theta} = r_4 = k_1\,pP - k_{-1}\,pOpH + 3k_2\,pO - 3k_{-2}\,pApH^3 - 2k_3\,pO$$

Where θ = W/F = gm cat h/ g mol paraffin feed

The kinetic parameters were estimated by minimization of the root mean square value of the residuals of calculated rate and experimental values of rate using the polymath software based on Levenberg-Marquardt (LM) algorithm. Various models for rate equation have been tested by the integral method of analysis.

6.5.2Langmuir-Hinshelwood-Hougen-Watson Model

The LHHW model has been derived based on the assumption that among the chemical steps, the slowest is the rate controlling. When one step is rate controlling the other steps are summed to be at equilibrium. Diffusion steps of the porous catalytic system are neglected.

The reaction scheme corresponding to the three major dehydrogenation reactions have steps for adsorption, surface reaction and desorption as shown in **Figure 6.17**. The symbol L denotes the active site of the catalyst surface.

Step 1: Adsorption of decane on catalyst active site

Step 2: Decane reacts with another active site to form decene and hydrogen

Step 3: Desorption of decene & hydrogen

Step 4: Readsorption of Decene

Step 5: Decene reacts with another active site to form aromatics and hydrogen

Step 6: Desorption of aromatics & hydrogen

First 3 steps have shown in **Figure 6.15** bellow

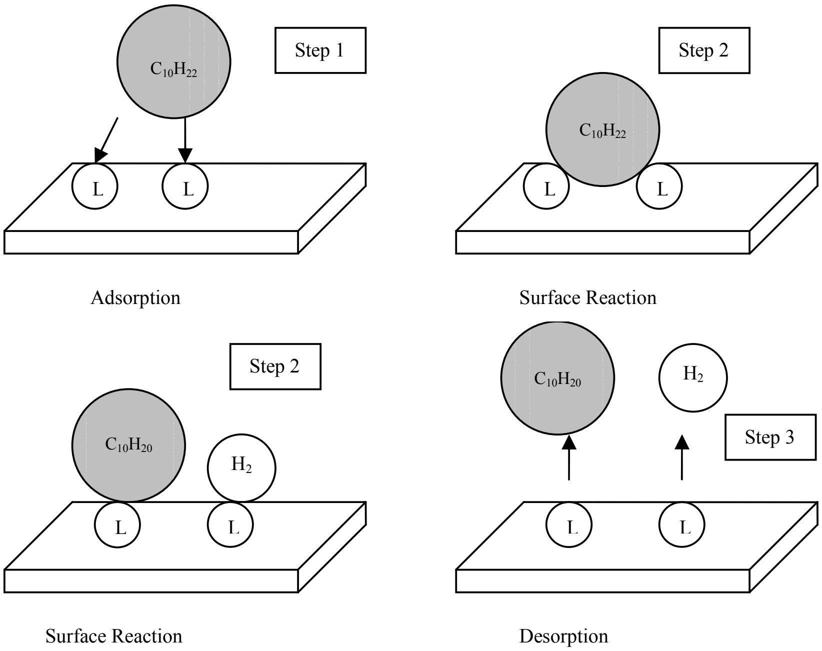

Figure 6.15 Schematic diagram of decane conversion to decene

All the reactions are assumed to have a step that is slower than the other steps, i.e. rate determining step (rds). For example, if adsorption on dual sites is considered as rate determining, then step 1 and step 4 are rate determining steps. The rate equations are derived in the same way similar to a single reaction. The derivation of rate equation for all the three steps of adsorption, surface reaction and desorption control for a single reaction is given in **Appendix-2**.

Rate equations were written for the rate determining step of each of the three reactions in terms of the concentrations of the adsorbed species. These concentrations were then eliminated by means of the Longmuir equilibrium relations and a balance on the active sites including those left vacant and those covered by adsorbed species. This gives rate equations in terms of accessible gas-phase partial pressures and contains a denominator resulting from the adsorption of reacting species. Since all the three reactions are assumed to take place on the same active sites, the three rate equations have the same denominator.

Various sets of rate equations can be generated with different assumptions. In the present work six sets of rate equations were generated assuming adsorption, surface reaction, desorption on dual sites (LHHW model)**(Figure 6.16)** as rate controlling steps and single site (Rideal and Eley models) with adsorption, surface reaction and desorption as rate controlling steps. In Rideal–Eley mechanisms one adsorbed species reacts with another species in the gas phase. The reaction scheme based on the single site mechanism is given in **Figure 6.17**. The derivation of the rate equations for adsorption, surface reaction and desorption based on the Rideal – Eley mechanism is given in **Appendix-3**. The final rate models tested are presented in **Figure 6.18** and **Table 6.19**.

$$\begin{array}{lcllc}
\mathrm{C_{10}H_{22} + L} & \leftrightarrow & \mathrm{C_{10}H_{22}L} & \text{Adsorption} & \\
\mathrm{C_{10}H_{22}L + L} & \leftrightarrow & \mathrm{C_{10}H_{20}L + H_2L} & \text{Surface Reaction} & \{P \leftrightarrow O\} \\
\mathrm{C_{10}H_{20}L} & \leftrightarrow & \mathrm{C_{10}H_{20} + L} & \text{Desorption} &
\end{array}$$

$$\begin{array}{lcllc}
\mathrm{C_{10}H_{20} + L} & \leftrightarrow & \mathrm{C_{10}H_{20}L} & \text{Adsorption} & \\
\mathrm{C_{10}H_{20}L + L} & \leftrightarrow & \mathrm{C_{10}H_{14}L + H_2L + 2H_2} & \text{Surface Reaction} & \{\mathrm{O} \leftrightarrow \mathrm{A}\} \\
\mathrm{C_{10}H_{14}L} & \leftrightarrow & \mathrm{C_{10}H_{14} + L} & \text{Desorption} &
\end{array}$$

$$\begin{array}{lcll}
\mathrm{H_2L} & \leftrightarrow & \mathrm{H_2 + L} & \text{Desorption}
\end{array}$$

Figure 6.16 Dual site mechanisms (LHHW Model)

$$\begin{array}{lcllc}
\mathrm{C_{10}H_{22} + L} & \leftrightarrow & \mathrm{C_{10}H_{22}L} & \text{Adsorption} & \\
\mathrm{C_{10}H_{22}L} & \leftrightarrow & \mathrm{C_{10}H_{20}L + H_2} & \text{Surface Reaction} & \{P \leftrightarrow O\} \\
\mathrm{C_{10}H_{20}L} & \leftrightarrow & \mathrm{C_{10}H_{20} + L} & \text{Desorption} &
\end{array}$$

$$\begin{array}{lcllc}
\mathrm{C_{10}H_{20} + L} & \leftrightarrow & \mathrm{C_{10}H_{20}L} & \text{Adsorption} & \\
\mathrm{C_{10}H_{20}L} & \leftrightarrow & \mathrm{C_{10}H_{14}L + 3H_2} & \text{Surface Reaction} & \{\mathrm{O} \leftrightarrow \mathrm{A}\} \\
\mathrm{C_{10}H_{14}L} & \leftrightarrow & \mathrm{C_{10}H_{14} + L} & \text{Desorption} &
\end{array}$$

Figure 6.17 Single site (Rideal Eley Model) mechanisms

Adsorption as rate controlling step

$$r_1 = K_1(p_P - p_O p_H / K_{E1})/\mathrm{DEN}$$

$$r_2 = K_4(p_O - p_D {p_H}^3 / K_{E2})/\mathrm{DEN}$$

$$r_3 = K_3 p_D$$

$$\mathrm{DEN} = (1 + K_P p_O p_H / K_{E1} + K_O p_D + K_A p_A + K_H p_H)$$

Surface Reaction as rate controlling step

$$r_1 = K_2(K_P p_P - p_O p_H / K_{E1})/\mathrm{DEN}$$

$$r_2 = K_2(p_O - p_D p_H / K_{E2})/\mathrm{DEN}$$

$$r_3 = K_3 p_D$$

$$\mathrm{DEN} = (1 + K_P p_p + K_O p_O + K_D p_D + K_A p_A + K_H p_H)^2$$

Desorption as rate controlling step

$$r_1 = (K_3 p_O)/\mathrm{DEN}$$

$$r_2 = K_6(K_{E2} p_O / (K'_O p_H^3) - K_A p_A)/\mathrm{DEN}$$

$$r_3 = K_3 p_D$$

$$\mathrm{DEN} = (1 + K_P p_P + K'_O p_O + K_{E2} p_O / (K_{O'}\, p_H^3) + K_{E1} p_P / (K_{OA} p_P p_{H3}))$$

Figure 6.18 Rate equations for LHHW model

Adsorption as rate controlling step

$$r_1 = K_1(p_P - p_O p_H/K_{E1})/DEN$$

$$r_2 = K_4(p_O - p_D p_H^{3}/K_{E2})/DEN$$

$$r_3 = K_3 p_D$$

$$DEN = (1 + K_P p_O p_H/K_{E1} + K_O p_D + K_A p_A)$$

Surface Reaction as rate controlling step

$$r_1 = K_2(p_P - p_O p_H/K_{E1})/DEN$$

$$r_2 = K_5(p_O - p_D p_H^{3} /K_{E2})/DEN$$

$$r_3 = K_3 p_D$$

$$DEN = (1 + K_P p_p + K_O p_O + K_D p_D + K_A p_A)$$

Desorption as rate controlling step

$$r_1 = K_3(K_{E1} p_P/p_H - p_O)/DEN$$

$$r_2 = K_6(K_{E2} p_O/(p_H^{3}) - p_A)/DEN$$

$$r_3 = K_3 p_D$$

$$DEN = (1 + K_P p_P + K_O K_{E1} p_P/(K_H) + K_O K_{E1} p_P/(K_{OA} p_H^{4}))$$

Figure 6.19 Rate equations for Rideal Eley model

6.5.3 Model discrepancy and Parameter Estimation

The rate of reaction in above all model was calculated from the W/F vs conversion data as stated earlier. The conversion of each reaction was calculated by material balance. The kinetic parameters were estimated by minimization of the root mean square value of the residuals of calculated rate and experimental values of rate of each component by using Polymath 5.1 academic version.

The program uses the Levenberg-Marquardt (LM) algorithm for finding the parameter values, which minimize the sum of squares of the errors. A detailed explanation of this method can be found at some where else **[7]**. Two different implementations of the LM method are included. The LM technique is an iterative solution method that usually converges very rapidly, except when the Hessian matrix becomes nearly singular. In such cases, the algorithm switches to the steepest descent method, the convergence of which can be very slow. A nearly singular Hessian matrix often indicates that there are more parameters in the model than are justified by the data. In case of slow convergence, it is recommended to stop the iterations and check the display of statistical analysis to verify the correctness of the number of model parameters. Various models for rate equation have been tested by the integral method of analysis.

The conditions used to discriminate between the above described various models are (1) if negative values are obtained for one or several parameters, the model should rejected (2) Root mean square difference (RMSD) value should be the least of all the models (3) when models are in competition, the model with less number of parameters is considered

Table 6.9 Model discrepancy and parameter estimation

	Predicted Models						
Parameter value	Power Low	LHHW model Controlling Step			Rideal-Eley model Controlling Step		
		Adsorption	Surface reaction	Desorption	Adsorption	Surface reaction	Desorption
k_1	0.075						
k_{-1}	0.031						
k_2	0.1030						
k_{-2}	$1.89*10^{-6}$						
k_3	0.6030						
k_{-3}							

K_{11}		0.0681			-0.0033		
K_{22}			-0.169			0.0198	
K_{33}				0.10			
K_{44}		0.0071			0.0288		0.098
K_{55}						0.6111	
K_{66}				-0.0508			0.377
K_{O}			31.30		31.26	6.406	
K_{P}		0.5669	-1.039	0.1998	2.4617	-0.6326	0.2
K_{A}		28.9058	-30.03	-0.0626	26.6449	2.7789	
K_{H}		1.9442	0.4429				
K_{E1}		0.6086	0.4928	0.0032	1.3361	46.4498	0.1212
K_{E2}		1.032	0.6470	-37.032	46.4409		26.03
K'_{O}			0.3535	0.3188			0.3259
K_{OA}				0.0121			4.480
RMSD	**109.9**	**0.0509**	**1.101**	**0.045**	**0.0497**	**0.023**	**0.053**

Of the Power law, LHHW models and Rideal - Eley models tested, the RMSD value of the model for adsorption on double site mechanism is minimum, how ever the RMSD value is not satisfactorily minimum it is still quantitatively higher value to discriminate the model. The desorption as controlling step of Rideal – Eley mechanism is also showing positive parameters, while all other model where having at least one parameter value as negative so they are eliminated. But out of the entire model, model with adsorption as rate controlling for dual site has some what physical significance. At supercritical condition high solvent power of reactant fluids always tends to desorb the components present in the system. So with this reason it could be stated that adsorption would be slowest step.

Thus no model gives good fitting of the experimental data with very high accuracy..

6.6 Catalyst Coking and Deactivation

The spent catalysts discharged after 5 hrs of run from the reactor were crushed along to a homogeneous powder and analyzed for the following. Coke content of spent catalysts was determined by temperature programmed coke oxidation by using thermo gravimetric technique (TPCO). In a typical TPCO experiment, oxygen stream at constant flow rat of 120cm^3/ min is fed into the sample cell under ambient conditions. The sample temperature is increased linearly at the desired heating rate from room temperature to the desired temperature at which complete oxidation of all the carbon deposits occurs.

In this technique the reference sample was pure alpha-Al_2O_3 against the spent catalyst sample which is taken after the 5 hrs of reaction. The result of the coke formation by the various parameter studies, like Temperature (°C) Pressure (atm) and W/F (gm/gmole/hr) is shown in **Table 6.10**, **figure 6.20, 6.21** and **6.22**.

Table 6.10 Effect of process variables on coke formation

P = 21 atm, LHSV = 25 h^{-1}		T = 475° C, LHSV = 25 h^{-1}		P = 21 atm, T= 475° C	
Temp (°C)	Coke, (wt %)	Pressure (atm)	Coke (wt%)	W/F	Coke (wt%)
445	2.383	17	18.73	5.2240	4.463
460	2.76	19	2.35	3.5615	3.347
475	3.45	20	3.45	3.1845	2.678
490	3.63	23	2.08	2.6105	2.231
505	10.68	25	3.44	2.2384	1.912

As shown in the Figure below the coke content has increased as the temperature increment. Higher temperature leads to the higher rate of formation of the reactions and so successive dehydrogenation occurs which result in the coke precursor and remains on the catalyst surface. How ever it is observed that coke content decreased as we move towards the supercritical condition and there is drastic change in the coke content. This also supports the pervious observation done for the time effect on the conversion and selectivity. Here this might be due to the high extraction power of the supercritical fluid which extract the olefin as it form from paraffin on the active site. Thus further dehydrogenation can be controlled. Mainly coke precursors are these further dehydrogenated products only and also some cracked product.

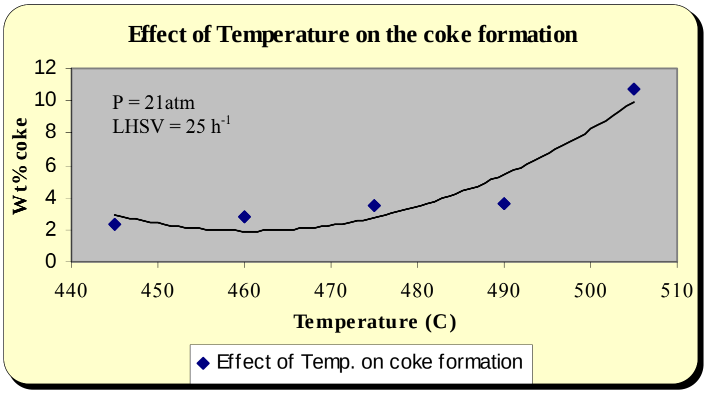

Figure 6.20 Effect of temperature on coke formation (P=21atm, LHSV=25h^{-1})

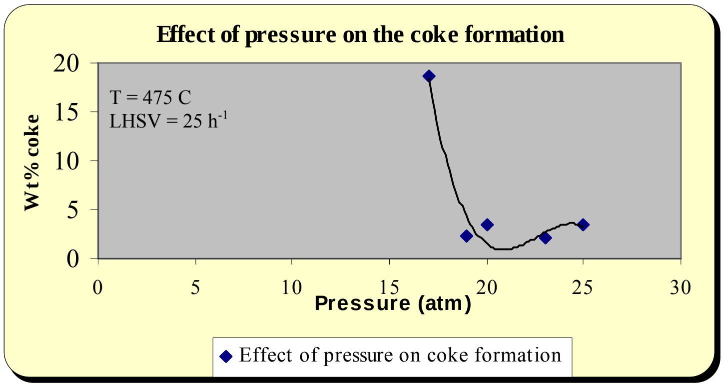

Figure 6.21 Effect of pressure coke formation

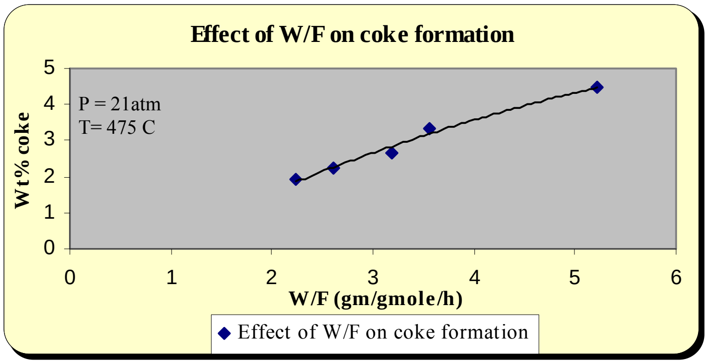

Figure 6.22 Effect of W/F on coke formation

More over coke content increases as increase in the W/F ratio. Higher the ratio there is more contact time available for reaction, so these gives higher rate of reaction which results in the byproduct formation and coke precursors.

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7. Summary and Conclusions

- High pressure reaction system was designed and fabricated for “Selective dehydrogenation of n-paraffins”.
- Process parameters were chosen to generate the data to study kinetics of the reaction.
- Modified Box-Wilson experimental design was used to find out the effect of process parameters (temperature, pressure, and LHSV) on conversion of n-paraffin and selectivity of mono-olefins.
- Surface response method was used to establish Quadratic Response Surface Models to correlate selectivity of the products and operating conditions. These correlations can be used for optimization of operating conditions.
- Kinetic experiments were carried out at one temperature by varying W/F over a wide range of constant pressure of 21atm.
- Reaction network was established based on the product distribution obtained.
- A kinetic model based on LHHW dual site and Rideal-Eley single site was derived assuming adsorption, surface reaction, and desorption as rate controlling step.
- All the proposed kinetic models were tested using non-linear modeling for kinetic parameter estimation.

7.1Conclusions

- Results indicated that the (Pt-Sn/γ Al_2O_3) is highly active and selective for dehydrogenation of n-Decane.
- Box Wilson design method is found to be suitable for modeling conversion and selectivity as a function of operating conditions.
- At supercritical condition deactivation minimized due to dual property and solvent power of fluid.
- However, total deactivation can not be eliminated but in absence of hydrogen, it is **significant reduction in coke formation** on the catalyst.
- Hence it is possible to waiver use of hydrogen, highly hazardous gas, leading to support one of the twelve principles of Green chemistry, e.g. minimization of material use and elimination of hazardous material usage This support one

of the twelve principles of Green chemistry, e.g. minimization of material use and elimination of hazardous material usage

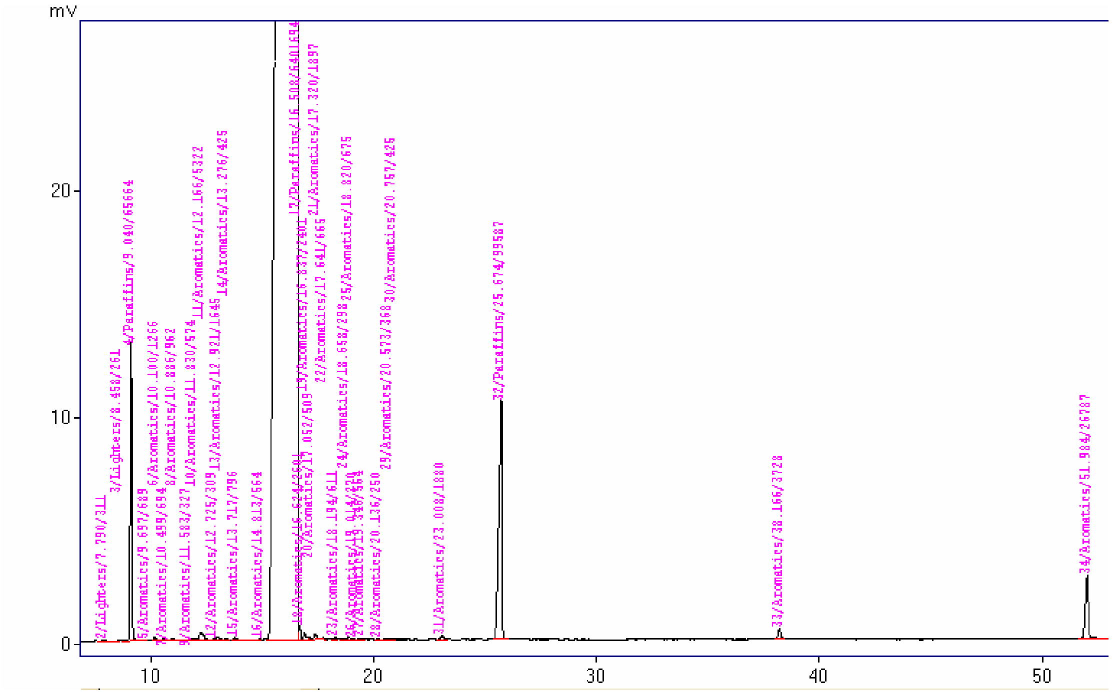
- Intrinsic rate equations were derived for dehydrogenation of n-Decane to propose various models, out of which LHHW models with adsorption as rate controlling step and Rideal - Eley with desorption as rate controlling step only yielded positive parameter value, even though they are not statistically significant enough to propose the reaction mechanism.
- More over it seems logical that in presence of high pressure and solvent power of supercritical fluid the more tendencies is towards desorption rather than absorption. These can explain the more possibility of LHHW model with adsorption as slowest and rate controlling step for this reaction mechanism.

7.2 Further Work

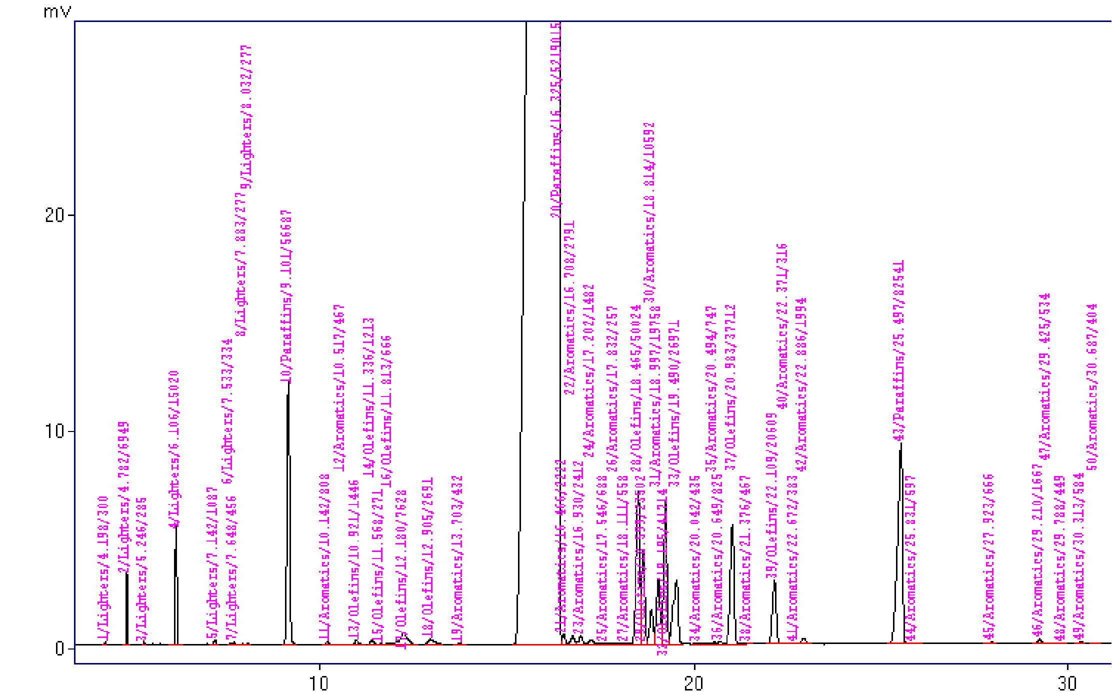
- As in the present work the reactant itself has taken in supercritical phase, but the out put is not still satisfactorily. As n-Decane might not possess enough solvent power in the supercritical region as observed, the study could be extended to C_{10}-C_{13} fraction as reactants to get clearer picture.
- High extraction power can also be improved by using CO_2 as solvent in the reaction

APPENDIX-1

Gas Chromatograph for feed



Gas Chromatograph for Product



APPENDIX-2

Derivation of Rate Equations for LHHW Model based on Dual Site Mechanism

Dehydrogenation of n-Decane

$$P \leftrightarrow O + H_2$$

$P + L \leftrightarrow PL$ $\quad K_1 = C_{PL}/(p_p * C_L)$

$PL + L \leftrightarrow OL + H_2L$ $\quad K_2 = C_{OL}*C_{HL}/(C_{PL}*C_L)$

$OL \leftrightarrow O + L$ $\quad K_3 = p_O*C_L/C_{OL}$

$H_2L \leftrightarrow H_2 + L$ $\quad K_7 = p_H*C_L/C_{HL}$

$K_{E1} = K_1*K_2*K_3*K_7 = p_O*p_H/p_P$

A . Adsorption is rate controlling

$K_1 \neq C_{PL}/(p_p * C_L)$

$C_{PL} = p_O*p_H*CL/ (K_2*K_3*K_7) = K_1*p_O*p_H*C_L/K_{E1}$

$C_{OL} = p_O*C_L/K_3$; $C_{HL} = p_H*C_L/K_7$

$C_t = C_L + C_{PL} + C_{OL} + C_{AL} + C_{HL}$

$C_t = C_L(1+ K_1*p_O*p_H/K_{E1} + p_O/K_3 + p_A/K_6 + p_H/K_7)$

$r = k_1(p_P *C_L – C_{PL}/K_1)$

$\quad = k_1*C_L(p_P - p_O*p_H/K_{E1})$

$$\mathbf{r = K_{11}(p_P – p_O*p_H/K_{E1})/(1+ K_P*p_O*p_H/K_{E1} + K_O*p_O + K_A*p_A + K_H*p_H)}$$

where $K_{11} = k_1*C_t$, $K_A = K_1$, $K_O = 1/K_3$, $K_A = 1/K_6$, $K_H = 1/K_7$

B. Surface reaction is rate controlling

$K_2 \neq C_{OL}*C_{HL}/(C_{PL}*C_L)$

$C_{PL} = K_1*p_P*C_L$; $C_{OL} = p_O*C_L/K_3$; $C_{HL} = p_H*C_L/K_7$

$C_t = C_L + C_{PL} + C_{OL} + C_{AL} + C_{HL}$

$C_t = C_L(1+ K_1*p_P + p_O/K_3 + p_A/K_6 + p_H/K_7)$

$r = k_2(C_{PL} * C_L - C_{OL} * C_{HL}/K_2)$

$= k_2(K_1 * p_P * CL * C_L - p_O * p_H * C_L * C_L/(K_2 * K_3 * K_7)$

$= k_2 K_1 * C_L^2(p_P - p_O * pH/K_{E1})$

$= k_2 * K_1 * C_t^2(K_{P*} p_P - p_O * p_H/K_{E1})/ (1+ K_1 * p_P + p_O/K_3 + p_A/K_6 + p_H/K_7)^2$

$\mathbf{r = K_{22}(K_P * p_P - p_O * p_H/K_{E1})/(1 + K_P * p_P + K_{O*} p_O + K_A * p_A + K_{H*} p_H)^2}$

where $K_{22} = k_2 * C_t^2 * K_1$

C Desorption of product O is rate controlling

$K_3 \neq p_O * C_L/C_{OL}$

$C_{PL} = K_1 * p_P * C_L;\ C_{HL} = p_H * C_L/K_7$

$C_{OL} = K_2 * C_{PL} * C_L/C_{HL} = K_2 * K_1 * K_7 * p_P * C_L/p_H$

$= K_{E1} * p_P * C_L/(K_3 * p_H)$

$C_t = C_L + C_{PL} + C_{OL} + C_{AL} + C_{HL}$

$C_t = C_L(1+ K_1 * p_P + K'_O * pO + K_{E2} * p_P/(K'_O * p_H^3) + K_{E1} * pP/(K_{OA} * pA * pH^3))$

$r = k_3(C_{OL} - p_O * C_L/K_3)$

$= k_3 Ct * (K_4 - 1/K_3) * pO/(1+ K_1 * p_P + K'_O * pO + K_{E2} * p_P/(K'_O * p_H^3) +$
$K_{E1} * pP/(K_{OA} * pA * pH^3))$

$\mathbf{r = K_{33} * pO/(1+ K_p * p_P + K'_O * pO + K_{E2} * K'_O * p_O/(p_H^3) + K_{E1} * K_{OA} * pP/(pA * pH^3))}$

where $K_{33} = k_3 Ct * (K_4 - 1/K_3),\ K'_O = 1/K_4,\ K_{OA} = 1/K_5$

APPENDIX-3

Derivation of Rate Equations for Rideal – Eley Model based on Single Site Mechanism

$$\mathbf{P \leftrightarrow O + H_2}$$

$P + L \leftrightarrow PL \qquad K_1 = C_{PL}/(p_P * C_L)$

$PL \leftrightarrow OL + H_2 \qquad K_2 = C_{OL}*p_H/C_{PL}$

$OL \leftrightarrow O + L \qquad K_3 = p_O*C_L/C_{OL}$

$K_E = K_1*K_2*K_3 = p_O*p_H/p_P$

A. Adsorption is rate controlling

$K_1 \neq C_{PL}/(p_p * C_L)$

$C_{PL} = p_O*p_H*CL/(K_2*K_3) = K_1*p_O*p_H*C_L/K_{E1}$

$C_{OL} = p_O*C_L/K_3;$

$C_t = C_L + C_{PL} + C_{OL} + C_A$

$C_t = C_L(1 + K_1*p_O*p_H/K_{E1} + p_O/K_3 + pA/K_6)$

$r = k_1(p_P *C_L - C_{PL}/K_1)$

$\quad = k_1*C_L(p_P - p_O*p_H/K_{E1})$

$$\mathbf{r = k_1*C_t (p_P - p_O*p_H/K_{E1})/(1 + K_1*p_O*p_H/K_{E1} + p_O/K_3 + pA/K_6)}$$

where $K_{11} = k_1*C_t$

B. Surface reaction is rate controlling

$K_2 \neq C_{OL}*p_H/(C_{PL})$

$C_{PL} = K_1*p_P*C_L; \; C_{OL} = p_O*C_L/K_3;$

$C_t = C_L + C_{PL} + C_{OL} + C_{AL}$

$C_t = C_L(1 + K_1*p_P + p_O/K_3 + pA/K_6)$

$r = k_2(C_{PL} - C_{OL}*p_H/K_2)$

$\quad = k_2*K_1*C_L(K_1*p_P - p_O*p_H /K_{E1})$

$\quad = k_2*C_t*K_1(p_P - p_O*p_H/K_{E1})/(1 + K_1*p_P + p_O/K_3 + pA/K_6)$

r = K_{22} (p_P – p_O*p_H/K_{E1})/(1+ K_p*p_P + p_O*K_O + pA*K_A)

Where K_{22} = k_2*C_t*K_1

C Desorption of product O is rate controlling :

$K_3 \neq p_O*C_L/C_{OL}$

$C_{PL} = K_1*p_P*C_L$;

$C_{OL} = K_2*C_{PL} /p_H = K_2*K_1*p_P*C_L/p_H$

$C_t = C_L + C_{PL} + C_{OL} + C_{AL}$

$C_t = C_L(1+ K_1*p_P + K_{E1} *p_P/ (K_3*p_H)+ K_5* K_{E1}*p_P/(K_3*p_H^4)$

r = $k_{-3}(C_{OL} – p_O*C_L/K_3)$

= $k_{-3}(K_{E1}*p_P*C_L/(p_H) - p_O*C_L/K_O)$

r = K_{33}*(KE1*p_P/p_H – p_O)/(1+ K_p*p_P + K_{E1}* K_O* p_P/ p_H+ K_O* K_{E1}*p_P/(K_{OA}*p_H^4)

where K_{33}= k_{-3} *C_t

APPENDIX-4

Material Balance for a typical run:

Basis: 1 hr

Temperature = 475 °C

Pressure = 21 atm

LHSV = 25 hr^{-1}

Cat wt, gm = 0 .4

Cat density gm/ml = 0.4

Feed inlet:

P = 99.2237%

A = 0.77%

LE = 0.0075%

Feed rate g/h = 18.1587 g/h

Product out let Total (liquid) = 17.5 g/h

Material balance Yield for liquid product = 96.37%

Assumptions:

The material balance was calculated by following assumptions.

- Paraffin is converted into normal olefin and then olefin converted in to aromatics.
- We consider only olefin cracking no isomerisation present and the product is Lighters.
- Gaseous and liquid product mass are based on the difference of the inlet and outlet of material.

	Paraffin	**Olefin**	**Arom.**	**LE**	**H_2**	**total**
Mol.wt	142.28	140.28	134.28	35.27	2.016	-
Wt%	86.961	6.6531	5.359	1.0275	-	100
Wt g/h	15.22	1.164	0.968	0.1798	0.659	18.1908
Gmol/h	0.107	0.0083	0.007	0.00188	0.279	0.3267
Mol%	23.55	1.8272	1.5381	1.1228	71.956	99.996
Conv(%)	12.359	-	-	-	-	-
Selectivity	-	54.253	37.421	8.318		
Yieldwt/wtf%	-	6.705	5.401	1.036		

APPENDIX-5

Some of the important definitions used in the present work and literature has given bellow

1) **Refractive Index (n):** It is a ratio of velocity of light in a particular substance to the velocity of light in vacuum. (It is unit less)

2) **Dipole Moments (D):** The permanent dipole moment of an isolated molecule depends on the magnitude of the change and on the distance separating the positive and negative charges. It is defined as $\mu = \Sigma\ q_i r_i$, where summation extends over all charges (electron and nuclei) in the molecule.

Unit = debye (cgs)

1D = 3.33564 x 10^{-30} (c)(m)(coulomb.meter)

3) **Dielectric Constant (ε):** According to coulomb's law for two oppositely charge plates

$$F = \frac{1}{4\pi\,\varepsilon_o}\frac{q_1 q_2}{\varepsilon\, r^2}$$

Where F = Force (N)

ε = Dielectric constant of the medium between plates

ε_o = Permittivity of free space

q_1 q_2 = Charge (Colulombs)

r = meter

If another substance such as solvent is in the space separating those charges (or ions in a solution), their attraction for each other is less. The dielectric constant is a measure of the relative effect a solvent has on the force with which tow oppositely charged plates attract each other. It is unit less number.

4) **Viscosity (η):** It is define as the force per unit area necessary to maintain a unit velocity gradient at right angles to the direction of flow between two parallel planes a unit distance apart.

SI unit = (Pascal)(Second) or N.S/m^2

CGS unit = CP, 1CP = 1 (m.N.s)/m^2

Kinematic Viscosity = η/ρ m^2/s (in SI)

Stroke (cm^2/s) (CGS)

Fluidity is reciprocal of dynamic viscosity (η)

5) **Surface tension (r)**: It is the force per unit length on the surface that opposes the expansion of the surface area.

Unit = dyn/cm

1dyn/cm = 1 m.N/m

6) **Reaction co-ordinates**: Reaction co-ordinates characterizes the extent or degree to with a reaction has taken place

7) **Reduced Temperature and Pressure**: Ratio of existing pressure to the critical pressure is called reduced pressure (P_r) and ratio of existing temperature to critical temperature is called reduced temperature (T_r)

8) **LHSV**: It is known as Liquid hourly space velocity, it means amount (m^3) of liquid feed per hour per amount (m^3) catalyst.