Design and Fabrication of Mini Synthetic Rubber Plant

By

Muhammad Usama	**CIIT/FA19-BME-020/WAH**
Huraira Nadeem	**CIIT/FA19-BME-034/WAH**
Ashan Akhtar	**CIIT/FA19-BME-052/WAH**
Muhamamd Irfan Riaz	**CIIT/FA19-BME-073/WAH**

Final Year Design Project Report

Bachelor of Science in Mechanical Engineering

COMSATS University Islamabad
Wah Campus - Pakistan

Spring 2023

COMSATS University Islamabad
Wah Campus
Department of Mechanical Engineering

PROJECT ID	FA2019-FYDP-		NUMBER OF MEMBERS	4

TITLE	Design and Fabrication of a Mini Synthetic Rubber Plant

SUPERVISOR NAME	Dr Muhammad Shoaib Naseem

MEMBER NAME	REG. NO.	EMAIL ADDRESS
Muhammad Usama	FA19-BME-020	usamaawan4586@gmail.com
Huraira Nadeem	FA19-BME-034	Hurairanadeema@gmail.com
Ashan Akhtar	FA19-BME-052	ashanakh012@gmail.com
Muhamamd Irfan Riaz	FA19-BME-073	muhammadirfanriaz1@gmail.com

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Muhammad Usama   CIIT/FA19-BME-020/WAH

Huraira Nadeem   CIIT/FA19-BME-034/WAH

Ashan Akhtar   CIIT/FA19-BME-052/WAH

Muhamamd Irfan Riaz   CIIT/FA19-BME-073/WAH

Date: _____

Supervisor Signature: _____

Secretary FYDP Committee Signature: _____

ABSTRACT

Our research aims to design and construct a compact synthetic rubber manufacturing facility. Synthetic rubbers, produced from 1,3-butadiene (BD) and its derivative monomers, have a wide range of applications in products like tires, rigid plastics, and various industrial processes due to the simplicity of polymerizing/copolymerizing these monomers and the resultant material's high stability. This project specifically concentrates on the gas-phase production of butadiene from either ethanol or a combination of ethanol and acetaldehyde. The synthesis process involves converting ethanol or the ethanol and acetaldehyde blend in the presence of a unique catalyst. Notably, this approach diverges from established techniques by employing a solid catalyst composed of a metal selected from silver, gold, or copper, and a metal oxide chosen from magnesium, titanium, zirconium, tantalum, or niobium oxides.

Experimental work has been carried out concerning the one-step catalytic conversion of ethanol to butadiene, which involves concurrent dehydrogenation and dehydration processes. The selected catalyst, Al_2O_3:ZnO (60:40), also known as the binary oxide catalyst or heterogeneous catalyst, has been examined for its effectiveness in both stationary and fluidized beds. The proposed approach is applied in a continuous flow fluidized bed reactor for the condensation process. The design is configured to achieve a high yield and selectivity for butadiene, along with a substantial level of feed conversion. The reaction occurs within the fluidized catalyst bed, allowing for adaptability in catalyst composition, temperature, ethanol flow rate, and variations in ethanol concentration.

Ethanol, a byproduct in the sugar industry, is abundant in Pakistan, the 9th largest global producer of sugar with 81 sugar industries as of 2020. Notably, Pakistan ranks as the 33rd largest importer of Synthetic Rubber, spending $78.3 million on imports in the same year. Thus, the overarching goal of our project is to address the growing demand for synthetic rubber in Pakistan by establishing a localized production facility.

SUSTAINABLE DEVELOPMENT GOALS:

Sustainable Development Goal 9: (Industry, Innovation, and Infrastructure):

It Centers on advancing inclusive and sustainable industrial development, cultivating innovation, and enhancing infrastructure. By aligning our project with this goal, we can explore ways to enhance the sustainability and efficiency of synthetic rubber synthesis processes, as well as contribute to the development of innovative solutions within the rubber industry.

Here are some specific aspects of SDG 9 that can be relevant to our project:

1. **Sustainable Industrialization:** Investigate and propose strategies to reduce the environmental impact associated with synthetic rubber production. This can include exploring alternative feedstock sources, optimizing energy consumption, minimizing waste generation, or implementing greener manufacturing practices.

2. **Research and Development:** By contribute to the advancement of knowledge and innovation within the rubber industry. We can explore novel formulations, manufacturing techniques, or material properties that improve the performance and sustainability of synthetic rubber. We can emphasize the importance of research and development in driving progress towards sustainable industrial practices.

3. **Infrastructure Development:** The infrastructure required for the synthesis of synthetic rubber, including facilities, transportation systems, and waste management. We can provide ways to optimize infrastructure to reduce environmental impacts, enhance resource efficiency, or support sustainable supply chain management.

4. **Inclusive Industrialization:** After analyzing the social and economic implications of synthetic rubber production, such as employment opportunities, working conditions, and community engagement.

By focusing our project on the synthesis of synthetic rubber in alignment with Sustainable Development Goal 9, we can contribute to the broader sustainability agenda, promote responsible industrial practices, and support the development of innovative solutions within the rubber industry.

ACKNOWLEDGEMENTS

First and foremost, we express our sincere thanks to Almighty Allah for granting us the courage and good health needed to successfully finalize this dissertation. Our heartfelt gratitude goes out to all those who played a vital role in the successful completion of this project, the design and fabrication of a mini synthetic rubber plant. This endeavour would not have been possible without the unwavering support, guidance, and encouragement of numerous faculty members and COMSATS.

We express our sincere thanks to our final year project supervisor **Dr. Muhammad Shoaib Naseem**. His expertise, guidance, and constant encouragement were instrumental in shaping this research. His invaluable insights and mentorship were pivotal in steering the project in the right direction. We faced failures in achieving wanted results, but thanks to his experience which guided and boosted our engineering skills.

Lastly, we are grateful to the faculty members of the Department of Mechanical Engineering, CUI Wah Campus for their invaluable feedback and suggestions during the course of this research. Their collective wisdom greatly enriched us understanding of the subject matter and refined the project's outcomes.

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Chapter 1

Introduction

Rubber is an important material and plays an important role in our daily life and used in many industries ranging from automotive and aerospace to consumer goods and healthcare. Trees are the main source of the natural rubber derived from the latex of the trees. However due to increase in the demand of rubber and limited supply originated the need of an alternative product and a product with specific performance requirements to be used in different industries. The synthesis of synthetic rubberhas revolutionized industries, providing a reliable and versatile alternative to natural rubber.

1.1 Uses:

In Pakistan synthetic rubber is widely used to make different types of products:

Rubber products are typically categorized into three primary classes: Tires and rubber products used in the automotive, aircraft, and ship construction industries, as well as agricultural machinery, railroad transport, and construction. Industrial rubber goods utilized in various sectors, including motor-vehicle manufacturing. Rubber products designed for consumer goods, such as footwear and other everyday items[1].

- Synthetic rubber is often chosen over natural rubber in certain applications, provided the price difference is not substantial.
- The transportation industry, particularly tire manufacturing, is the primary consumer of rubber.
- The construction sector utilizes rubber in various forms such as elevator belts, hoses, tubes, and seismic bearings.
- Rubber is extensively employed by consumer goods industries for manufacturing quality footwear, erasers, sports equipment, and more.

Industries in Lahore Pakistan use synthetic rubber to make:

1. Anti-Vibration-Mounting
2. Canvas Seals:
3. Concrete-pumps-piston-ram.
4. Oil Seals
5. Rubber-Diaphragm
6. sandwich-mount--Isolators-Buffers:
7. Carbon Seals
8. Rubber Gaskets
9. O Ring
10. Polyurethane-Seals
11. PTFE-Diaphragm
12. Rubber-Track-Pad
13. Star-Coupling
14. Spare-Tire-Couplings
15. Clutches
16. engine bearings
17. conveyor belts

To make all these types of products and many more we import synthetic rubber in large quantity. In the year 2020, Pakistan held the 33rd position as one of the largest global importers of Synthetic Rubber, with total imports valued at $78.3 million. During the same period, Synthetic Rubber ranked as the 117th most imported product in Pakistan. Pakistan's primary sources for Synthetic Rubber imports were South Korea ($13.8 million), China ($10.4 million), Chinese Taipei ($8.72 million), Russia ($6.85 million), and the United Arab Emirates ($5.73 million).

Notably, the most rapidly expanding markets for Synthetic Rubber imports into Pakistan between 2019 and 2020 were Indonesia ($2.46 million), China ($2.24 million), and South Korea ($2.08 million).

1.2 PRODUCTION METHOD:

Synthetic gas produced from the polymerization of 1,3-butadiene derivatives or the copolymerization of 1,3-butadiene with unsaturated monomers is derived from

petroleum and natural rubber. Our Goal is to fulfill the wide range of need and to synthesize the synthetic rubber in Pakistan. As we know that Pakistan is not fuel rich country so it is difficult to synthesize the synthetic rubber by hydrocarbons.

We have developed an alternative method to produce rubber using ethanol as Pakistan is the 9th largest producer of sugar and there are 81 sugar industries located in Pakistan. So, we can make synthetic rubber using ethanol waste product of Sugar industries[2].

1.3 INTRODUCTION TO PROCESS:

Ethanol is predominantly obtained through the sugar fermentation and is acknowledged as among the most plentiful and ecologically friendly feedstocks. This is particularly significant given the CO_2 emissions and human-induced global warming associated with the manufacturing and handling of several industrial feedstocks. Ethanol's transformation into industrial materials holds crucial importance in the field of chemistry. Among the various products derived from this conversion, 1,3-butadiene plays a pivotal role in the process of making polymers and their intermediates, such rubbers made of styrene and butadiene.

1,3-butadiene ($CH_2 = CH - CH_=CH_2$)is used as the main raw ingredient to make synthetic rubber. Various techniques are currently utilized on an industrial scale for the production of 1,3-butadiene, including the pyrolysis of hydrocarbons. In countries where ethanol is abundantly accessible in substantial volumes and at a comparatively affordable price, frequently as a byproduct of the sugar sector, using it as the principal feedstock for butadiene production can present unique benefits. 1,3-butadiene, frequently known as butadiene C_4H_6 or BD, is essential to the production of several elastomers, such as polybutadiene, acrylonitrile-butadiene-styrene, and rubber styrene-butadiene, among other important compounds. It is also an essential reagent in organic chemistry, especially in processes like the Diels-Alder reaction.

Presently, the primary source of butadiene is the C4 steam cracker byproduct within petroleum industry. Nevertheless, this method of butadiene production is

vulnerable to market fluctuations and variations in the petroleum sector, influenced by factors such as the growing use of shale gas, which could potentially result in butadiene shortages. Moreover, the limited availability of fossil fuel reserves emitting greenhouse gases presents long-term challenges to the present butadiene production approach, regarding its economic feasibility and environmental sustainability.

Consequently, there has been a resurgence of interest in the century-old method of catalytic conversion of ethanol into butadiene using heterogeneous catalysts. This process entails transforming gaseous ethanol into butadiene by employing multifunctional materials. There are two established commercial approaches to accomplish this conversion: the two-step and the one-step processes. The two-step process, widely used in the United States, comprises a sequence of reactions conducted in two distinct catalytic units[3].

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$

$$CH_3CH_2OH + CH_3CHO \rightarrow CH_2 = CH - CH_-CH_2 + 2H_2O$$
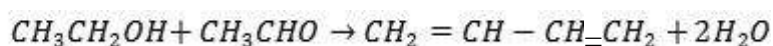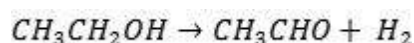
Extensive investigations conducted by American researchers (6-8) have been documented, stating that the two-stage process yields superior conversion rates and leads to a more refined end product. On the other hand, the single-step process implemented in Russia integrates dehydrogenation and dehydration in a single reactor with an appropriate catalyst possessing both dehydration and dehydrogenation properties[4].

$$2C_2H_5OH \rightarrow CH_2 = CH - CH_-CH_2 + 2H_2O + H_2$$
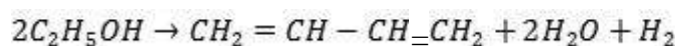
The latter method is evidently simpler to operate, although it typically results in lower purity and yield of butadiene. The single-step process has been commercially successful in East European nations for an extended period. Nevertheless, the precise operational particulars, particularly the catalyst's nature, have been tightly protected through patent mechanisms.

1,3-Butadiene (BD) holds significant importance as a raw material in various industries, particularly with the growing advancements in the automotive and defense industries. The production of butadiene holds not just economic importance but also

carries strategic relevance. Poly-butadiene rubber market segmented based on its applications and geographical regions. Regarding applications, it can be categorized into tire manufacturing, footwear, sports accessories, and various other uses. Polybutadiene rubber is extensively utilized in diverse applications such as tire manufacturing, clutches, engine bearings, conveyor belts, industrial machinery, seals for potable water systems, and the manufacturing of synthetic rubber items [5].On the basis of the one-step catalytic transformation of ethanol into butadiene in a fluidized bed reactor as described in a published research paper by "**S. K. B H A T T A C H A R Y Y A A N D B. N. A V A S T H I ".** According to his paper, the authors have identified the following catalysts as effective for the conversion of ethanol to butadiene in fixed-bed reactors.

Mono-component Catalyst Systems:

$$Al_2O_3, Fe_2O_3, ZrO_2, ThO_2$$

Binary catalysts Systems:

$$Al_2O_3:ZnO, Al_2O_3:Cr_2O_3, Al_2O_3:MgO, Al_2O_3:CaO$$
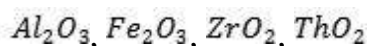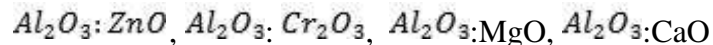
Ternary Catalysts Systems:

$$Al_2O_3:Fe_2O_3:Cr_2O_3$$
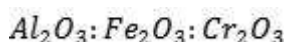
The single oxide catalysts mentioned above were evaluated for their effectiveness in converting ethanol into butadiene. In the case of alumina, the liquid product primarily consisted of water, with no traces of ethanol or aldehyde.

We conducted a thorough investigation into the influence of various operating conditions on each of the single oxide catalysts. Temperature, ethanol feed rate, ethanol feed concentration, height of the catalyst bed, deactivation and reactivation of the catalyst were all included in this list. Zirconia was shown to be the most effective catalyst out of all those that were investigated.

1.3.1 Single Oxide Catalyst:

1.3.1.1 EFFECT OF TEMPERATURE:

We conducted a study to examine the ethanol-to-butadiene conversion rates when employing alumina, ferric oxide, zirconia, and thoria as catalysts at temperature between $375^{\circ}C$ and $450^{\circ}C$. The optimum temperature in each case was $425^{\circ}C$.

1.3.1.2 EFFECT OF ETHANOL FEED RATE:

With the presence of alumina, ferric oxide, zirconia, and thoria as catalysts, we studied the effect of the ethanol feed rate on the conversion of ethanol to butadiene. For every one of these catalysts, a different feed rate was optimal.

1.3.1.3 IMPACT OF ETHANOL FEED CONCENTRATION:

In case all single oxide catalysts investigated, it was observed that the butadiene process yield decreased when the ethanol feed's water content rose. Furthermore, when zirconia and thoria were used as catalysts, the percentage of aldehydes in the product increased as ethanol was diluted. Conversely, when ferric oxide was employed as the catalyst, the proportion of aldehydes declined with the dilution of ethanol.

1.3.1.4 IMPACT OF CATALYST DEACTIVATION:

Deactivation investigations unveiled a uniform pattern across all catalysts: the butadiene process yield decreased with repeated catalyst usage. This deactivation was attributed to the accumulation of carbon, which was probably produced through the ethanol cracking process and some of the reaction byproducts. Notably, there were no notable alterations detected in the percentage of aldehyde formation.

1.3.2 Binary Oxide Catalyst:

In-depth investigations carried out by Bhattacharyya and colleagues (3-5) have resulted in the finding that only oxides that exhibit reactivity in the butadiene manufacturing process are those that have both dehydrating and dehydrogenating properties. Furthermore, through the thoughtful selection of combinations of two or more oxides with these dual properties, the activity level can be significantly

enhanced. In our study, we conducted an extensive examination of the effectiveness of binary oxide systems, initially identified as the most favorable by Bhattacharyya and Ganguly (3-5), through the utilization of a fluidized bed reactor. When using single oxide catalysts, The study's conclusions showed that the process yield of butadiene dropped as feed's water content rose. On the other hand, we also assessed the activity of several ternary and binary oxide catalyst systems, which include components with dehydrogenating and dehydrating properties and are employed in fixed bed reactors to convert ethanol to butadiene [6].

Among the binary catalysts tested, the alumina-zinc oxide combination (60:40) demonstrated the highest performance, achieving a maximum process yield of 55.8% for ethanol to butadiene conversion. Among the 40 various ternary oxide catalyst systems investigated, only the 80:5:15 alumina-chromium oxide-ferric oxide composition exhibited noteworthy activity, achieving a butadiene process yield of 35.7% under optimal conditions In general, it was observed that ternary oxide systems tended to be less active compared to their binary oxide counterparts.

1.4 Motivation:

We have chosen this project due to following reason:

1. To provide cheap synthetic rubber in Pakistan and to cut the millions dollar worth of yearly import of synthetic rubber as we know that our country is not in that to import so many things.

2. Environment sustainability: By avoiding the use of hydrocarbons and components associated with oil, our approach to synthetic rubber production significantly reduces or eliminates environmental pollution compared to conventional methods. This commitment to environmentally friendly practices allows us to contribute to a greener future for our country.

3. Improvement in quality: Our method to produce synthetic rubber is different and it will very helpful to produce rubber with improved quality and we will be able to change the different properties of the rubber using this method. So in this way we will be able to provide a better quality rubber.

4. Moreover we have a great interest to make a production company in Pakistan which will use synthetic rubber as a raw material to different useful daily life products.

1.5 Research Question:

""What are the most effective alternative methods and formulations for synthesizing synthetic rubber without the use of hydrocarbons or oil-based substances, while achieving improved mechanical properties and promoting environmental sustainability?"

Chapter 2

Literature Review

2.1 Fixed Bed Catalytic Conversion Method:

Avasthi, B. N., & Bhattacharyya, S. K. (1962) explored the single-step catalytic transformation into butadiene from ethanol (in a fixed bed). Investigated different oxide catalysts, operational parameters, and acknowledged the potential complexity and endothermic nature of the reaction flow in the fixed bed[7].

Ghaziaskar, H. S., & Xu, C. C. (2013) examined the continuous catalytic transformation into gases from ethanol using a vertically mounted fixed bed tubular reactor. The reactor, connected to various instruments, facilitated continuous ethanol feeding at temperatures ranging from 150 to 300℃. Gas analysis using a Micro GC revealed the presence of carbon dioxide, methane, hydrogen, ethane, and a little proportion of propane[8]. In the conducted trials, ethanol was pumped as the sole reactant at different temperatures and pressures. A solid catalyst was consistently used throughout the study. To ensure precision in calculating the actual flow of mass during the reaction, the feed-stock container was placed on a top-weighted balance[8].

Bojang and Wu (2020) employed a fixed bed reactor system less than basic pressure and temperature. A 0.4 g sample of the impetust was put into a clean cylinder (R 1/4 22 mm) and put it in the heater. Controlled SiO_2 was activated to exceed the bed length, facilitating the course condition. Ethanol, induced with nitrogen gas at a flow rate of 30 cm^3/min, was directed in the bed reactor(fixed). The bubbler temperature was adjusted with the changing of WHSV ($0.75h^{-1}$, $1.25\ h^{-1}$, $2.5\ h^{-1}$, and $6.0\ h^{-1}$). Prior to the chemical reaction, the impetus was operated by heating upto 400 ◦C. This process of heating, at a rate of 15°C/min, was maintained at 400°C for 1h below a 30 cm^3/min flow of nitrogen. The major results (ethylene, 1,3-butadiene, and acetaldehyde) were analyzed with an FID detector using GC-14B[9].

2.2 Fluidized Bed Catalytic Conversion Method:

Bhattacharyya, S. K., & Avasthi, B. N. (1963) explored the use of a fluidized bed catalyst in the single-step catalytic transformation into 1,3 butadiene from ethanol. The study investigated reactions execute in the fluidized catalyst bed with the the use of single, binary, and ternary catalyst systems in the presence of various conditions like temperature, catalyst composition, ethanol feed rate, catalyst deactivation, ethanol concentration variation and bed height[7].

2.3 One step Catalytic Conversion Method:

2.3.1 Ag-ZrO$_2$/SiO$_2$ Catalysts:

Dagle et al. (2020) examined $\mathrm{Ag} - ZrO_2$ catalysts with balanced metal and Lewis acid sites. Direct transformation into n-butene from ethanol (blends of 1 and 2 butene) occurred with atypical butene-rich olefins selectivity (88% at 99% transformation). The study revealed that C4 product placement, particularly n-butene and 1,3-butadiene, could be tailored by adjusting partial pressure of hydrogen input and other process parameters. Under maximum partial pressure of hydrogen, 1,3-butadiene was fully and selectively hydrogenated to produce n-butene. The conversion from acetaldehyde into ethanol dehydrogenation over metallic Ag, abide by aldol condensation into crotonaldehyde from acetaldehyde over the acid sites of ZrO_2/SiO_2, and subsequent reduction of crotonaldehyde into butadiene over Lewis acid sites via a MPV type depletion with ethanol as the source of H_2 [10]. The synthesis of a series of xAg-4 ZrO_2 / SiO_2 impetus involved incipient moisture impregnation, drying, and calcination steps[10].
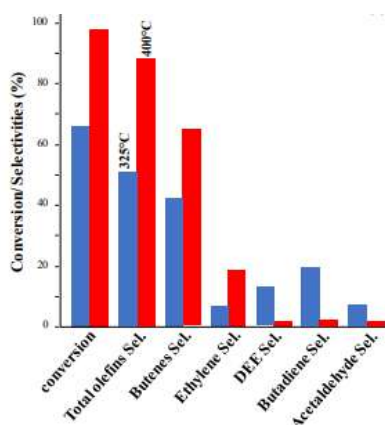
Figure 1:Contrast of the selectivities and conversion[10]

2.3.2 Bifunctional Zn-Y/Beta zeolite:

Yan, Wu, Dai, Lang, Guan, Hunger, and Li (2018) explored the tranformation mechanism into butadiene from ethanol using a bifunctional catalyst Zn Y/Beta. The investigation aimed to discern the roles of Zn and Y practical sites in each step of reaction. An extremely vigorous and selective Zr/MCF impetus was applied for 1,3-butadiene production with the use of ethanol in a dual based fixed bed system of reactor. In single fixed bed reactor systems employing Zr on a silica support, additional metals (e.g., Ag, Zn, Cu) were needed as dopants to catalyze and form the BD with the use of EtOH reaction. These metals of dopant facilitated the dehydrogenation of ethanol to form the acetaldehyde, while Zr catalyzed subsequent aldol condensation and MPV for BD production. The study by Sushkevich et al. revealed that increasing Ag content in a Zr/silica impetus enhanced the conversion of EtOH, but excessive Ag loading increased byproduct formation, reducing BD selectivity[11].

Controlling intricate reactions in a single bed reactor with the bimetallic catalyst by adjusting metal quantity to achieve a first rate AcH quantity for high BD production is challenging. To address this, Klein et al. proposed a two-stage process for prodution of butadiene wit the use of ethanol. The study concluded a Cu/SiO_2 and MgO/K/zeolite-β system[11].
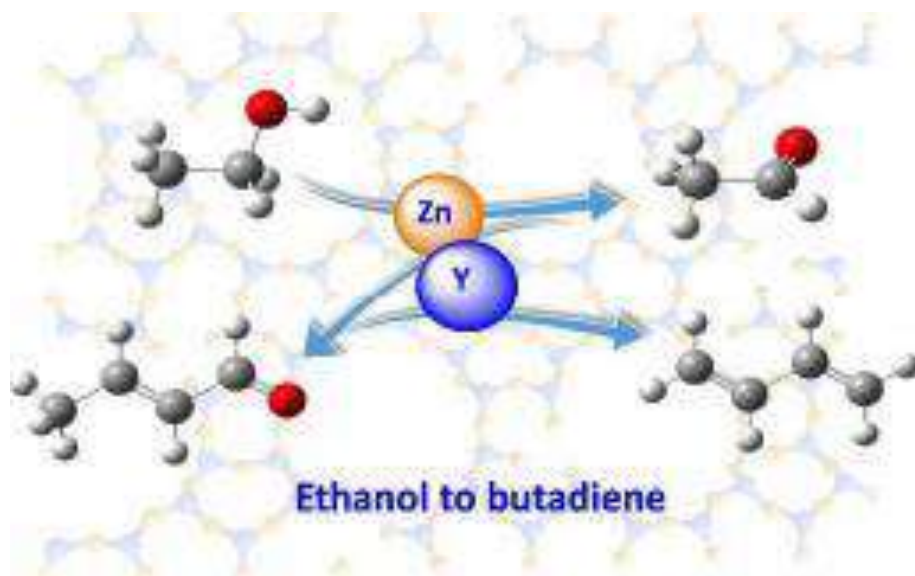
Figure 2:Conversion of ethanol to butadiene[11]

2.4 Ternary Ag/MgO-SiO₂ Catalysts:

Janssens, Makshina, Vanelderen, Clippel, Houthoofd, Kerkhofs, Martens, Jacob, and Sels investigated the use of an MgO-SiO₂ system tampered with silver as an active impetus from ethanol to butadiene production. The saturation method, introducing silver, likewise framed a shapeless magnesium silicate layer on the silica stage. Optimal impetus outcomes were obtained from corporate silica (SiO_2) with stable silica structure and pore architecture, and an optimal silver loading of 1–2 wt%. Larger temperatures positively affected ternary catalyst activity. The largest butadiene production reached 0.29g Butadiene gCatalyst1h1 with 1.0Ag/MgO-SiO₂ at 753 K and a WHSV of 1.2 h1, corresponding to a Butadiene production and selectivity of 42% and half, respectively[12].
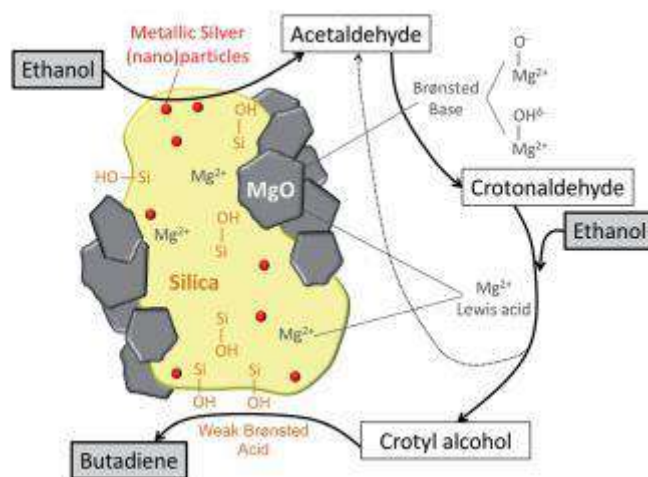
Figure 3: Demonstration of the suggested model to interpret the catalytic activity[12]

The comprehension of catalytic results was facilitated through the integration of characterization findings related to studied catalysts. In a first rate catalyst structure, a notable presence of attainable silver nanoparticles and abundant basic sites (MgO pairs and basic OH groups) was discerned. Both these species played essential roles in efficiently catalyzing the dehydrogenation of ethanol and the condensation of aldol, pivotal steps in butadiene production. These steps emerged as the rate-limiting factors in the butadiene formation process across different magnesia-silica catalysts. Specifically, the ethanol dehydrogenation was recognized as the rate-limiting step in silver-free catalysts, whereas in highly dynamic silver-containing impetuses,

condensation of aldol assumed the role of the rate-limiting step.The consecutive aqueous saturation of silver proved to be a remarkably effective procedure. This method not only introduced dehydrogenation action as silver species but also elevated Lewis acidity while preserving sufficient basicity. This dual functionality enabled the catalysis of the gas-phase transformation into butadiene from the ethanol. The amalgamation of these novel insights into the impetus production of silver-advanced MgO-silica impetuses was blended into a complete model.This model aimed to elucidate the distinct active sites involved in various reaction steps of butadiene formation and their respective locations on the surface of the dynamic impetuses.[12].

2.5 Magnesia–silica acidic–basic bi-functional catalysts:

In a study conducted by Gao, Liu, Zhang, and Tong, the mechanism of production of 1,3-butadienefrom ethanol was investigated using magnesia-silica acidic-fundamental bifunctional impetuses. The catalyst was formed through a wet working cycle, and exploratory response was examined utilizing Drive Reaction and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The experimental setup included essential components, for example, a quartz tube, heater, six-way valve, mass stream meter, warm conductivity finder, test circle, auto switch, and a 10-gas indicator. The catalytic transformation into butadiene from the ethanol took place within a quartz tube. Before the reaction initiation, the catalyst underwent a 2-hour treatment with nitrogen gas. Subsequently, ethanol with the use of helium was impulsively presented into the reactor, and the resultant products were analyzed through mass spectrometry (MS). The detailed examination of the mechanism involved sequential steps. Initially, ethanol was dehydrogenated, leading to the formation of acetaldehyde. Subsequently, the condensation of acetaldehyde changed into the production of acetaldol, followed by the dehydration of acetaldol to generate crotonaldehyde. Finally, ethanol underwent a second reaction involving a hydrogen exchange with crotonaldehyde, ultimately resulting in the formation of 1,3-butadiene[2].

Sun and Wang investigated the development of mixed metal oxides, exemplified by $Zn-Zr_{10}O_2$, featuring balanced acid−base pairs for the direct conversion into isobutene from ethanol, concurrently producing hydrogen as a

valuable byproduct. Co-taking care of fluid ethanol with hydrogen on metal oxides like Sc-altered and Y/has been accounted for to yield propylene over zeolites specifically. Acid−base impetuses have been read up for the change of 1-butanol and 1,3-butadiene at different response temperatures (200−400 °C). The ethanol to 1,3-butadiene response is accomodated at moderately high temperatures (300−400 °C), while the Guerbet response overwhelms creation of 1-butanol from ethanol at lower temperatures (200−300 °C). Acid−base and redox properties are recognized as restricting variables overseeing the two responses, with fundamental locales accepted to catalyze dehydrogenation and buildup responses, shaping critical intermediates like acetaldehyde and crotonaldehyde. Notwithstanding, waiting inquiries persevere in regards to key intermediates, response pathways, energy engaged with creation of 1-butanol/butadiene/isobutene/propylene from ethanol change on acid−base impetuses, and their relationship with the idea of acid−base dynamic sites[13].

2.6 Two-Step Catalytic Conversion Method:

Dimian, Bezedea, and Bildea delved into a two-stage method utilizing a particular CuO/Cr2O3 impetus for ethanol dehydrogenation and a high return Ta2O5 impetus for butadiene combination. In the first stage, ethanol dehydrogenation using the CuO/Cr_2O_3 catalyst produced acetaldehyde with 100% selectivity in a multi-tubular reactor operating at 280 °C and 3 bar. A Dowtherm vapor system supplied the heat required for the endothermic reaction, achieving a catalyst productivity of 0.258 kg acetaldehyde per kg catalyst/hr. A byproduct with 99.8% by weight purity was obtained, and hydrogen contributed approximately 6% to RM costs despite a mass yield of only 2%. The acetaldehyde was separated through absorption in an ethanol aqueous solution after a series of flashes, resulting in a 2:1 mass ratio ethanol/acetaldehyde mixture ready in stage 1 for stage 2. The development of an intensity recuperation plot solely around the synthetic reactor prompted a general energy investment funds of 38.5%, with hot utility reserve funds of 42.5%, fundamentally marvellous the most not entirely set in stone by squeeze examination by 87.7%[14].
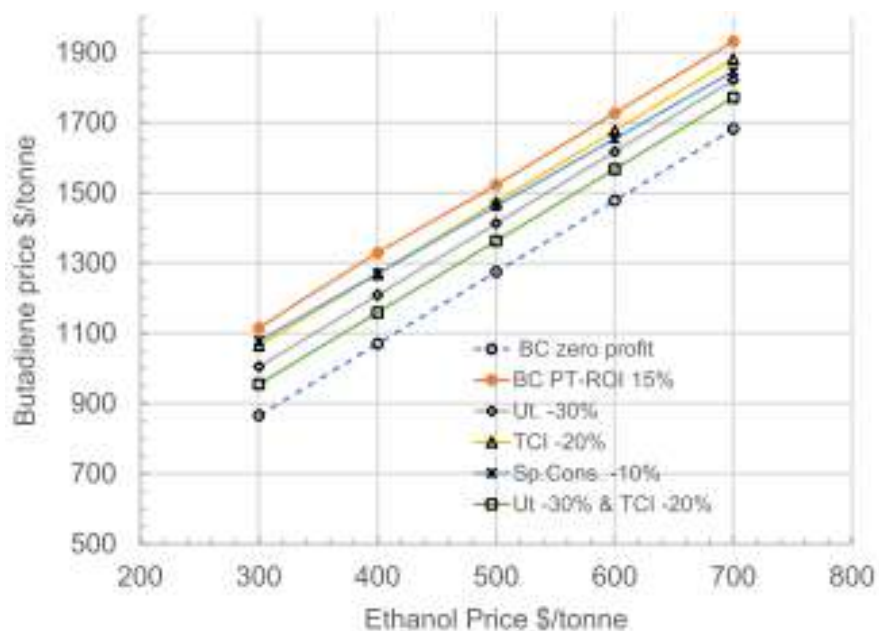
Figure 4:Assessment of the profitability by butadiene manufacture[14]

The effective Ta_2O_5 catalyst played a pivotal role in the synthesis of butadiene from ethanol and acetaldehyde. Under reaction conditions of 330 °C, 3 bar pressure, and a mass ratio of 3:1 between ethanol and acetaldehyde, a comprehensive kinetic model comprising 27 parallel consecutive reactions and 24 species was employed in designing the catalytic reactor. This model provided a realistic depiction of the outlet reaction mixture. Simulation results indicated that 60% of butadiene originated from aldol condensation via CRA, while 40% resulted from MVK. The aldol condensation method produced 1-butene, which could be easily extracted through distillation, while the MVK method yielded 2-cis-butene, necessitating extractive distillation. The perplexing response network created soaked and unsaturated hydrocarbons, oxygenated species (alcohols, aldehydes, ketones, ethers, and esters), and a significant amount of water as byproducts and impurities. Azeotropes and a wide range of volatilities were observed in these components.In rundown, the material equilibrium with shut reuses uncovered mass yields of 50.7% butadiene, 38.5% water, 4.7% C2/C3 olefins, 4.2% oxygenated species, and 1.2% waste in kilograms of item per kilogram of ethanol. The impetus' efficiency was determined at 0.253 kg butadiene/kg impetus.[14].

2.7 Reaction Details of Ethanol to Butadiene Conversion:

2.7.1 Kagan Mechanism:

Over the course of several decades, multiple research teams engaged in the exploration of the kinetics of the process have formulated the widely accepted pathway for butadiene synthesis from ethanol. The current iteration of this mechanism is specifically denoted as such in the new study to differentiate it from alternative mechanisms, initially presented by Kagan et al. and subsequently modified by Niiyama et al., Natta et al., and Bhattacharyya et al. The comprehensive representation of the entire reaction pathway is illustrated in Figure 5.

The sequence of reactions is as follows:

1. Non-oxidative dehydrogenation partially converts ethanol into acetaldehyde.

2. The aldol condensation of two acetaldehyde molecules leads to the formation of 3-hydroxybutanal (acetaldol).

3. Acetaldol undergoes dehydration to produce acetaldehyde.

4. Crotonaldehyde undergoes an MPVO reduction with ethanol, resulting in the production of crotyl alcohol and acetaldehyde.

5. Subsequently, crotyl alcohol undergoes dehydration to produce butadiene.

The identification of the rate-limiting reaction might vary based on chemical characteristics. For basic catalysts with low redox characteristics, dehydrogenation of ethanol is commonly recognized as the limiting step. Conversely, in the case of Lewis acids, it is believed that the MPVO reaction serves as the limiting step[15].
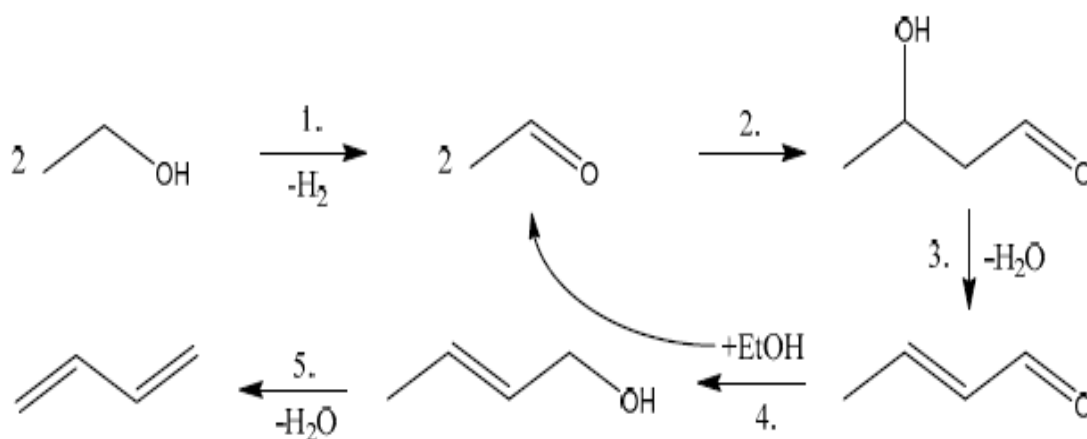
Figure 5: Ethanol to Butadiene Reaction Proposed by Kagan[15]

2.7.2 Generalities Mechanism:

Numerous theories have been put forth and extensively discussed to shed light on the conversion of gaseous ethanol (or an ethanol/acetaldehyde mixture) into butadiene. The long-standing debate found resolution through the widespread acceptanceof a cycle fixated on the condensation of acetaldehyde as the wellspring of C4 species. However, Cavani et al. have recently introduced an innovative and internally consistent mechanism, incorporating an intermediary carbanion species in the synthesis of C4 molecules. This proposition is grounded in their findings with simply basic MgO catalysts. Both mechanisms will be briefly explored later on. Despite the ongoing controversy surrounding these methods, it is commonly acknowledged that both ethanol and acetaldehyde play roles in various steps of the reaction.

In the two-step procedure, the addition of acetaldehyde often leads to an increase in butadiene production. For the Lebedev process, the reaction can be succinctly described as a dehydrogenation, condensation, and dehydration sequence (refer to Figure 6). Additionally, Sels et al. and Weckhuysen et al. have extensively delved into thermodynamic factors pertaining to the conversion of ethanol to butadiene[16].
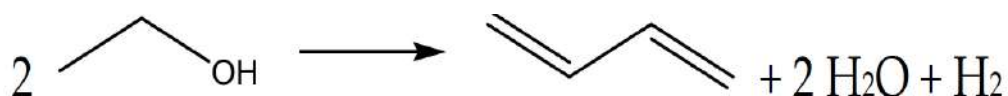
Figure 6: Ethanol to Butadiene Stoichiometric Reaction[16]

2.7.3 The Cavani Mechanism:

The process is also known as the "Guerbet reaction," and the previously mentioned ETB mechanism encompasses the conversion of ethanol to 1-butanol. According to the Kagan theory, C4 carbonaceous intermediates are formed through the aldol condensation of acetaldehyde, resulting in the production of 1-butanol in the absence of dehydration active sites. However, aldol condensation's significance was recently challenged by Meunier et al. In light of this perspective, Cavani et al. conducted investigations on both reactions using purely basic MgO catalysts with

short contact times. Their findings led to the proposal of new reaction pathways, substantiated by calculations utilizing density functional theory (DFT), diffuse-reflectance infrared Fourier transform spectroscopy analysis (DRIFTS), and mass spectroscopy (MS).

In simpler terms, the study revealed that the production of crotonaldehyde followed, in kinetic order, the production of butanol and crotyl alcohol (the precursor to butadiene). Ethylene could also be synthesized in the absence of acid sites, indicating that ethanol dehydration was not the sole process leading to the production of this light olefin. Moreover, when acetaldol and ethanol were converted, butadiene was not produced; instead, acetaldehyde and crotonaldehyde were formed. To reconcile this disparity with the Kagan mechanism, a novel reaction model was developed (refer to Figure 7)[17].

1) This model, which is based on measurements made over MgO, predicts that adsorbed ethanol might split into acetaldehyde and hydrogen.

2) Ethoxide species adsorbed on unambiguous MgO deformities may likewise encounter proton deliberation to frame a carbanionic animal groups balanced out by surface Mg cations.

3))This carbanion fills in as the essential transitional for the union of different items during an ETB response.

4) When attacked by the carbanion, an adjacent adsorbed acetaldehyde molecule transforms into crotyl alcohol.

5) Subsequently, crotyl alcohol undergoes dehydration to produce butadiene.

6) If reacted by the carbanion, an adjacent adsorbed ethanol molecule instead forms 1-butanol.

7) Then 1-butanol can be dehydrated into 1-butene.
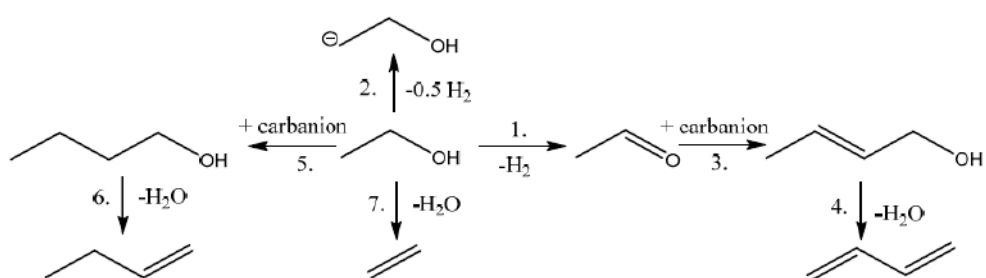
Figure 7: Reaction Pathway for Ethanol to Butadiene conversion proposed by Cavani[17]

2.8 Catalysts Used in Ethanol to Butadiene Conversion:

2.8.1 Magnesium-Silica System:

Szukiewicz was the pioneer in 1944 to identify magnesium combined with silica as an effective catalyst for the direct conversion of ethanol to butadiene. The catalyst for the ETB reaction has undergone extensive examination due to numerous studies. The ETB reaction, presumed to involve dehydrogenation, dehydration, and condensation phases, necessitates multifunctional catalysts, as mentioned earlier. The double usefulness of magnesium-silica impetuses is accepted to emerge from the mix of fundamental and acidic attributes. While the basicity of magnesium oxide is deep rooted, the acridity is remembered to result from associations between magnesium oxide and silica. It has been reliably exhibited that optimizing butadiene synthesis requires careful balancing of chemical characteristics, often achieved by changing the molar proportion of Mg to Si in a given material. Albeit the idea of dynamic destinations is discussed, K Visle et al. have shown that contact between magnesia and silica is essential for catalytic activity[18].

The MgO-SiO2 system does exhibit a vulnerability to deactivation due to coke production, which is likely a consequence of the high basicity of MgO. Various active sites and their characteristics have been proposed, contingent upon the mechanistic subscription. In the approach presented by Cavani et al., the MgO surface accommodates a stable carbanion formed through ethanol proton abstraction (see Figure 3, step 2). The subsequent condensation of acetaldehyde with this carbanion yields crotyl alcohol, which, upon interaction with acid sites (see Figure 1, steps 3 and 4), dehydrates into butadiene. Dehydrogenation of ethanol is believed to take place over the bare magnesium-silica interface. Baba et al. contributed to our understanding of the magnesia-silica system by exploring the potential of talc containing zinc as a catalyst. Their investigation involved the assessment of two MgO catalysts, one produced through calcination and the other through hydrothermal treatment, with the aim of elucidating the role of magnesia. Intriguingly, hydrothermally treated magnesia exhibited a notable ethanol conversion rate of 36.6% and a selectivity of 47.1% toward butadiene at a Weight Hourly Space Velocity (WHSV) of 0.19 h^{-1} at 673 K. In contrast, calcined MgO did not result in butadiene formation, leading multiple

researchers to conclude that the acidity contributed by SiO_2 was indeed crucial. Examination of X-ray Photoelectron Spectroscopy (XPS) spectra of O1s for the two examples uncovered a connection between's the combination of butadiene and the presence of a particular oxygen animal categories in the MgO stage. Baba et al. state that this trademark assumes an essential part in the ETB response by going about as a functioning site for the MPVO decrease of crotonaldehyde to crotyl liquor and the age of acetaldehyde through heterolytic separation including ethanol.

$$CH_3CH_2OH + O\text{-}Mg\text{-}O\text{-}Mg \rightarrow O\text{-}Mg\text{-}H + H\text{-}O\text{-}Mg + CH_3CHO$$
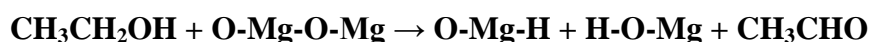
2.8.2 Zirconium Catalytic Systems:

Toussaint et al. conducted a comprehensive study focusing on Lewis acid catalysts applied in the Ostromislensky process. These catalysts comprised tantalum, zirconium, and niobium oxide supported on silica. Jones et al. reached the conclusion that catalysts composed of zinc and zirconium oxide supported on silica displayed notable activity in the Lebedev process. This enhanced activity was attributed to a combination of Lewis acidity and the catalytic ability of ZnO in promoting ethanol dehydrogenation, as determined through a screening investigation. Ivanova et al. introduced a distinctive methodology for the fabrication of catalysts tailored for the Lebedev process, resulting in highly efficient materials for the one-step MPVO (Meerwein-Ponndorf-Verley-Oppenauer) reduction. Their approach involved combining metal oxides known for their action in aldol buildup and MPVO decrease (like ZrO2, MgO, Al2O3, Nb2O5, TiO2) with metal advertisers fit for changing over ethanol into acetaldehyde (counting Ag, Cu, Ni). Resulting research distinguished the silver/zirconium framework as the best impetus for butadiene creation. Further examinations included the MPVO decrease of crotonaldehyde utilizing an impetus containing zirconium, aldol buildup of acetaldehyde over silica-upheld zirconium oxide, and the dehydrogenation of ethanol over silica-upheld silver. These cycles are accepted to be vital to the Kagan response pathway[19].

2.8.3 Catalysts for the One-Step Process:

To bolster their catalytic system featuring Ag and Zr(IV), Ivanova et al.investigated the usage of requested microporous zeolite beta polymorph A (BEA) and mesoporous MCM-41 as options in contrast to silica [21]. The BEA-supported catalyst exhibited significantly higher activity than its silica-supported counterpart and slightly surpassed the MCM-41 catalyst at similar silver and zirconium concentrations. The higher movement saw with atomic sifters was credited to the expanded convergence of separated Zr(IV) destinations accomplished through direct consolidation during the combination method, as proven by XPS and 29Si MAS NMR, as opposed to silica impregnation where zirconium is thought to be as ZrO2. The quantity of Lewis corrosive destinations, distinguished by FTIR utilizing deuterated acetonitrile (CDCN3) and related with separated Zr(IV) locales, connected with the butadiene yield. The optimal particle size for ethanol dehydrogenation on silica-supported catalysts is 2 to 5 nm, a characteristic achieved through dry impregnation of silver in all samples [19]. Despite similar activity, Ag/Zr/MCM-41 generated more dehydration products than Ag/Zr/BEA, owing to the larger number of surface silanol groups in the former, acting as Bronsted acid sites. Subsequent investigations delved extensively into the nature of Zr/BEA active sites[20][21].
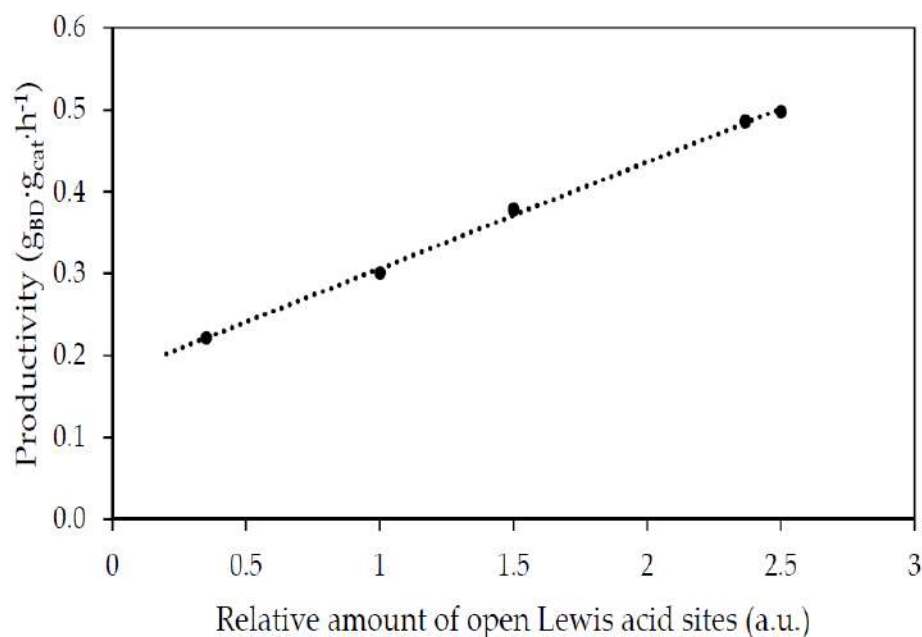
Figure 8: Relation between the relative amount of open Lewis acid Zr sites with the rate of Butadiene [20]

2.8.4 Catalysts for the Two-Step Process:

Han et al. investigated ZrO_2/SiO_2 catalysts for the Ostromislensky process, employing the sol-gel technique and nitric acid to induce hydrolysis and jellification of tetraethyl orthosilicate (TEOS). Catalysts with ZrO_2 contents up to 8.4 wt% were produced, yielding mesoporous materials with a high surface area, diminishing as ZrO_2 levels increased. Despite the absence of a discernible ZrO2 phase by XRD, it was inferred that ZrO_2 was widely distributed, corroborated by TEM revealing a leaf-like catalyst shape. Pyridine-FTIR spectroscopy identified Lewis acid sites, with no observable growth in Bronsted acid sites as Zirconium concentration increased. Catalytic activity was assessed under controlled factors, including temperature, WHSV, and the ethanol-to-acetaldehyde ratio. Enhanced ethanol conversion from 593 to 683 K correlated with increased butenes selectivity at the expense of butadiene production. WHSV reduced ethanol conversion at shorter contact times but had no impact on butadiene selectivity. Notably, at high Zirconium loadings, there was an unexpectedly high selectivity towards butenes, reaching up to 25%. Butene formation was influenced significantly by the ethanol/acetaldehyde ratio, surpassing butadiene selectivity at high acetaldehyde levels for the 2% Zr/SiO_2 catalyst at 593 K and WHSV = 1.2 h^{-1}.
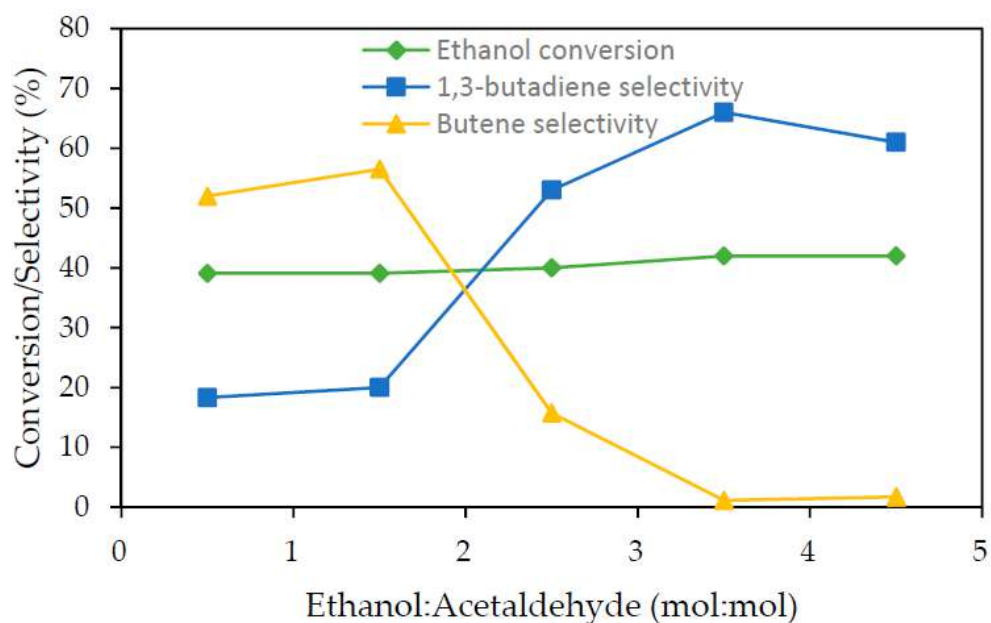
Figure 9: Effect of ethanol/acetaldehyde ratio in the feed over 2% Zr/SiO2 (T = 593 K, WHSV = 1.2 h^{-1})

The data suggested that butenes were not derived from the hydrogenation of butadiene, hinting at a potential origin through the dehydration of 1-butanol. The sol-gel-manufactured ZrO_2 demonstrated some activity in the Guerbet reaction, or an alternative route may be involved. However, questions remain regarding the origin of butenes species, particularly considering the unlikely preference of an acidic material to hydrogenate crotyl alcohol without a dopant to inhibit acidity. Alkali-doped ZrO_2/SiO_2 has been recognized for its activity in the Guerbet reaction as well.[20]

2.8.5 ZrO_2-MgO-SiO_2 Catalyst:

The scholarly work titled "Synthesis of 1,3-Butadiene from Ethanol/Acetaldehyde over ZrO2-MgO-SiO2 Catalyst: The Thermodynamics and Reaction Kinetics Analysis," authored by Cheng Liu, Yan Li, Linlin Wu, and Zhongfeng Geng, delves into the intricate domain of catalytic chemistry and kinetics. It focuses on the conversion of ethanol into 1,3-butadiene utilizing a ZrO2-MgO-SiO2 catalyst, shedding light on sustainable chemical synthesis and unraveling the underlying mechanisms governing this transformation[19]. Historically, 1,3-butadiene, a versatile compound crucial in polymer materials and organic synthesis, has been derived from petroleum-based processes, raising environmental concerns. The depletion of petroleum sources has spurred exploration into alternative routes, with the conversion of ethanol into 1,3-polybutadiene emerging as an attractive and sustainable prospect[19].

The catalytic synthesis into 1,3-butadiene with the use of ethanol can occur through a single step or a two-step process. The one-step process includes the direct synthesis of 1,3-butadiene wth the use of ethanol, while the two-step process, proposed by Ostromislensky, introduces acetaldehyde to enhance 1,3-butadiene yield. This study addresses the kinetics of the conversion of ethanol into 1,3-butadiene, providing a comprehensive investigation using a ZrO2-MgO-SiO2 catalyst developed by the authors. The experimental investigation employs an isothermal integral reactor for precise control of reaction conditions, spanning temperatures from 573 to 613 K and various space velocities. The study extends beyond the main reaction to explore the kinetics of byproduct reactions, providing a holistic view of the complex network

of reactions involved. Proposed mechanisms for rate-deciding advances incorporate the Langmuir-Hinshelwood component and the Eley-Rideal instrument.[19][22].

Key findings include the activation energy for the aldol condensation step (54.6 kJ/mol), offering crucial insights into the energy barrier for product formation. Kinetic models derived from these mechanisms are validated by comparing theoretical and experimental values, showcasing their accuracy and applicability. The implications extend to industrial settings, offering valuable insights for reactor design in large-scale synthesis. The choice of the ZrO2-MgO-SiO2 catalyst emphasizes its potential for sustainable chemical production. As industries globally strive for greener processes, this study contributes valuable knowledge for the development of efficient and environmentally friendly methods for 1,3-butadiene synthesis[19].

In summary, this journal article by Cheng Liu, Yan Li, Linlin Wu, and Zhongfeng Geng advances our understanding of catalysis, kinetics, and sustainable chemical synthesis. By investigating the conversion of ethanol into 1,3-butadiene, it not only uncovers intricate mechanisms but also provides practical insights for a greener chemical industry. This research contributes both academically and practically to the field of catalytic kinetics and sustainable chemistry.[19].

2.8.6 Catalytic Potential of Sepiolite:

To advance the production of 1,3-butanediol (1,3-BD), Kitayama and collaborators conducted a catalytic exploration involving sepiolite in 1981 [2]. Sepiolite, a mineral represented by the chemical formula $\{(H_2O)_4(OH)_4Mg_8Si_{12}O_{30}.8H_2O\}$, was selected for its ability to exchange Mg (II) centers with transition metals. In their study, the Mn(II)-exchanged sepiolite exhibited superior results at 300°C, producing a selectivity of 33.4% for 1,3-BD and 41.4% for ethene, a marked improvement compared to the 2.4% selectivity of pure sepiolite. However, the high ethene content posed a challenge.In a study by Fripiat, vanadyl or silver cations were considered as potential replacements for sepiolite. When subjected to pure ethanol, vanadyl exhibited modest selectivity for 1,3-BD, whereas in the presence of abundant acetaldehyde, it demonstrated an impressive 80% selectivity. The Prins reaction was proposed as one of the potential mechanisms.This research highlights sepiolite's catalytic potential, especially when modified with Mn(II), for the

selective production of 1,3-BD. Additionally, the exploration of alternative cations, such as vanadyl or silver, underscores the ongoing efforts to optimize catalytic systems for enhanced selectivity.

The Prins mechanism was supported by the linearly rising ethene and 1,3-BD selectivities of silver-aluminated sepiolite with conversion. However, the role of the Prins response has not been well examined. Due to excessive ethene produced by zeolite acidity, zeolite usage was restricted. Materials made of magnesium and silica were efficient 1,3-BD catalysts [4]. The basic and acidic silica sites that magnesium added improved the corresponding stages in the process. MgO-to-SiO$_2$ ratio and preparation technique were important. The best catalyst was produced by wet kneading Mg(OH)$_2$ with SiO$_2$, surpassing MgCl$_2$-based catalysts, according to Ohnishi's studies. By lowering acidity, adding 0.1 wt% Na$_2$O or K$_2$O boosted 1,3-BD selectivity. Similar catalysts were investigated by Kvisle, who discovered that increasing ethanol flow reduced conversion and selectivity, which was reversed by acetaldehyde or oxygen. Wet-kneaded catalysts outperformed mechanical mixes and it appeared that the pre-MPV step determined the rate. A 10 wt% NiO content was added to the catalysts throughout development, and it was discovered that an ideal Si/Mg ratio of 1.5 resulted in a 31% yield of 1,3-butanediol (1,3-BD) and a meager 0.5% selectivity for ethene. This ratio was believed to offer the ideal acid-to-base site balance, improving 1,3-BD selectivity by lowering acid sites. Sels recently added transition metal centers to materials made of MgO:SiO$_2$ [4]. According to their research, selectivity was increased by using a Mg/Si ratio of 2, CuO, ZnO, and Ag (at 350°C, EtOH concentration = 1.5 104 ppm). MgO:SiO$_2$ had to be prepared first, then transition metals had to be added[23].

Bimetallic (ZnO/ZrO$_2$) supported MgO:SiO$_2$ catalysts were created by Jones and colleagues [5]. In contrast to the undoped version at 2:1, the bimetallic catalyst's ideal Mg:Si ratio moved to 95:5. SiO$_2$ was crucial, as 100% MgO only provided 5% conversion and 19% 1,3-BD selectivity, compared to 30% conversion and 68% selectivity in the 95:5 ratio. The MgO-SiO$_2$ ratio was also emphasized in earlier work by Niiyama [4]. They determined an ideal ratio of 85:15, with basic sites promoting the synthesis of acetaldehyde, highlighting the necessity of controlling catalyst acidity and basicity. The use of MgO in Takezawa's research on the synthesis of ethanol to

acetaldehyde aids the identification of ethoxide species by IR spectroscopy[23]. SiO_2 and Al_2O_3 supports have been used throughout the past three years [6]. Jones created bi- and tri-metallic catalysts and discovered that a catalyst consisting of ZrO_2, ZnO, CuO, and SiO_2 (1 wt% each) obtained 67.4% 1,3-BD selectivity at 375°C. Greater 1,3-BD selectivity was achieved in porous SiO_2 due to larger pore sizes and lower acidity[23].

Dehydrogenation was ascribed to ZnO and aldol coupling to ZrO_2. Ordomskiy obtained up to 82% 1,3-BD yield by patenting Au, Ag, or Cu with metal oxide (Mg, Ti, Zr, or Ta) over SiO_2. Coking, or carbon formation, is a possibility and might lower catalyst activity, requiring renewal. H_2O_2 addition showed potential for reducing coking problems. Ezinkwo demonstrated that adding H_2O_2 as a "process initiator" prolonged catalyst activity, enabling continuous operation. Chae's work in 2014 used Ta_2O_3 on ordered mesoporous silica, achieving 47% conversion and 80% selectivity for 1,3-BD. Catalysts based on these ordered materials displayed greater resistance to coke and higher activity[23].
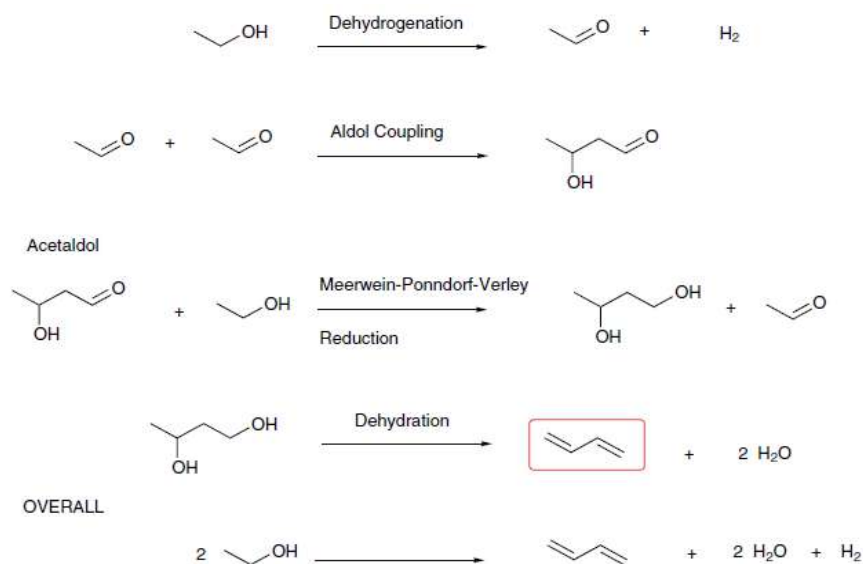
Figure 10: Steps involved in the conversion of ethanol to 1,3-Butadiene Adapted From [1], Chemistry Central Journal

2.8.7 Catalyst Development and Kinetic Study:

The research article titled "Direct Catalytic Conversion of Ethanol to 1,3-Butadiene: Catalyst Development and Kinetic Study" provides a comprehensive exploration of an innovative pathway for producing 1,3-butadiene (BD), a critical compound employed in the production of various polymers. BD finds applications in diverse industries, including the manufacturing of styrene-butadiene rubber, acrylonitrile-butadiene-styrene polymers, and polybutadiene. Traditionally, BD is obtained from the C4 fraction of naphtha steam crackers as a by-product, where ethylene is the primary product. However, shifts in feedstock preferences in steam cracking processes may lead to reduced BD yields, while escalating market demand for BD raises concerns about potential shortages. In this context, the study delves into other substitute technologies for BD synthesis, specifically focusing on a renewable and non-petroleum-based route[3].
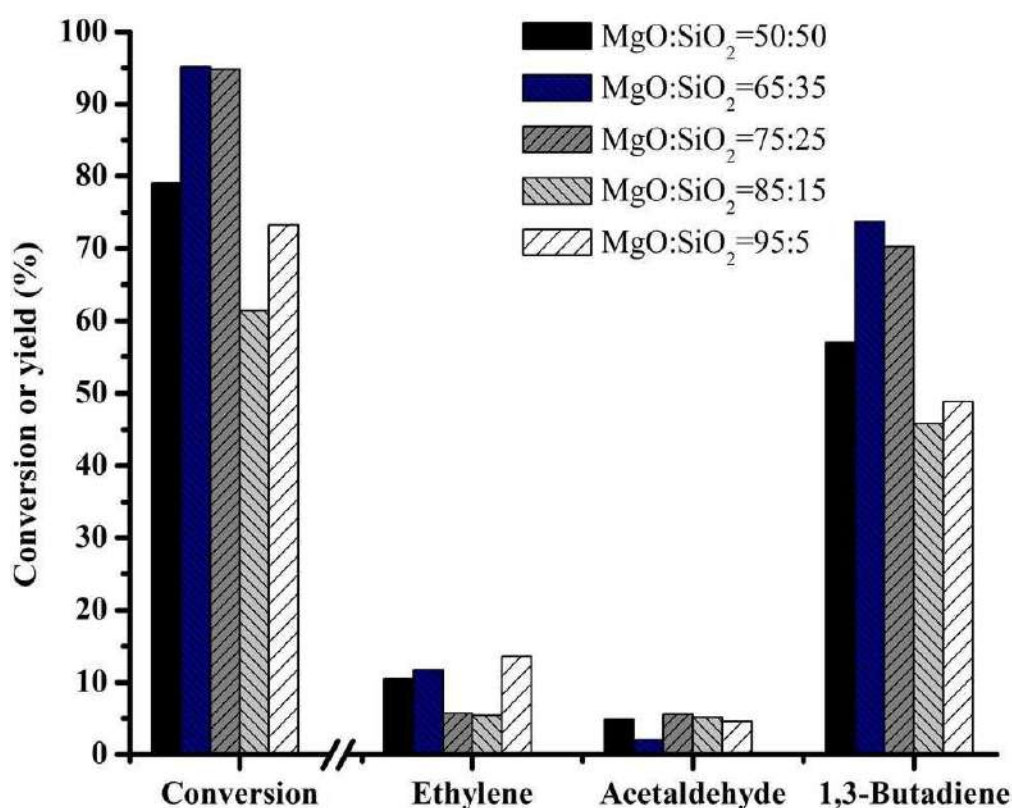
Figure 11: Conversion(%) of Ethanol to 1,3-Butadiene[3]

The driving force behind the exploration of this alternative route lies in the increasing awareness of sustainability and the need to minimize reliance on fossil

fuels. The article underscores the significance of developing pathways that utilize bio-ethanol as a precursor for BD production. Bio-ethanol can be derived from carbohydrate sources through fermentation, presenting an environmentally friendly alternative to traditional petroleum-based feed stocks. This approach aligns with global efforts to transition towards greener and more sustainable chemical production processes.

The historical perspective provided in the article sheds light on the evolution of BD production methods. While the direct catalytic conversion of ethanol to BD dates back to the 1920s, it fell out of favor with the rise of conventional oil production. However, with the resurgence of interest in renewable resources and the availability of bio-ethanol, the feasibility of direct ethanol-to-BD conversion has been revisited. The study explores the potential of the one-step process, pioneered by Lebedev, utilizing mixed metal oxide catalysts.

Central to the research is the development and characterization of catalysts suitable for the conversion of ethanol to BD. The article offers detailed insights into the preparation of magnesium oxide (MgO) and magnesium oxide-silica (MgO-SiO_2) catalysts through different methods. The identification of crystalline phases using X-ray powder diffraction and the determination of textural properties using nitrogen adsorption-desorption isotherms contribute to understanding the catalysts' structural characteristics[3].

The study delves into the acid and basic properties of the catalysts through NH_3- and CO_2-temperature-programmed desorption (TPD) methods. The analysis of Fourier-transform infrared (FT-IR) spectra and UV-Vis diffuse reflectance (DR) spectra further illuminates the functional groups and surface properties of the catalysts. Additionally, the morphology of the catalysts is examined using field emission-scanning electron microscopy (FESEM), providing visual insights into their physical structure[3]. The catalytic production of the developed materials is evaluated through experimentation involving the conversion of ethanol to BD. A fixed-bed quartz tube reactor is employed, and the reaction temperature is meticulously monitored. The article emphasizes the importance of catalyst selection and preparation methods in influencing catalytic efficiency. The effluent gas products are

subjected to thorough analysis using gas chromatography (GC), yielding valuable data on the effectiveness of the catalysts in facilitating the desired conversion[3].

In conclusion, the research article presents a holistic exploration of the direct catalytic synthesis of ethanol to 1,3-butadiene, aligning with the paradigm shift towards sustainable chemical processes. The article bridges historical context, catalyst development, characterization, and experimental analysis to offer a comprehensive view of this innovative approach. As industries increasingly seek greener alternatives to traditional chemical production methods, the findings of this study have the potential to drive advancements in sustainable BD production, contributing to the broader sustainability goals of the chemical industry[3][17].

2.8.8 Water Vapor Effect on ZnO/MgO-SiO$_2$ Catalysts in Ethanol-to-Butadiene Conversion:

The study titled "Water Vapor Effect on ZnO/MgO-SiO$_2$ Catalysts in Ethanol-to-Butadiene Conversion" explores the critical realm of sustainable chemistry by investigating the evolution of high volume chemical processes based on bio-raw materials as a means to replace processes reliant on fossil fuels. Within this context, a particularly significant focus of research is the creation and enhancement of catalytic processes that involve coupling carbon-carbon (C–C) bonds through the utilization of bio-alcohols. Specifically, the paper delves into the conversion of ethanol to 1,3-butadiene (BD) using the ethanol to butadiene process (ETB-process). This process holds promise as a pathway to harness renewable resources for the production of valuable chemicals[24].

The core of the study revolves around understanding the intricacies of the ETB-process, which encompasses a sequence of reactions. These reactions include the dehydrogenation of ethanol into acetaldehyde, the aldol-crotonic condensation of acetaldehyde yielding crotonaldehyde, the Meerwein–Ponndorf–Verley (MPV) reduction of Crotonaldehyde using ethanol to produce crotyl alcohol, and finally, the dehydration of crotyl alcohol leading to the formation of 1,3-butadiene. The efficiency of this process is intricately tied to the acidic & basic characteristics of the catalyst employed[24].

An essential dimension explored in the paper pertains to the influence of water vapor within the feed mixture. This consideration stems from the potential to employ more aqueous concentrated (50–80%) ethanol, which can be obtained through rapid membrane filtration of fermentation broth. The study's investigation into the effect of water content on product selectivity and the overall efficiency of the process proves to be a critical aspect of optimizing its practical viability[24]. Central to this research is the examination of the catalysts used for the ETB-process. The catalysts are prepared through a multistep process involving the impregnation of magnesium oxide, silica gel, and their mixtures with zinc acetate solutions, followed by drying and calcination. The acid-base characteristics of these catalysts are systematically evaluated through temperature-programmed desorption (TPD) experiments involving carbon dioxide (CO_2) and ammonia (NH_3) as probe molecules[24].

These experiments offer valuable appreciation into the nature of acid and base properties on the catalyst surface and how they interact with reactants.
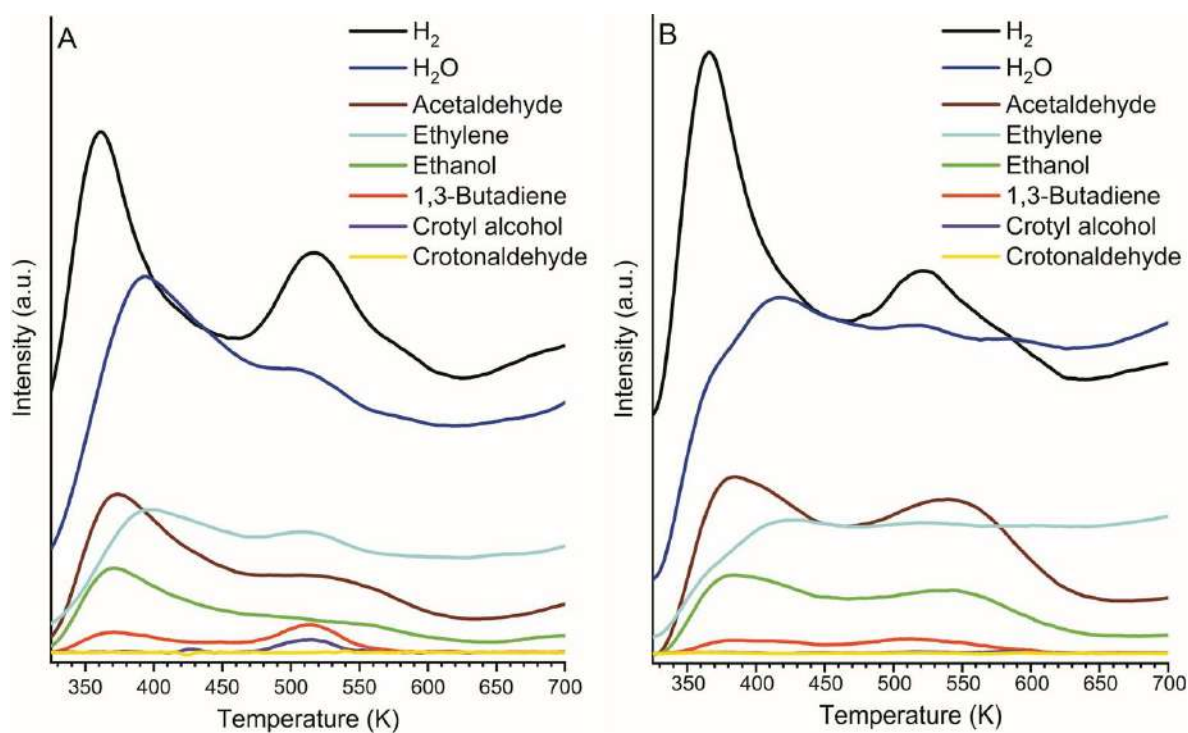
Figure 12: Temperature(K) vs Intensity(a.u.)[24]

To comprehensively understand the impact of water vapor, the study conducts a series of experiments. Water vapor adsorption and desorption experiments,

alongside temperature-programmed surface reaction (TPSR) experiments involving ethanol and iso-propanol, are carried out. These experiments provide a holistic view of how water vapor interacts with the catalyst's surface and influences reaction outcomes. The research findings demonstrate that the adsorption of water vapor induces changes in the surface's acid-base properties. Consequently, this has an impact on the generation of C–C coupling products, possibly as a result of water vapor attaching to the active sites involved in aldol condensation. Intriguingly, the investigation highlights that the active sites, formed at the interface between magnesia and silica, maintain their activity even when exposed to water vapor. This suggests that these catalysts retain their functionality even when subjected to water-rich conditions, emphasizing their potential utility in practical applications.

In conclusion, the study's findings carry important implications for sustainable catalytic processes and the development of bio-based alternatives to traditional fossil fuel-dependent methods. By addressing the influence of water vapor on catalyst performance, the research provides a deeper understanding of the underlying mechanisms at play. Moreover, achieving a BD selectivity of over 60% in the conversion of an ethanol-water mixture (80 vol% ethanol) using specific ZnO/MgO-SiO$_2$ catalyst compositions underscores the practical significance of these findings[24].

Ultimately, this research contributes to the broader discourse on sustainable chemistry and catalysis by shedding light on the complex interplay between catalyst composition, acid-base characteristics, and water vapor effects. The study underscores the need for continued exploration in this area, which holds the potential to revolutionize industrial processes, reduce environmental impact, and promote a more sustainable future. As the world seeks innovative solutions to address the challenges posed by climate change and dwindling fossil fuel reserves, research endeavors such as these are crucial in guiding the transition to more sustainable and environmentally friendly alternatives[24].

2.8.9 MgO-SiO$_2$ Bifunctional Catalysts for Cascade Conversion of Bio-Ethanol to 1,3-Butadiene:

The paper titled "MgO-SiO$_2$ Bifunctional Catalysts for Cascade Conversion of Bio-Ethanol to 1,3-Butadiene" delves into the innovative approach of utilizing renewable resources for the synthesis of 1,3-butadiene (BD), a key tetramer in polymer manufacturing. BD plays a pivotal role in the production of various polymers, including styrene-butadiene rubber, polybutadiene, and acrylonitrile butadiene styrene (ABS) rubber. The conventional method of obtaining BD through naphtha steam cracking has encountered challenges due to shifts in feed stocks and the rise of alternative sources like shale gas. Therefore, exploring an alternative, sustainable route for BD production has gained significant attention[25].

The Lebedev reaction pathway, which involves the direct conversion of bioethanol into BD, has emerged as a promising solution. Bioethanol can be derived from carbohydrate fermentation or cellulosic sources, making it a renewable and environmentally friendly precursor for BD production. The paper investigates the potential of this approach and explores various catalysts and preparation methods to achieve efficient and selective BD synthesis[26]. The primary catalyst under investigation is magnesium oxide-silicon dioxide (MgO-SiO$_2$), which has shown promising catalytic activity for the ethanol-to-BD conversion. The choice of catalyst and its preparation method play a crucial role in determining the efficiency and selectivity of the reaction. The researchers explore several catalyst preparation techniques, including the wet-kneading method, sol-gel method, and incipient wetness impregnation method. Each method offers unique advantages and challenges in terms of catalyst morphology and performance[26].

One of the intriguing catalyst morphologies studied is the flower-like MgO precursor. This morphology is synthesized through a hydrothermal process using surfactants like ethylene glycol and polyvinylpyrrolidone (PVP). Additionally, nanodisk and nanosheet MgO precursors are synthesized using similar methods with different surfactants. These various morphologies are carefully characterized to understand their structural and functional properties[26].
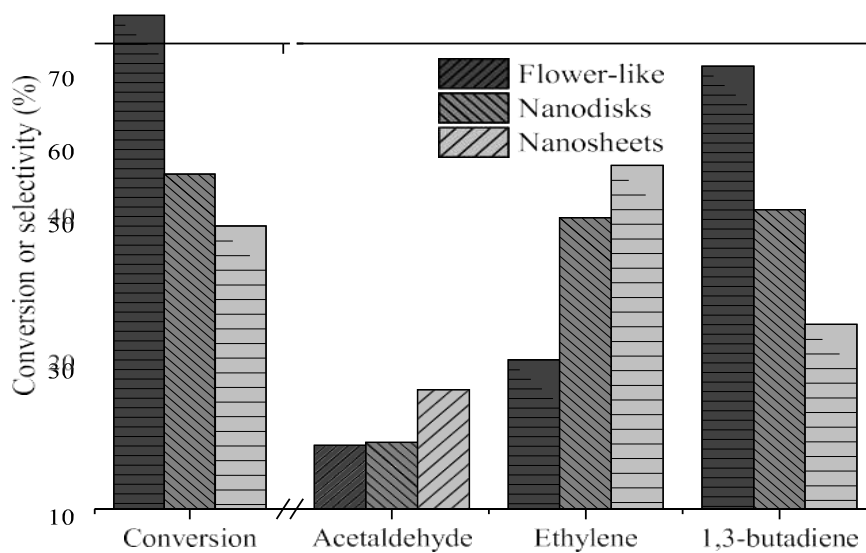
Figure A: Conversion (%) of Ethanol to 1,3-Butadiene

Techniques for characterizing materials, such as X-ray diffraction (XRD), offer valuable insights into crystal structures, whereas the specific surface area can be determined through the Brunauer-Emmett-Teller (BET) method. Scanning electron microscopy (SEM) offers visualizations of the catalyst's morphology, while Fourier-transform infrared (FT-IR) spectroscopy aids in analyzing catalyst composition. UV-vis diffuse reflectance spectroscopy and magic angle spinning nuclear magnetic resonance (MAS NMR) further contribute to a comprehensive understanding of the catalysts' properties[27].

Additionally, this research delves into the acidity and basicity of the catalysts through the utilization of CO_2-temperature-programmed desorption (CO_2-TPD) and NH_3-temperature-programmed desorption (NH_3-TPD). The temperature-programmed desorption of ethanol (ethanol-TPD) provides insights into the progression of the 1,3-butadiene production reaction. Real-time monitoring of products using mass spectrometry provides valuable insights into the reaction dynamics[27]. The findings of the study emphasize the pivotal role of catalyst morphology in the conversion of bioethanol to 1,3-butadiene. Notably, the flower-like MgO-SiO_2 catalyst exhibits exceptional performance with high BD selectivity and minimal ethylene formation. This can be attributed to the unique layered architectures of this morphology, which facilitate the production of interfacial MgO-Si species and enhance Lewis basicity. The relation between MgO and SiO_2 contributes to the catalyst's enhanced activity[27].

In conclusion, the paper's significance lies in its exploration of sustainable pathways for the synthesis of 1,3-butadiene. By utilizing bio-ethanol as a renewable precursor and tailoring catalyst morphology for optimal performance, the study paves the way for greener and more efficient chemical processes. As industries worldwide seek alternatives to fossil-fuel-based production, the research offers insights into advancing sustainable practices in the chemical manufacturing sector. By understanding the intricate interplay between catalyst properties and reaction mechanisms, researchers can contribute to the development of cleaner and more resource-efficient synthesis routes. The findings of this study are poised to impact the field of catalysis and sustainable chemistry, driving the shift towards more eco-friendly and economically viable production methods[27].

2.8.10 Tuning Surface Properties of MgO-SiO$_2$ Catalysts for Enhanced Conversion of Ethanol and Acetaldehyde to Butadiene:

The research study titled "Tuning Surface Properties of MgO-SiO$_2$ Catalysts for Enhanced Conversion of Ethanol and Acetaldehyde to Butadiene" delves into the promising potential of utilizing ethanol as a renewable feedstock for the production of butadiene, a critical building block in the production of synthetic rubbers, elastomers, and resins. Traditionally, the extraction of butadiene involves resource-intensive processes, prompting researchers to explore alternative, sustainable routes using bio-ethanol[26].

The research concentrates on two primary pathways for transforming ethanol into butadiene: the one-step approach pioneered by Sergey Lebedev and the two-step method involving ethanol's conversion into acetaldehyde, followed by the subsequent transformation of the ethanol-acetaldehyde mixture into butadiene. However, the primary focus of this investigation lies in the intricate catalytic aspects of the one-step process, with specific emphasis on the role of catalysts containing MgO-SiO$_2$ and ZrO$_2$-SiO$_2$, as well as the two-step process using Ta-SiO$_2$ catalysts. The versatile nature of MgO-SiO$_2$ catalysts renders them particularly appealing for potential large-scale application in ethanol-to-butadiene conversion [26].

The study illuminates the pivotal factors influencing the catalytic efficacy of these procedures, encompassing catalyst composition, preparation techniques, and reaction conditions. Previous research has already pointed out that the interaction between MgO and SiO_2 within these catalysts plays a crucial role in determining their activity and selectivity in facilitating the conversion of ethanol into butadiene.. The experimental methodology is outlined comprehensively, detailing the process of catalyst preparation through impregnation, utilizing ethanol as a solvent. The study involves synthesizing various catalysts, each with distinct MgO/SiO_2 ratios, and characterizing them using a range of advanced techniques. These include nitrogen adsorption-desorption measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), 29Si magic-angle spinning nuclear magnetic resonance (MAS NMR), and X-ray photoelectron spectroscopy (XPS)[25].

The key findings of the study highlight the potential for enhancing the catalytic execution of MgO-SiO_2 catalysts by tailoring their surface properties through carefully controlled calcination temperatures. The addition of water to the ethanol and acetaldehyde feed mixture is also demonstrated to be advantageous. This addition not only enhances butadiene selectivity but also curbs the formation of undesirable byproducts, contributing to the overall efficiency of the conversion process[25]. Of particular significance is the discovery that the catalyst exhibiting the highest butadiene selectivity (measuring at an impressive 80.7%) possesses a distinct composition. This composition features a notable concentration of amorphous magnesium silicates, coupled with minimal crystalline magnesium silicates. The existence of specific Si-O-Mg bonds, characterized by particular binding energies, emerges as a key factor in bolstering the catalytic performance of these catalysts.

Moreover, the study underscores the essential role played by Lewis acidic sites and a balanced presence of basic sites in enhancing the productivity of the two-step conversion process. This intricate interplay of surface properties and active sites serves to amplify the production of butadiene while minimizing the formation of undesired byproducts.

In conclusion, the research study significantly contributes to the field of sustainable chemical production by addressing the challenges and opportunities

associated with converting ethanol into butadiene. By meticulously investigating the interaction between MgO and SiO$_2$ and optimizing surface properties, the study paves the way for the development of more efficient and selective catalysts. Ultimately, these catalysts have the potential to revolutionize the synthesis of butadiene, enabling a more sustainable and environmentally friendly approach to chemical production. As industries continue to seek alternatives to resource-intensive processes, the findings of this study hold significant promise for future advancements in catalysis and chemical engineering[25].

2.8.11 Catalysts based on magnesium oxide (MgO) and silicon dioxide (SiO$_2$) for the conversion of ethanol to butadiene:

The research at hand delves into a pressing concern of the modern world: the adverse effects of oil consumption and the consequent rise in greenhouse gas emissions. As industries grapple with the need to transition towards more sustainable practices, there is a growing focus on identifying renewable raw materials for chemical production. Among these alternatives, bio-ethanol, derived from the fermentation of sugars, emerges as a promising candidate with vast potential in the chemical sector. Particularly intriguing is its application as a foundational component for producing chemicals, with 1,3-butadiene standing out due to its significance in the manufacturing of engineering polymers, tires and latex products[28].

The pivotal challenge lies in deciphering the complex mechanisms involved in the conversion of ethanol to 1,3-butadiene. Traditional wisdom has dictated the use of catalysts possessing both acidic and basic characteristics to facilitate this transformation. However, recent research casts doubt on the role of aldol condensation in this process, prompting a reevaluation of existing mechanisms. This catalytic conversion holds great importance, given that 25% of global rubber manufacturers rely on butadiene in their operations, underscoring the urgent need for sustainable production methods[28].

The study systematically explores catalysts based on magnesium oxide (MgO) and silicon dioxide (SiO$_2$) for the conversion of ethanol to butadiene. Critically, the composition and preparation of these catalysts emerge as pivotal factors influencing their efficacy. Conventional catalysts based on MgO and SiO$_2$ have been employed historically, with their performance strongly influenced by the Mg/Si atomic ratio.

Prior research has emphasized a ratio greater than unity as essential for attaining high selectivity towards butadiene. However, this study takes a novel approach by proposing that even a minimal quantity of Si can significantly enhance catalytic performance, challenging previous assumptions[28].

The method chosen for synthesizing these catalysts is the sol-gel technique. This approach enables the precise mixing of components, yielding materials with tailored properties. The catalysts are subjected to rigorous characterization using diverse techniques, such as X-ray diffraction (XRD), which provides insights into the crystalline structure, and the BET method, which measures specific surface area. Furthermore, NH3-temperature-programmed desorption (TPD) measurements offer valuable information about the acidity of the catalysts, a crucial factor in their performance[28].

The reactivity experiments are conducted within a continuous flow reactor under barometric pressure. This setup allows for the systematic evaluation of different catalysts and reaction conditions. The study pays meticulous attention to detail, varying the residence time and inlet feed molar ratios while maintaining consistency. Gas chromatography, outfitted with flame ionization detection (FID) and thermal conductivity detection (TCD), allows for precise and simultaneous analysis of gas samples, is employed for the analysis of downstream products. The mass balances are meticulously determined, ensuring accurate and reliable results[28]. In-situ **Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)** studies offer a deeper understanding of the reaction intermediates and the catalyst's behavior under reaction conditions. The researchers employ this technique to investigate the surface interactions and transformations during the catalytic process. By monitoring specific mass spectroscopy signals, they gain insight into the various products formed, aiding in deciphering the intricate pathways involved in ethanol conversion[28].

The conclusion of these studies offers profound insights into the characteristics of active sites within the MgO-SiO2 catalysts. According to the research, Lewis acid sites, which are defined by Mg-O-Si pairs, hold a crucial role in the conversion process. These sites transition into Bronsted acid sites when they interact with water generated during the reaction, thereby enhancing the effective dehydration of alkenols into butadiene. The study presents an enhanced model that

takes these discoveries into consideration, elucidating the intricate interplay of acid-base sites in the catalytic process[28].

In conclusion, the study stands as a testament to the meticulous exploration of catalysts for the conversion of bio-ethanol to 1,3-butadiene, a compound integral to various industrial applications. The research challenges conventional assumptions about catalyst composition and performance, proposing that even trace amounts of Si can significantly enhance catalytic activity. Through rigorous characterization techniques and reactivity experiments, the study uncovers the optimal catalyst composition and mechanisms governing the transformation. By elucidating the complex interplay of acid-base sites, the research contributes to the broader goal of sustainable chemical production and underscores the importance of innovative catalyst design[28].

2.9 Concluding Remarks

In this chapter, we have given an overall review about the literature related to the synthesis of synthetic rubber. One step catalytic conversion method for the conversion of ethanol to butadiene is highlighted, used and recommended by many of the research paper because of its benefits in cost as well as its applications.

CHAPTER 3

Experimental Methodology

A popular polymer used in the creation of synthetic rubber, plastics, and other products is polybutadiene. Traditionally, butadiene, a feedstock obtained from petroleum, has been used to make polybutadiene. However, there is a need to investigate alternate sources for the synthesis of polybutadiene because of the rising demand for sustainable and renewable resources. A viable possibility for the synthesis of polybutadiene has been found as ethanol, a commonly available bio-based feedstock. The goal of this research is to create a brand-new method for making polybutadiene from ethanol.

For the synthesis of polybutadiene, we designed the fluidized bed reactors. The main designing parameters of Mini Synthetic Rubber Plant are given by:

3.1 Fluidized bed catalytic reactor:

The Al_2O_3-ZnO catalyst's reaction conditions and process size determine the reactor that will be utilized to convert ethanol to butadiene. However, a fluidized-bed catalytic reactor can be a typical reactor utilized for this procedure. The Al_2O_3-ZnO catalyst is the catalyst material used in this fluidized bed catalytic reactor, which is a cylindrical vessel. To boost reaction efficiency and enhance interaction between the catalyst and reactants, the reactor may have numerous beds of the catalyst.

Through an intake, the reactants and ethanol are fed into the reactor and passed through the catalyst bed. Butadiene is generated during the reaction, which takes place on the surface of the catalyst particles, and the products exit the reactor through an outlet. To reach the necessary reaction temperature, the reactor is heated using heating elements or other heating techniques. To improve the performance of the reaction, we adjusted reaction parameters such as temperature, pressure, and reactant flow rate. Temperature and pressure sensors are used to monitor and regulate the reaction. In general, the reactor used to convert ethanol to butadiene using the Al_2O_3-ZnO catalyst should be built to efficiently provide contact between the

reactants and catalyst, preserve the optimal reaction conditions, and make process monitoring and control simple.

3.2 Components of Mini Synthetic Rubber Plant:

For the synthesis of polybutadiene, we designed the synthetic rubber plant by assembling and designing following components:

1. Nitrogen Cylinder

2. Evaporator

3. Fluidized Bed Reactor

4. Cyclone Collector

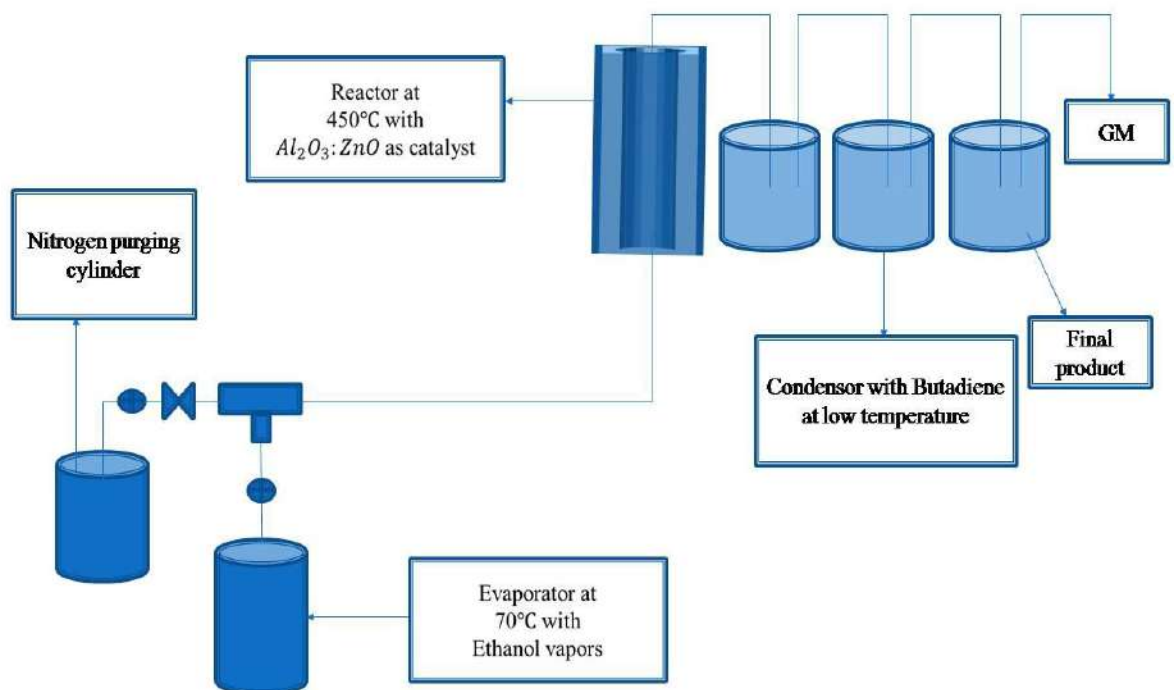5. Condenser

6. Temperature & Pressure Controller

Figure 13: 2D Model of Synthetic Rubber Plant

Now we discuss, designing parameters and details of these components.

3.2.1 Nitrogen Cylinder:

The utilization of nitrogen gas cylinders to purge and create an oxygen environment plays a role in the production of high quality polybutadiene. Typically polybutadiene is manufactured by polymerizing butadiene monomers resulting in a rubber known for its mechanical properties. Nitrogen gas is introduced into the reaction vessel, Fluidized bed reactor to displace any oxygen or reactive gasses establishing a controlled and oxygen free atmosphere that facilitates the polymerization process. This purging step is essential as oxygen can lead to side reactions, contaminants and alterations in the properties of the polymer. By eliminating oxygen from the system through its nature and lack of reactivity, nitrogen minimizes the risk of oxidation and maintains stable conditions for polymerization. Additionally, this nitrogen flow aids in removing any vapors or odors produced during the addition of monomers contributing to a controlled setting for polymerization. Researchers can fine tune synthesis parameters such as pressure, temperature and other factors by adjusting the nitrogen flow to achieve desired properties, for the polybutadiene polymer. This process is crucial in producing top notch polybutadiene that possesses characteristics ideal for applications, like tire manufacturing, industrial rubber products and adhesives.

Figure 14: Nitrogen Cylinder

3.2.2 Evaporator:

For the synthesis of poly-butadiene we used 90% pure ethanol. An evaporator is used to increase the concentration of the 90% pure ethanol after additional purification. The evaporator receives the initial ethanol, which contains a sizable proportion of water and other volatile contaminants. The ethanol is heated under control inside the evaporator, increasing its temperature and pressure. The outcome is that the liquid phase is vaporized above by the volatile components, mostly water and other contaminants. The liquid ethanol is separated from this vapor, which has been enhanced with the volatile contaminants. The volatile contaminants are then successfully removed by cooling the vapor back into a liquid form. Distillation, a process of evaporation and condensation, uses the distinctions in boiling points between ethanol and contaminants to separate the two. The distillate is collected when the distillation process is complete, and as more pure ethanol is added, the initial 90% concentration of ethanol is exceeded With its increased purity, ethanol is now even more appropriate for usage in a variety of processes, such as serving as a crucial precursor in the production of polybutadiene, a synthetic rubber with several industrial applications. By using an evaporator for further purification, it is possible to produce ethanol that is of outstanding quality, free of substantial contaminants, and better suited for labor-intensive industrial operations.

Figure 15: Evaporator

3.2.3 Fluidized bed reactor (FBR):

A fluidized bed reactor (FBR) is necessary and helpful equipment for the polymerization process in the manufacture of polybutadiene. A fluidized bed reactor (FBR) is a type of chemical reactor that utilizes a fluidized bed of solid particles to support various chemical reactions. It offers several advantages over traditional fluidized-bed reactors, including better heat and mass transfer, enhanced mixing, improved reaction kinetics, and the ability to handle a wide range of feed stocks. The FBR facilitates effective mixing and contact between the reactants and catalyst, improving heat and mass transfer while also improving the reaction kinetics in general. In the FBR configuration, the bed material is supported by solid particles in a rectangular box with a distributor plate at the bottom.

Figure 16: Fluidized Bed Reactor

The two heating elements are carefully positioned around the reactor to evenly distribute heat and keep the bed at a consistent temperature. During the polymerization process, the two heating elements are crucial for accurate temperature

control. Together, they help the fluidized bed reactor reach the desired reaction temperature of 450 °C, assuring ideal reaction conditions and averting any thermal gradients. The exothermic polymerization reaction may be efficiently controlled by carefully controlling the heating mantle temperatures. This lowers the possibility of runaway reactions and improves the overall safety and effectiveness of the synthesis. Additionally, the use of a fluidized bed reactor allows for continuous operation, making it appropriate for the high reproducibility, large-scale manufacture of polybutadiene. The fluidized bed reactor and the two heating mantles work together to create an efficient and scalable platform for the synthesis of polybutadiene, allowing for the creation of a flexible synthetic rubber material with a wide range of industrial uses.

In a fluidized bed reactor, solid particles are typically held in a fluidized state by an upward flow of gas or liquid. The fluidization process occurs when the upward fluid flow is sufficient to balance the weight of the particles, causing them to exhibit fluid-like behavior. This state is characterized by the formation of a dense bed of particles with suspended particles or bubbles dispersed within. The fluidized bed reactor operates under controlled conditions of temperature, pressure, and residence time to promote the desired chemical reactions. The properties of the solid particles, such as size, density, and composition, are crucial in determining the reactor performance.

3.2.3.1 Advantages of a Fluidized Bed Reactor:

The key advantage of a fluidized bed reactor includes:

1. **Enhanced heat and mass transfer:**

   Between the reactants and the catalyst or solid particles, the fluidized bed enables effective mixing and interaction. This encourages improved heat transfer and diffusion rates, which boost reaction rates.

2. **Uniformly Distribution of Temperature:**

   Hot spots are less likely to emerge and reaction conditions are more consistent thanks to the fluidized bed's good temperature dispersion throughout the reactor.

3. High catalyst utilization:

In a fluidized bed reactor, the enormous surface area and effective mixing enable maximum catalyst utilization. This is especially advantageous in reactions that demand catalyst regeneration or have high catalyst costs.

4. Flexibility in feedstock and reaction conditions:

The fluidized bed allows for efficient mixing and contact between the reactants and the catalyst or solid particles. This promotes better heat transfer and improved diffusion rates, leading to enhanced reaction rates.

5. Scalability:

Fluidized bed reactors are easily scalable, from lab-scale setups to industrial-sized units, making them suitable for a range of applications.

3.2.4 Cyclone Separator

A cyclone collector is an essential component of the post-reaction procedure in the synthesis of polybutadiene because it ensures the effective removal of dust and residual catalyst particles from the product stream leaving the fluidized bed reactor (FBR). As previously mentioned, the FBR makes the mixing and reaction conditions ideal, which speeds up the polymerization process. However, the reactor may produce tiny catalyst particles as well as other types of dust during the process. A cyclone collector is strategically positioned after the FBR to stop these unwelcome particles from getting into the downstream condenser and impacting the quality of the finished product.

To separate solid particles from the gas stream, the cyclone collector uses the centrifugal force principle. The product stream is sent into an upward swirl when it reaches the cyclone, carrying dust and leftover catalyst particles. The catalyst and dust, which are heavier particles, are pushed outward by the centrifugal force produced inside the cyclone and hit the collector's walls. These divided particles are then prevented from accessing the condenser by sliding down the walls and being gathered at the cyclone's bottom. The cleaned gas stream, on the other hand, leaves the cyclone from the top and travels to the condenser for additional processing now that it is free of solid particles.

Figure 17: Cyclone Separator

In addition to ensuring the manufacture of high-purity polybutadiene, the cyclone collector's effective contamination removal also improves the process' overall effectiveness and safety. The cyclone collector helps to produce high-quality polybutadiene with regulated characteristics and reduces the chance of fouling and deterioration in the downstream condenser by efficiently eliminating dust and leftover catalyst particles. By using the cyclone collector, polymer synthesis has advanced significantly, improving knowledge of process optimization and the creation of effective post-reaction systems for the creation of novel, high-performance materials.

3.2.5 Condenser:

The condenser is an essential component in the conversion of ethanol to polybutadiene, due to its vital function in cooling and condensing the gaseous stream carrying butadiene, which is the primary product of interest. The purpose of the condenser is to effectively transfer heat from the gaseous mixture to a cooling medium, resulting in the liquidization of the gaseous butadiene. We talk about the multi-stage condensation process and emphasize how important it is for increasing yield and improving product quality. Using an Al_2O_3-ZnO catalyst, ethanol is transformed into polybutadiene through a series of chemical reactions where the

intermediate product, butadiene, is produced in gaseous form. The mini synthetic rubber plant uses a condenser as a crucial component to efficiently recover the gaseous butadiene. The main job of the condenser is to exchange heat with the gaseous stream, which enables the conversion of butadiene from a vapor to a liquid phase. The condenser separates and collects butadiene through the process of condensation, permitting further downstream processing for the creation of synthetic rubber.

The butadiene-containing gaseous mixture is brought into contact with a cooling medium, such as water, in the condenser according to the principle of heat exchange. Thermal energy is transferred from the vapor to the cooling medium as the hot gaseous stream passes through the condenser. The butadiene gas loses heat as a result of this exchange, goes through a phase change, and condenses into a liquid state. The remaining uncreated ethanol and other impurities are subsequently gathered and removed from the condensed butadiene. A multi-stage condensation process is used in complex processes that need to produce large yields and satisfy high purity requirements. This design offers numerous alternatives for effective cooling and condensation through the use of various stainless steel boxes as independent condensation units. Further butadiene condensation is encouraged as the gaseous mixture moves through each box due to increased cooling capacity and extended interaction with the cooling medium. Higher yields of high-quality polybutadiene are ensured by the multi-stage condensation process, which also improves process efficiency and helps to optimize product separation.

Figure 18: Condensers

3.3 Catalyst Preparation:

A catalyst is a material that speeds up a chemical reaction without being consumed in the process by lowering the activation energy needed for the reaction to happen. Catalysts function by offering a different reaction pathway or mechanism with lower energy barriers, allowing more reactant molecules to participate in the reaction. There are two types of catalysts, Homogeneous catalysts & Heterogeneous catalysts. Homogeneous catalysts are in the same phase as the reactants, while heterogeneous catalysts are in a distinct phase. Catalysts are used in chemical processes to boost productivity, lower energy usage and enable the production of particular products.

Al_2O_3-ZnO is a heterogeneous catalyst made up of a combination of zinc oxide (ZnO) and aluminum oxide (Al_2O_3). It is generally used in a variety of chemical processes, including the production of methanol, the dehydration of alcohols, and the transesterification of vegetable oils. The ratio of Al_2O_3 to ZnO, the technique of manufacture, and the calcination temperature all affect the catalyst Al_2O_3-ZnO's characteristics. The catalyst is typically strong mechanically, has a large surface area, and is thermally stable. It is also known for having strong basic and acidic properties, making it a versatile catalyst for a range of activities.

The catalytic activity and selectivity of the Al_2O_3-ZnO catalyst have been shown to be affected by a number of factors, including the reaction conditions, reaction time, and catalyst particle size. It has been found, for instance, that the catalyst is more active for the dehydration of alcohols at lower temperatures and higher pressures than it is for the synthesis of methanol at lower temperatures and higher pressures. Al_2O_3-ZnO is a suitable catalyst material for many catalytic processes due to its high activity, selectivity, and stability.

The following procedures can be used to prepare the Al_2O_3-ZnO catalyst for converting ethanol to polybutadiene:

3.3.1 Preparation of aluminium oxide:

Aluminium hydroxide, for example, can be oxidized at high temperatures (500–800°C) for several hours to produce aluminum oxide (Al_2O_3). Strong mechanical properties and high surface area are desired in the final product.

3.3.2 Preparation of zinc oxide:

To make zinc oxide (ZnO), a suitable zinc compound, such as zinc carbonate or zinc oxide hydroxide, is oxidized for several hours at high temperatures (400–600°C). Additionally, the final product should have a large surface area and strong mechanical properties.

3.3.3 Combining aluminium oxide and zinc oxide:

To create the Al2O3-ZnO catalyst, the manufactured aluminium oxide and zinc oxide are combined in an appropriate ratio (for example, 3:1). Ball milling or the impregnation process might be used to combine the ingredients.

3.3.4 Activation of the catalyst:

The catalyst is then activated by being calcined at a high temperature (for example, 500–800°C) for a number of hours in an inert atmosphere. This procedure aids in boosting the catalyst's surface area and catalytic activity.

3.3.5 Conversion of ethanol to polybutadiene:

The produced catalyst can be used to convert ethanol to polybutadiene by mixing it with ethanol, a suitable solvent, and other required reagents. To produce polybutadiene, the reaction can be carried out under the proper circumstances (such as temperature, pressure, and reaction time).

In conclusion, the Al_2O_3-ZnO catalyst for converting ethanol to polybutadiene can be made by mixing aluminium oxide and zinc oxide in an appropriate ratio, activating the catalyst through calcination, and afterwards using it in the reaction mixture. The ideal ratio of zinc oxide (ZnO) to aluminium oxide (Al_2O_3) for the synthesis of butadiene might vary based on a number of variables, including the particular reaction conditions and the desired catalyst qualities. The best Al_2O_3-ZnO catalyst ratio, which is utilized to produce butadiene, often lies between the ratios of 3:1 and 5:1.

Due to the Lewis acidity of the aluminium cations, a larger concentration of Al_2O_3 in the catalyst can produce stronger acidic characteristics and increase activity for the conversion of ethanol to butadiene. However, too much aluminum oxide can result in the creation of catalytically inactive species such $Al(OH)_3$, which can reduce

the activity of the reaction. The dehydration of ethanol to acetaldehyde, a crucial intermediate in the formation of butadiene, can be enhanced by a larger ZnO content in the catalyst due to its stronger basic characteristics. However, excessive zinc oxide might result in the development of ZnO aggregates, reducing the catalyst's surface area and lowering its catalytic activity.

As a result, the ideal Al_2O_3 to ZnO ratio for the synthesis of butadiene depends on a balance between the catalyst's acidic and basic properties as well as on the stability of the catalyst under the particular reaction circumstances. Most experts agree that a ratio between 3:1 and 5:1 offers a fair mix of these characteristics for the manufacture of butadiene from ethanol. It is crucial to remember that the ideal ratio can change based on the particular reaction conditions and the catalysts desired qualities.

Al_2O_3-ZnO catalyst activity and selectivity in the conversion of ethanol to butadiene may be greatly influenced by the ratio of Al_2O_3 to ZnO in the catalyst. The ideal Al_2O_3 to ZnO ratio for the synthesis of butadiene from ethanol is about 3:1, according to research by Wang et al. (2016). In this work, the authors developed a variety of Al_2O_3-ZnO catalysts with different Al_2O_3 to ZnO ratios, assessed their catalytic activity and selectivity during the synthesis of butadiene from ethanol, and discussed their results. At a temperature of 523 K and a feed flow rate of 1 mL/min, they discovered that the 3:1 catalyst had the maximum selectivity for butadiene. The synergistic interactions between Al_2O_3 and ZnO, which may increase the catalyst's acidity and basicity and facilitate the adsorption and activation of ethanol and intermediate species in the process, were credited by the scientists as the cause of the 3:1 catalyst's increased catalytic activity and selectivity.

3.4 Polymerization:

Living anionic polymerization is used to create polybutadiene. The solvent will be anhydrous ethanol, and the polymerization will take place in a dry, oxygen-free atmosphere. Using a Schlenk line and an inert gas environment, the polymerization process will be conducted. Prior to usage, ethanol will be nitrogen gas-purged and vacuum-degassed.

Several techniques may be used to polymerize butadiene utilizing the Al_2O_3-ZnO catalyst to convert ethanol into polybutadiene. According to a research by Liu et al. (2020), under specific reaction conditions, the polymerization may be accomplished utilizing a solution polymerization approach. In this work, a suitable solvent, such as tetrahydrofuran (THF), was employed together with an Al_2O_3-ZnO catalyst to polymerize butadiene whilst under a nitrogen environment. 100:1 monomer to catalyst was used in the reaction, which was conducted at 50°C for 4 hours. The authors discovered that the Al_2O_3-ZnO catalyst had strong butadiene polymerization catalytic activity and selectivity, and that the resultant polybutadiene had a high molecular weight and narrow molecular weight dispersion. The catalyst's strong acidity and basicity, which might facilitate the adsorption and activation of butadiene and intermediate species in the process, was credited with the excellent activity and selectivity of the catalyst.

3.5 Ethanol to Polybutadiene Conversion:

The conversion of ethanol to polybutadiene will take place with the help of the catalyst that was previously created. In a reactor, ethanol and the catalyst will be combined under predetermined reaction parameters, such as temperature, pressure, and space velocity. Gas chromatography (GC) analysis will be used to track the reaction and quantify how much ethanol is converted to butadiene. Using an Al_2O_3-ZnO catalyst, ethanol may be converted to butadiene by a catalytic dehydrogenation process. The scientific approach listed below can be used:

3.5.1 Materials:
- catalyst Al_2O_3-ZnO
- Ethanol
- Inert gas for purging, such as nitrogen

The following equipment is used for product analysis:

- reactor vessel
- heating element
- gas chromatography (GC)

- stirring device

- separation funnel

- Filter.

3.5.2 Steps:

1. Use an inert gas i.e. Nitrogen to completely purge the reactor vessel of any air or moisture.
2. Place the catalyst made of Al_2O_3 and ZnO in the reactor vessel.
3. Fill the reactor vessel with the appropriate amount of ethanol.
4. Under an inert gas flow, heat the reactor vessel to an appropriate temperature, usually between 300 and 450 °C.
5. Evaluate the reaction's development by periodically obtaining samples.
6. Gather the butadiene product and keep the uncreated ethanol and other reaction products separate.

It should be noted that depending on the particular catalyst and desired reaction parameters, reaction circumstances such as temperature, flow rate, and catalyst loading may change. For high conversion and selectivity, these parameters might need to be optimized.

3.5.3 Polybutadiene Synthesis:

The butadiene produced during the ethanol conversion will be utilized to create polybutadiene through a process known as live anionic polymerization. A specified set of reaction parameters, such as temperature, pressure, and the ratio of monomer to catalyst, will be used to carry out the polymerization once the butadiene has been introduced to the reactor containing the catalyst. By first synthesizing ethanol to butadiene with the use of an Al_2O_3-ZnO catalyst, and then polymerizing butadiene to create polybutadiene, it is possible to create polybutadiene from ethanol. It should be noted that depending on the intended molecular weight and characteristics of the polybutadiene, the polymerization parameters, such as temperature, initiator concentration, and reaction time, may change.

Chapter 4

Result and Discussion

4.1 Result:

The primary aim of this project is to design the mini synthetic rubber plant and investigate the feasibility of using aluminum zinc oxide (Al_2O_3-ZnO) catalyst in the single step transformation into butadiene from the ethanol, a crucial intermediate chemical in the production of synthetic rubber. By exploring the catalytic activity and selectivity of Al_2O_3-ZnO in this process, this study seeks to contribute to the development of more sustainable and efficient methods for butadiene synthesis.

The present study employed a quantitative research for the design and the fabrication of a mini synthetic rubber plant. The experiment has been done on the mechanism of the single-step catalytic transformation of ethanol into butadiene, which means that the dehydrogenation and dehydration occur at the same time, on Al_2O_3 & ZnO (60:40) catalyst, which is being called as the binary oxide catalyst or heterogeneous catalyst and is being studied as the best catalyst in static as well as fluidized beds. The Al_2O_3: ZnO (60:40) catalyst excelled in delivering the necessary conversion with high efficiency and selectivity, according to the comparative study of binary oxide systems. These results have important relevance for the creation of more efficient and environmentally friendly processes for synthesizing polybutadiene, an essential component of the synthetic rubber industry.

The findings in this thesis not only advance knowledge of the catalytic mechanisms involved in the synthesis of polybutadiene, but they also pave the way for future investigation and invention in the manufacture of synthetic rubber. This research is a significant step in developing polybutadiene production methods that are both economically and ecologically sound, eventually enhancing the rubber industry's sustainability.

The experiments were done under indistinguishable states of temperature and ethanol feed-rate (for example 1.8 ml/hr/G), and the similar movement of the double oxide frameworkswhich are recorded as follows:

Catalyst System and Composition	Total Ethanol Conversion (%)	Total Volume of gas at S.T.P. (Liters)	Process yield of Butadiene (%)
Al_2O_3:ZnO (at 425°C)			
80:20	92.47	8.85	33.6
60:40	94.38	12.52	55.8
40:60	95.13	14.89	31.0
20:80	96.92	15.52	25.6

Table 1: Catalyst Composition and Percentage Yield

The presentation attributes of alumina-zinc oxide (60:40), the best quality impetus, were concentrated on in more noteworthy details which are being discussed below:

1. As we know that, the response includes drying out and dehydrogenation too, the combination of a getting dried out impetus with a dehydrogenating one (in ideal extent) normally lead to better synergist change of ethanol to butadiene,

2. The presence of one part adjusts the primary and surface properties of the other as well as the other way around, and thus shows the better reactant action of the paired impetuses.

4.2 Performance Curves:
4.2.1 Catalyst Composition (Ratio) vs Ethanol Conversion (%):

The curve shows how the ratios of zinc oxide (ZnO) to aluminum oxide (Al_2O_3) in the catalyst composition affected the conversion of ethanol. These findings demonstrate a distinct pattern whereby ethanol conversion grows as zinc oxide content in the catalyst increases. In particular, the conversion of ethanol improves gradually when the ratio changes from 80% Al_2O_3 and 20% ZnO to 20% Al_2O_3 and 80% ZnO. This trend shows that the catalyst's makeup significantly affects how well ethanol is converted. To understand the processes underlying this phenomenon and to

improve catalyst compositions for ethanol conversion applications, more study and analysis may be necessary.
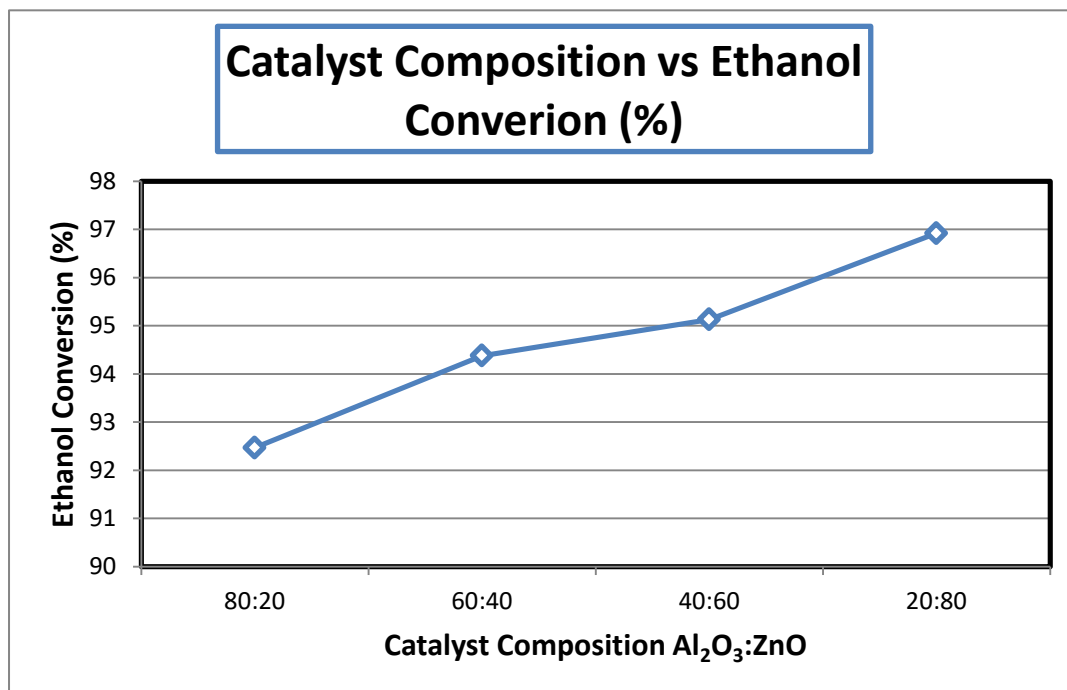

Figure 19 Catalyst Composition (Ratio) vs Ethanol Conversion (%) Performance Curve

Understanding the findings of the experiment for ethanol conversion with various catalyst compositions depends critically on maintaining a constant temperature throughout. The kinetic energy of the interacting molecules stays constant throughout the experiment while temperature is maintained constant. In this situation, temperature serves as a controlled variable that enables researchers to focus on the impact of catalyst composition on the conversion of ethanol. The greater ethanol conversion in this instance shows that ZnO functions better than Al_2O_3 in these circumstances as a catalyst for the ethanol conversion process. This could be the result of several things, such variations in the two materials' acidity, basicity, or redox characteristics.

4.2.2 Catalyst Composition (Ratio) Vs Yield of Polybutadiene (%):

The information given is the outcome of a study on how the composition of the catalyst, especially the ratios of aluminum oxide (Al_2O_3) to zinc oxide (ZnO),

affects the production of polybutadiene. The % yield of polybutadiene is calculated for each catalyst composition, and the findings are as follows: Based on these findings, it can be shown that the catalyst composition has a substantial impact on the yield of polybutadiene. An explanation of these observations is given below:

1. **80% Al_2O_3 : 20% ZnO:** This mixture produces 33.6% polybutadiene. Because of the comparatively reduced yield, it is possible that the catalyst composition is less efficient in promoting the required polymerization process.

2. **60% Al_2O_3 : 40% ZnO:** produces a substantially higher polybutadiene yield of 55.8%. It seems that the catalyst's ability to encourage butadiene's polymerization into polybutadiene, which increases yield, is better when it contains a larger percentage of ZnO.

3. **40% Al_2O_3 : 60% ZnO:** Despite having more ZnO than the 60% ZnO composition, this composition generates 31% less polybutadiene. This implies that the Al_2O_3 and ZnO ratio and combination in this catalyst may not be as favorable for the polymerization process.
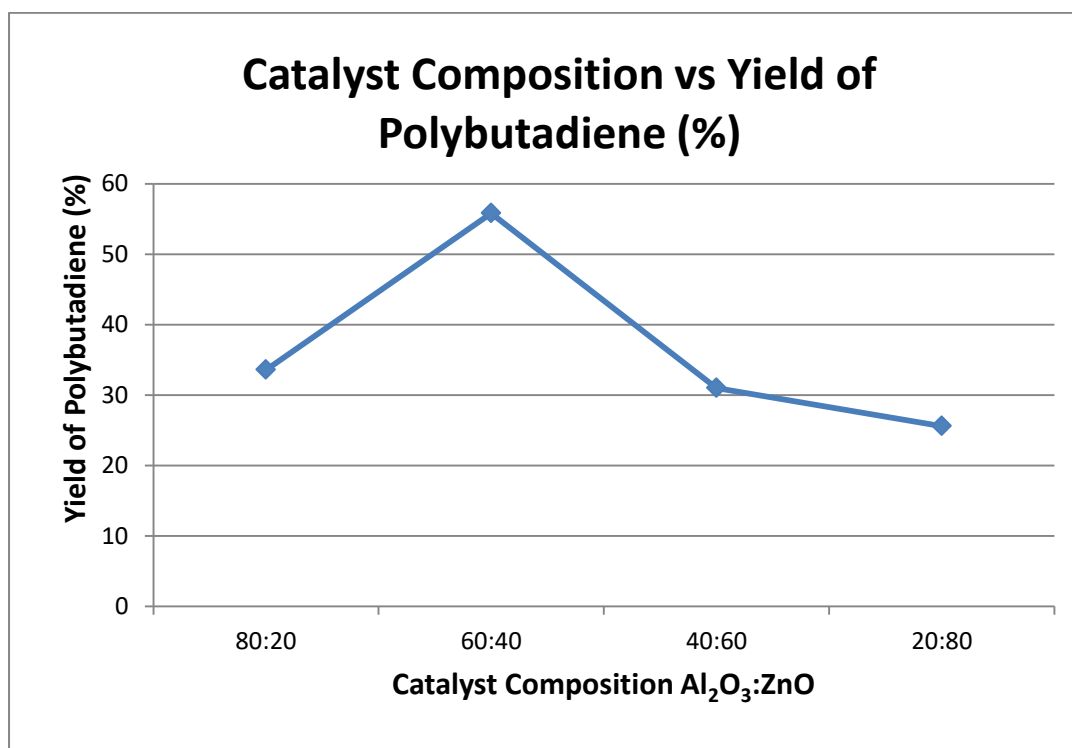

Figure 20 Catalyst Composition (Ratio) Vs Yield of Polybutadiene (%) Performane Curve

4. **20% Al_2O_3 : 80% ZnO:** This combination, which has the largest amount of ZnO, results in a polybutadiene yield of 25.6%. Although it still produces a sizable

output, it is less than the composition of 60% ZnO. This suggests that the reaction may not always be more positive with an extremely high ZnO fraction.

In conclusion, the findings show that the catalyst composition, particularly the ratio of Al_2O_3 to ZnO, significantly affects the yield of polybutadiene. It is important to choose the right catalyst composition to improve the polybutadiene manufacturing processes since different compositions have variable degrees of efficacy in driving the polymerization reaction.

4.2.3 Catalyst Composition vs Volume of Gas At STP:

The information presented here is the findings of a study on the production of synthetic rubber, with a particular emphasis on how the composition of the catalyst affects the amount of gas produced at Standard Temperature and Pressure (STP). The catalysts under research had four different compositions, ranging from 80% Al_2O_3 and 20% ZnO to 20% Al_2O_3 and 80% ZnO. The ratio of Al_2O_3 to ZnO in the catalysts varied. An association between the catalyst composition and the amount of gas generated at STP is suggested by the observed trend in the data. Notably, the volume of gas produced also showed a rising trend with increasing zinc oxide content in the catalyst.These results suggest that the catalyst composition is important for the synthesis of synthetic rubber, perhaps acting as a catalyst or affecting the kinetics of the reaction. With consequences for industrial procedures in the rubber production industry, further research and study of this connection may offer insightful tips for improving the synthesis of synthetic rubber.
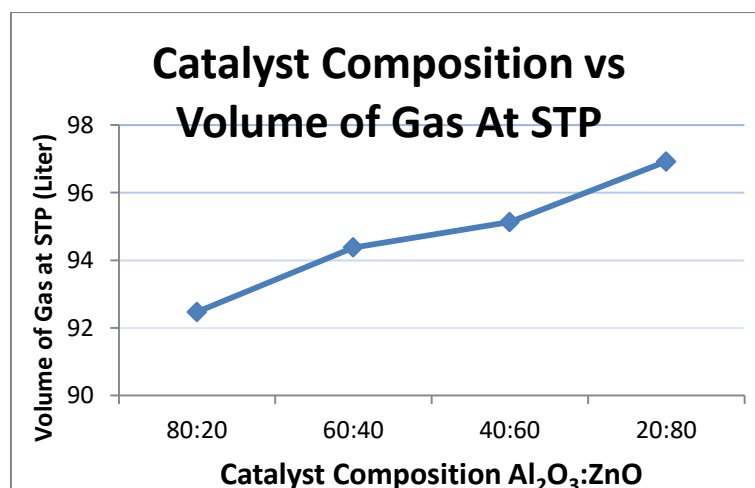

Figure 21 Catalyst Composition vs Volume of Gas At STP Performance Curve

4.2.4 Impact of Temperature and Ethanol Feed Rate on Polybutadiene Yield (%):

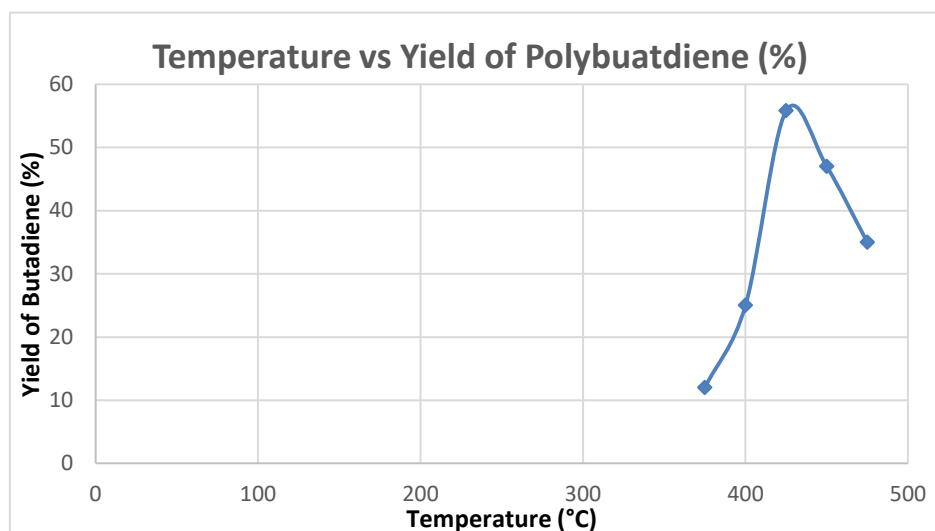In the presence of the catalyst alumina-zinc oxide **(60:40)** is as follows:

Figure 22 Temperature vs Yield of Polybuatdiene (%) Curve

From this graph, we came to know that when we increase the temperature up to 425°C, we get the highest butadiene yield of 55.8%.

4.2.5 Ethanol Feed Rate(ml/hr/g) Ethanol Feed Rate vs Polybuatadiene Yield (%)
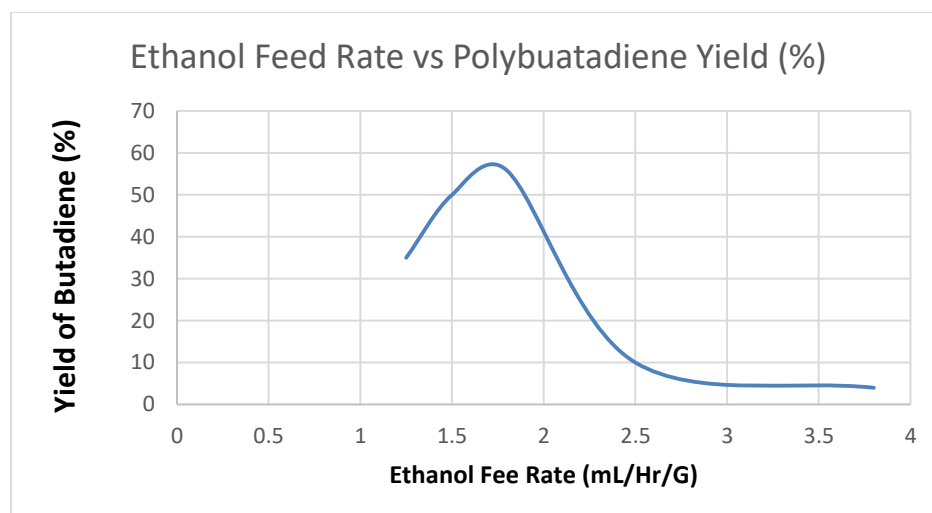

Figure 23 Ethanol Feed Rate vs Polybuatadiene Yield (%)

From this graph, we came to know that, we have to give the needed considered amount of the feed rate of 1.8 ml/h/g to get the highest butadiene yield of 55.8%.

4.3 Detail Discussion:

Based on the comprehensive research conducted on the one-step catalytic conversion of ethanol into butadiene using binary oxide catalysts, the following general conclusions can be drawn. Lebedev discovered that the most effective catalyst for the one-step conversion of ethanol into butadiene consisted of a composition with 75% dehydrogenating components and 25% dehydrating components. In the prevailing research the quality catalyst includes 60%, of dehydrating (Al_2O_3) and 40% of dehydrogenating (zinc oxide) component. Moreover, the catalyst blend consisting of 20% alumina and 80% zinc oxide exhibits significantly lower catalytic activity when compared to the superior catalyst.

(1) Optimum temperature:

The binary catalyst composed of aluminum and zinc oxide exhibits the highest activity within the temperature range of 425-450°C.

(2) The ideal ethanol feed rate:

In most cases, the ideal ethanol feed rate for binary catalysts ranges between 1.256 to 1.875 milliliters per hour per gram of catalyst, depending on the catalyst's characteristics.

(3) Ethanol concentration in the feed:

The study primarily focused on the ethanol concentration in the feed, specifically within the alumina-zinc oxide (60:40) system. Considering the reaction's nature and the catalysts' functions, it can be inferred that excessively diluting the ethanol feed with water will have a negative impact on butadiene yield. It is acceptable to dilute the ethanol down to 90% without experiencing any reduction in the process yield of ethanol to butadiene.

Figure 24: Complete Setup

CHAPTER 5

Conclusion

In conclusion, the synthesis of synthetic rubber has been a significant scientific and industrial achievement with far-reaching implications. Through meticulous research and technological advancements, scientists and engineers have successfully developed various types of synthetic rubber that mimic the properties of natural rubber, offering suitable substitutes for a variety of uses.

Development of synthetic rubber has played a vital role in addressing the growing demand for rubber-based products, especially during times of natural rubber shortages and economic fluctuations. The versatility, durability, and superior performance of synthetic rubber have allowed it to become an essential component in various industries, including automotive, aerospace, construction, medical, and consumer goods. As we know that it's not possible in Pakistan to synthesize the synthetic rubber with petroleum product as Pakistan is not a fuel rich country so in this thesis we have developed and discussed an alternative method to produce the synthetic rubber.

This work offers a fresh approach to ethanol-based polybutadiene production. The process entails employing a catalyst to convert ethanol into butadiene followed by the synthesis of polybutadiene via living anionic polymerization. The resulting polybutadiene will be characterized using a range of techniques to evaluate its physical properties. The findings of this investigation will aid in the creation of sustainable and renewable resources for the production of polybutadiene, paving the way for future research in this field.

As the global demand for rubber-based products continues to grow, the synthesis of synthetic rubber will remain a critical field of research. Future research in this field ought to concentrate on improving the performance and eco-friendliness of synthetic rubber, exploring new materials and manufacturing techniques, and promoting recycling and waste reduction.

In conclusion, the synthesis of synthetic rubber has revolutionized industries and daily life, serving as a testament to human ingenuity and innovation. As we move forward, continued advancements in this field will undoubtedly contribute to a more sustainable and technologically advanced society, ensuring that synthetic rubber continues to be a foundational material in various applications for years to come.

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