STREAM CONNECTION MATRIX MODELING AND SENSITIZED OPTIMIZATION OF REACTIVE DISTILLATION

Inhouse Research Project Report

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Chemical Engineering

Submitted By

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UNDER THE SUPERVISION AND GUIDANCE OF

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ABSTRACT

Oxygenated energies similar as alcohols and ethers have the eventuality to give dependable sources and environmentally friendly energy to world's adding unborn energy demands. They enhance energy combustion and thereby reduce exhaust emigrations while some of them also boost gasoline octane. Modeling is referred to as the mimic the behaviour of chemical processes under various operating conditions while simulation is referred to as the operation of an existing system. The stream connection matrix is an array with these entries per row and is a method of conversion of information diagram into numerical form where the stream number corresponding to the incoming and outgoing units are mentioned. Reactive distillation is a process in which chemical response and conventional distillation are integrated in a single outfit represents one of the best known exemplifications of the process intensification. This research paper outlines a comprehensive process involving the reactive distillation of oxygenated fuels resulting in the improved fuel recovery, along with the dynamic simulations were carried out. The result shows that purity of 95% and 65% for biodiesel and TAEE respectively is obtained in reactive distillation corresponding to reboiler duty of 2 kW and reflux ratio 4.

Keywords: Oxygenates, Reactive Distillation, Simulation, Modeling

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ACRONYMS

RVP	Reid Vapour Pressure
MTBE	Methyl tert-butyl ether
ETBE	Ethyl tert-butyl ether
TAME	Tertiary amyl methyl ether
TAEE	Tertiary amyl ethyl ether
IPA	Iso-Propyl Liquor, 2-Propanol
MMT	Methylcyclopentadienyl Manganese Tricarbonyl
RD	Reactive Distillation
CD	Cataytic Distillation
RWD	Reaction with Distillation
DAA	Diacetone liqour
TEL	Tetraethyl lead
TML	Tetra methyl lead
TMEL	Tetra methyl ethyl lead
EPA	Environmental Protection Agency
ISOM	Information Systems and Operations Management
RADFRAC	Radial Fractionation
RDC	Reactive Distillation Column
MATLAB	Matrix Laboratory
DWSIM	Dynamic Simulation of Chemical Processes in Steady State and Dynamic State
KW	Kilo Watt

NOMENCLATURE

Q_C	Condenser Heat duty
Q_W	Reboiler Heat duty
h_D	Enthalpy of distillate
h_w	Enthalpy of residue
H_w	Enthalpy of vapor leaving the reboiler
ΔHv	Heat due to vaporization
x_D	Mole fraction of distillate
M_D	Holdup of distillate
V_1	Vapor Molar flow rate on 1^{th} tray
$y_{n,i}$	Vapor mole fraction of component *i* on n^{th} tray
D	Distillate flow rate
RR	Reflux ratio
R	Reflux rate
$x_{n,i}$	Liquid mole fraction of component *i* on n^{th} tray
L_{n+1}	Liquid Molar flow rate of $n+1^{th}$ tray
V_{n-1}	Vapor Molar flow rate on $n-1^{th}$ tray
$y_{n-1,i}$	Vapor mole fraction of component *i* on $n-1^{th}$ tray
L_n	Liquid flow rate on n^{th} tray
M_n	Liquid holdup on n^{th} tray
$R_{n,i}$	Net reaction rate of component *i* on n^{th} tray
F_n	Input feed flow rate on n^{th} tray
$z_{n,i}$	Feed mole fraction of component *i* on n^{th} tray
$x_{w,i}$	Liquid composition of bottom product
M_W	Reboiler holdup
W	Residue Flow rate
V_W	Molar Flow rate of vapor leaving the reboiler
$Y_{W,i}$	Mole fraction of vapor leaving the reboiler
H_{n-1}	Enthalpy of liquid at n-1 th plate
H_{n+1}	Enthalpy of vapor at n+1^{th} plate
h_n	Enthalpy of liquid at n^{th} plate
H_n	Enthalpy of vapor at n^{th} plate
h_f	Enthalpy of the Feed
λ	latent heat of the reaction
V_R	Volume of the Reactive Zone

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CHAPTER 1: INTRODUCTION

1.1. Fuel Oxygenates:

Oxygenates play a veritably important part in high octane gasoline. By adding an oxygenate to a energy. Oxygenate is a chemical composition that contains oxygen. It is used as an octane booster to replace poisonous and carcinogenic composites such as lead; it has a positive impact on air quality and therefore has a direct positive effect on mortal health and the terrain.

The energy oxygenates are expected to retain the following parcels:

1. High energy content

2. It should have a high octane standing.

3. It should have low RVP.

The advantages of using the fuel oxygenates are:-

1. **Improved Combustion Efficiency:** Fuel oxygenates enhance the oxygen content of gasoline, leading to more complete combustion in engines. This results in increased fuel efficiency and reduced emissions of pollutants like carbon monoxide and unburned hydrocarbons, contributing to cleaner air quality.
2. **Higher Octane Rating:** Oxygenates can increase the octane rating of gasoline, which improves engine performance and prevents engine knocking or pinging. This allows for the use of higher compression ratios in engines, leading to greater power output and efficiency.
3. **Renewable Energy Source:** Many fuel oxygenates, such as ethanol, are derived from renewable biomass sources like corn, sugarcane, or cellulose. Using these renewable feedstocks reduces reliance on finite fossil fuels and helps mitigate greenhouse gas emissions associated with traditional gasoline production.
4. **Reduced Dependence on Petroleum:** Incorporating oxygenates into gasoline blends reduces the need for crude oil-derived components, enhancing energy security and diversifying fuel sources. This can lead to a more stable fuel supply chain and reduced vulnerability to fluctuations in oil prices or geopolitical tensions.
5. **Environmental Benefits:** Fuel oxygenates can decrease emissions of harmful pollutants, such as particulate matter, nitrogen oxides, and volatile organic compounds (VOCs). This

helps mitigate air pollution, smog formation, and their associated health impacts, leading to improved public health and environmental quality.

6. **Promotion of Sustainable Agriculture:** Ethanol production from crops like corn or sugarcane can provide additional revenue streams for farmers and support rural economies. Additionally, the cultivation of biomass for fuel production can promote sustainable agricultural practices and land management.
7. **Compliance with Regulations:** Many regions have regulations mandating the use of oxygenates in gasoline to meet air quality standards and reduce emissions. Using fuel oxygenates allows fuel producers and distributors to comply with these regulations and support efforts to address environmental challenges.

Some of the commonly used fuel oxygenates are:-

A. **Alcohols:** Methanol and ethanol are alcohols which have been used as octane booster. They work since both have a higher octane number than typical street gasoline. They are more effective in low octane gasoline than in high octane gasoline. Alcohol has an affinity for water.

- **Synthesis Process:**

Since ethanol is created from plants that saddle daylight, it is also considered a sustainable fuel. Ethanol is made by the aging of sugars. Alcoholic maturation, moreover referred to as ethanol maturation, is a natural prepare in which sugars such as glucose, 6 fructose, and sucrose are changed over into cellular vitality and subsequently create ethanol and carbon dioxide as metabolic squander items. Since yeasts perform this change in the absence of oxygen, alcoholic maturation is considered an anaerobic handle.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$$

$$2C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

- **Physical Properties:**

1. Ethanol is an alcohol, a group of chemical components whose molecules contain a hydroxyl group (-OH) bonded to a carbon atom.
2. Ethanol (CH_3CH_2OH) is a clear, colorless liquid with a specific pleasant odor, and it is soluble with water and most organic solvents in all proportions.
3. Ethanol has a boiling point of 173 °F and an energy content of 76,000 BTU per gallon.

- **Mixing Characteristics:**

1. Ethanol has an octane rating of 115 and a mixing RVP of 18.
2. Ethanol's mixing RVP is altogether higher than most of the ether.
3. The ethanol atom contains 34.8% oxygen by weight, nearly twice as much as MTBE. In this way, ethanol will give less weakening than other oxygenates when mixed at the equal oxygen level.

- **Limitations:**

1. Ethanol has a high affinity for water. If gasoline that has ethanol in it comes into contact with water, the ethanol and water will combine to form a separate phase, separating from the gasoline.
2. Another significant limitation to using ethanol in gasoline, especially during the summer months, is its impact on the Reid Vapor Pressure (RVP) of gasoline. Ethanol increases the RVP of the mixture by approximately 1 pound per square inch (psi) at the required levels.

B. **Ethers:** These have higher octane values than typical gasoline so like the alcohol they will increase the octane quality of street gasoline. Ethers do not have an affinity for water will not separate from gasoline, and blend like a hydrocarbon.

- **MTBE:** It stands for methyl tert butyl ether. It is generally blended in gasoline in volumes up to 15 percent.

- **Synthesis Process:**

MTBE, in recent times, is produced through a process involving isobutylene and methanol. The isobutylene used for ether production primarily comes from steam cracking during olefin production and fluid catalytic cracking during gasoline production. Methanol is mainly produced through the synthesis of carbon and hydrogen mixture.

$$CH_3OH + (CH_3)_2CCH_2 \rightarrow CH_3OC\ (CH_3)_3$$

- **Physical Properties:**

1. MTBE is a synthetic chemical used as a blending component in gasoline.

2. It is a colourless liquid at room temperature and is flammable,relatively non volatile and has a high octane value and is soluble in gasoline which means it disperses evenly and stays suspended without requiring physical mixing.
3. MTBE has a water water solubility of 4.3% and a boiling point of 131 °F while the energy content is about 93,000 British thermal units per gallon.

- **Mixing Characteristics:**

1. MTBE has an octane rating of 110 that makes it especially valuable as a gasoline octane booster since fragrant components such as benzene, customarily utilized to increment gasoline octane, are restricted beneath the reformulated gasoline regulations.
2. It moreover gives great weakening of undesirable components (aromatics, sulfur, olefin and benzene).
3. The MTBE atom contains 18.2% oxygen by weight.

- **Limitations:**

1. Because of leaking underground storage tanks or spills and because MTBE is soluble in water and does not biodegrade easily, there have been increasing detections of MTBE in ground waters and reservoirs.
2. MTBE dissolves easily in water and does not cling to soil very well, it migrates faster and farther in the ground than other gasoline components, thus making it more likely to contaminate public water systems and private drinking water wells.

- **ETBE:** It stands for ethyl tert butyl ether.Blending with ETBE, moves forward the combustion characteristics of petrol, and is moreover more consistent with pipelines and motors than ethanol.

- **Synthesis Process:**

The bio-ether ,ETBE is a subordinate from bioethanol, which is gotten from the refining of wheat and/or sugar beet. It is by distant the biofuel of choice nowadays. It is formed from ethanol and isobutylene in a catalytic reaction.

$$CH_3CH_2CH_3 + C_2H_5OH \rightarrow (CH_3)_3OC_2H_5$$

- **Physical Properties:**

1. ETBE is a colorless fluid with a characteristic gentle odor.
2. Its central characteristics are miscibility with gasoline, low mixing vapor weight, and good refining properties.
3. ETBE has a somewhat higher octane rating than MTBE while the energy substance of ETBE is almost 104,530 British warm units per gallon.

- **Mixing Characteristics:**

1. ETBE has an octane rating of 110 that makes it especially valuable as a gasoline octane booster.
2. The MTBE particle contains roughly 16.7 percent oxygen by weight.
3. RVP of ETBE is 4 which is much lower and octane RON is 120, much higher than MTBE and other alcohols and subsequently give way better octane boosting property.

- **Limitations:**

1. Since due to the azeotropic properties of ethanol, the ETBE framework contrasts particularly from that used for MTBE/TAME. Noteworthy sum of ethanol is display in the well-off from the reactor which has to be once more separated.
2. ETBE's reactivity contrasts from MTBE in one regard: it can shape peroxides in the presence of oxygen gas or oxidative specialists and subsequently a stabilizer is regularly included during manufacture.

- **TAME:** It stands for tertiary amyl methyl ether.It is considered to gotten to be a way better elective to a presently wrangled about MTBE and will supplant it as a favored oxygenate mixing component for green gasoline. It is made out from the light olefins like iso-amylenes.

- **Synthesis Process:**

  The essential TAME arrangement responses are:

$$CH_3OH + \text{2-methyl-1-butene} \leftrightarrow \text{TAME}$$

$$CH_3OH + \text{2-methyl-2-butene} \leftrightarrow \text{TAME}$$

Some TAME generation units employments tall virtue isopentane (minimum virtue 98%) in its generation process. This insurrection TAME's tall quality and gasoline execution characteristics. Methanol shapes an azeotrope with C5-hydrocarbons containing around 20% of methanol. On the other hand, the appropriate sum ought to not be surpassed much since the parcel of unreacted methanol which surpasses the sum required to build up the azeotropic composition at the beat, will conclusion up to the foot item, i.e. into the TAME product.

- **Physical Properties:**

1. TAME highlights a high octane number, measuring almost 112 communicated as RON enquire about octane number, demonstrative of ordinary street performance.
2. TAME too express octane number as MON Engine Octane Number, of 100 characteristic of high speed execution, a more extreme set of conditions.
3. Compounded or reformulated gasolines are prescribed to mix TAME in at a normal 15% by volume and has a warming esteem of 27900 KJ/l.

- **Mixing Characteristics:**

1. The TAME atom contains 15.6 percent oxygen by weight.
2. RVP of TAME is 10.34 KPa, least of all ethers and alcohols.
3. TAME has an octane rating of 112 which is middle between MTBE and ETBE.

- **Limitations:**

1. MTBE is a significant water pollutant and long-range transport potential of the oxygenates increased in the order of TAME, ethanol and MTBE.
2. TAME was shown to partition the least into water from a fuel phase, showing no co-solvency characteristics. TAME was found to be the most toxic of the three oxygenates investigated; however, it is not classified as a lethal agent.

- **TAEE:** It stands for tertiary amyl ethyl ether. TAEE is astonishing blending component due to its moo flimsiness, tall octane number and they do not contain aromatics and olefins. So the use of TAEE as characteristic welcoming and money related oxygenates is extending in afterward years.

- **Synthesis Process:**

The synthesis of TAEE from TAA and ethanol can be promising course as both reactants are derived from renewable resources.

$$2C_5H_{12}O + C_2H_5OH \rightarrow 2C_6H_{14}O + H_2O$$

It can in addition be made utilizing iso-amylenes in put of TAA but since of basic availability of TAA in the shape of by thing from other handle, iso-amylenes are once in a while used.

- **Physical Properties:**

1. TAEE has a MON of 98 and RVP of 6.9 which is unimaginably lower than other conventional oxygenates.
2. TAEE has outstandingly moo insecurity and is by and expansive collected at the foot; it has a tall bubbling point of 106 C.
3. It has uncommonly low water dissolvability around 4 gm/l at 20 C.

- **Blending Characteristics:**

1. Its oxygen substance is 13.8% by weight.
2. It has an octane rating of 112.
3. TAEE instantly mixes with other gasoline components and can be instantly transported through the existing gasoline transport system.

- **Limitations:**

1. Since TAEE burn in discuss exceptionally effectively, an evaluation of their potential dangers depends on flash focuses and start temperatures. It too tends to retain and respond with oxygen from the discuss to shape unsteady peroxides that may explode with extraordinary savagery when concentrated by vanishing or refining, when combined with other compounds that deliver a detonable blend, or when aggravated by warm, shock.
2. The exploratory conditions must be carefully chosen, since TAEE deterioration and a tall by-products arrangement happened if tall weights or D/F proportions were utilized during the column operation.

C. Other Fuel Oxygenates:

- **Tertiary Butyl Liquor;2-Methyl-2-Propanol (TBA):** Work amid the 1970s demonstrated the prevalent properties of TBA to other alcohols from the standpoint of gasoline compatibility. It is delivered inside the petrochemical industry as an middle of the road and for particular employments. The generation is little, basically in the US Inlet Coast and Europe. This can be produced in the same plant as MTBE and can frequently be a contaminant of trading MTBE. The little sum of TBA in the MTBE has small impact on the last mentioned additive's viability.

- **Iso Propyl Liquor, 2-Propanol (IPA):** It is as well utilized as a dissolvable and to convey other chemicals. At show a major divide of IPA is made from acetone (which in turn is conveyed as a byproduct from the create of phenol). Refineries can provide amazing sums of propylene and this can be the quick forerunner to the era of IPA.

- **Di-Iso-Propyl-Ether (DIPE):** It is a allowed added substance beneath US Government reformulated gasoline directions and the proposed Euro-3 and Euro-4 rules. It is obtained from propylene and water. Isopropanol is a byproduct. The world capacity is obscure but likely little.

- **Non-oxygenate octane boosters:** Organometallic compounds boost octane but contribute unimportant oxygen substance (in the event that any) to the wrapped up gasoline. Until presently, lead alkyls have been overwhelming. Numerous other organometallic compounds have been attempted, but as it were two have risen with potential. An press based additive, ferrocene, and a manganese added substance, MMT.

  i. **Ferrocene (dicyclopentadienyl iron):** Ferrocene is a dim orange coloured powder, openly dissolvable in hydrocarbons. It is ready to use from Related Octel as. To date, ferrocene added substance has struggled to pick up industry acknowledgment. The fundamental issue shows up to be the erosive nature of the combustion items.

  ii. **Methylcyclopentadienyl Manganese Tricarbonyl (MMT):** This is a fluid octane enhancer for unleaded and lead substitution petrol. It is a pure compound of moo vapor weight (0.05 mmHg @ 20 °C), tall streak point (96 °C) and thermally stable to its bubbling point (232 °C). It has amazingly moo solvency in water, but is freely soluble in gasoline. This has been broadly inquire about from the 1950s and is in broad use in a few nations.

D. **High octane hydrocarbons:** There are a few components of gasoline of tall octane which a broadly exchanged. They can be utilized as octane boosters and blendstocks, a few of these materials are: butane, benzene, toluene, xylenes, isooctane.

- **Biodiesel:**

Biodiesel is a renewable fuel derived from vegetable oils, animal fats, or recycled cooking grease through a process called transesterification. It is commonly blended with petroleum diesel to reduce greenhouse gas emissions and dependence on fossil fuels. Biodiesel can be used in diesel engines without modification and offers several environmental benefits, including lower emissions of carbon dioxide, particulate matter, and sulphur oxides. These can be produced from a variety of feedstocks, including soybean oil, canola oil, palm oil, and waste oils and fats. The choice of feedstock can impact the sustainability and environmental profile of biodiesel production. It is often blended with petroleum diesel in various proportions, with common blends including B5 (5% biodiesel, 95% petroleum diesel), B20 (20% biodiesel, 80% petroleum diesel), and higher blends for specialized applications. It offers significant environmental benefits compared to petroleum diesel, including lower emissions of greenhouse gases, particulate matter, and sulphur oxides. It is also biodegradable and non-toxic, thus making it safer for handling and transportation.

1.2.Reactive Distillation:

Reactive distillation (RD) is a process that combines catalytic chemical reactions and distillation (the fractionation of reactants and products) within a single apparatus. This technique is a part of process intensification technologies, aiming to enhance efficiency and performance. From a reaction engineering perspective, RD can be classified as a two-phase countercurrent fixed bed catalytic reactor.In literature, this integrated reaction-separation technique is also referred to as CD or RWD. Catalytic distillation specifically describes a process where a heterogeneous catalyst is situated in a distinct zone of a distillation column. The term reactive distillation is broader and encompasses both homogeneously and heterogeneously catalyzed reactions within distillation columns.Typically, a reactive distillation column consists of a reactive zone in the middle, a rectifying zone above the reactive zone, and a stripping section below the reactive zone. This setup allows for the simultaneous reaction and separation of components, enhancing overall process efficiency.

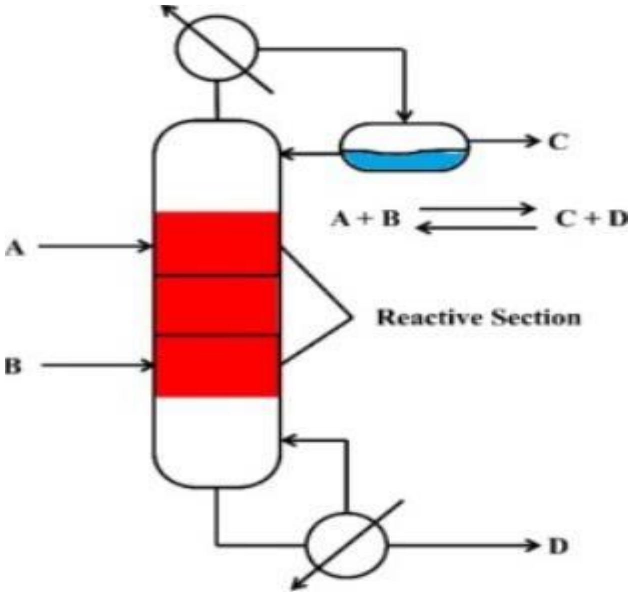

Fig.1. Illustrative diagram of Reactive Distillation

(Image Source:-Science Direct)

1.2.1. Advantages of Reactive Distillation:

RD technology has several advantages over conventional operating methods, such as a fixed bed reactor connected to a fractionating column, in which the distillate or bottoms have to be recycled after further separation steps for a total overall conversion.

1. **Improved Efficiency:** Reactive distillation eliminates the need for separate reactors and distillation columns, leading to reduced equipment costs, lower energy consumption, and higher overall process efficiency.
2. **Enhanced Selectivity:** The intimate contact between reactants and products within the distillation column promotes improved selectivity by minimizing side reactions and maximizing desired product formation.
3. **Reduced Footprint:** Integration of reaction and separation in a single unit operation reduces the overall footprint of the process, making it particularly attractive for space-constrained environments.

4. **Increased Yield:** Reactive distillation enables higher product yields by continuously removing products from the reaction zone, thereby shifting the equilibrium towards product formation.
5. **Flexibility:** It offers flexibility in process design and operation, allowing for optimization of reaction conditions, product purity, and yield.
6. **Environmental Benefits:** Reduced energy consumption and lower waste generation contribute to environmental sustainability, making reactive distillation an environmentally friendly option compared to traditional separation processes.

1.2.2. Constraints of Reactive Distillation:

Reactive distillation, despite its advantages, faces certain constraints and limitations that can affect its applicability and performance. Some key constraints associated with reactive distillation are :

1. **Equilibrium Limitations:** Reactive distillation operates based on the principles of chemical equilibrium. For reversible reactions, achieving high conversions may be limited by the equilibrium constant of the reaction. This can result in lower yields and selectivity compared to ideal conditions.
2. **Mass Transfer Limitations:** Mass transfer limitations can affect the efficiency of reactive distillation, particularly for systems with slow-reacting or bulky molecules. Poor mass transfer rates can lead to reduced conversion, selectivity, and overall process performance.
3. **Heat Transfer Limitations:** Efficient heat transfer is essential for maintaining optimal reaction conditions and column performance in reactive distillation. Heat transfer limitations can arise due to temperature gradients, fouling, or phase equilibrium effects, affecting process efficiency and control.
4. **Catalyst Compatibility:** The choice and management of catalysts in reactive distillation systems can be challenging. Catalyst deactivation, poisoning, or instability under reactive distillation conditions can impact process performance and longevity, requiring careful selection and maintenance.
5. **Kinetic Effects:** Kinetic limitations can influence the rate and extent of chemical reactions in reactive distillation. Systems with complex reaction mechanisms or multi-step reactions

may exhibit non-ideal behavior, leading to deviations from expected performance and complicating process optimization.

6. **Separation Efficiency:** Reactive distillation combines reaction and separation processes within the same unit, but achieving optimal separation efficiency can be challenging. Non-ideal phase equilibria, entrainment, and vapor-liquid disequilibrium can affect product purity and yield, requiring careful column design and operation.
7. **Design Complexity:** Designing reactive distillation systems requires consideration of multiple factors, including reaction kinetics, thermodynamics, mass transfer, and heat transfer. Balancing these factors to achieve desired performance can be complex and may involve trade-offs between conflicting objectives.
8. **Scale-Up Challenges:** Scaling up reactive distillation processes from laboratory or pilot scale to commercial production can be difficult due to differences in fluid dynamics, heat and mass transfer, and equipment performance. Ensuring consistent performance and product quality across different scales requires careful consideration of scale-up factors and process modifications.
9. **Operational Stability:** Maintaining stable operation of reactive distillation systems over extended periods can be challenging due to factors such as catalyst degradation, fouling, or process upsets. Robust control strategies and preventive maintenance measures are necessary to ensure reliable operation and product quality.

1.2.3.Applications of Reactive Distillation:

Reactive distillation column is generally employed for reversible reaction because the conversion for reversible reactions is limited in conventional reactors because of limitation of chemical equilibria which was improved in reactive distillation column. Some common applications include:

- **Acetylation:** Biodiesel generation from vegetable oil produces glycerol as by-product with the sum of almost 10 wt% of its item. This over the top sum of glycerol needs to be changed over into the higher important item. One of the planned glycerol’s derivatives is triacetin, a great bio-additive as anti-knocking operator. The generation utilizing 18 continuous receptive refining come about in glycerol change of 98.51% and 8.84% of triacetin selectivity.

- **Aldol condensation:** Aldol condensation of acetone in the nearness of corrosive catalyst gives diacetone liquor (DAA) as an middle of the road item, which advance dehydrates to provide mesityl oxide. By utilizing receptive refining (RD), one can make strides selectivity toward DAA, by persistently expelling it from the receptive zone and in this manner suppressing the parchedness reaction
- **Alkylation:** Reactive distillation innovation is connected for alkylation in case of ethyl benzene and cumene manufacturing.
- **Amination:** Coordinate amination of benzene to aniline where watery smelling salts was employed as aminating specialist with hydrogen peroxide as oxidant and copper doped catalyst, utilizing a receptive refining reactor beneath gentle conditions.
- **Lack of hydration:** Lack of hydration of glycerol was performed in the nearness of different metallic catalysts counting alumina, magnesium, ruthenium, nickel, platinum, palladium, copper, raney nickel, and copper-chromite catalysts to get acetol in a single-stage receptive distillation unit beneath mellow conditions.
- **Esterification:** In ordinary methyl acetic acid derivation generation, the yeild of methyl acetic acid derivation is low since of moo bubbling azeoptrope arrangement. This limitation is expelled in reactive distillation and almost immaculate methyl acetic acid derivation can be collected.
- **Etherification:** The application of reactive distillation innovation is restricted to union of methyl tert butyl ether, ethyl tert butyl ether, tert amyl ethyl ether and tert amyl methyl ether. Because of their great octane moving forward capacity, these ethers are great mixing component.
- **Hydrolysis:** Receptive refining tests have been performed for the union and hydrolysis of methyl acetic acid derivation utilizing the organized catalytic pressing Katapak-S with an acidic ion-exchange gum (Amberlyst 15) as the heterogeneous catalyst.
- **Isomerization:** a-isophorone and b-isophoroneinspite of being isomer can be exceptionally well separated by responsive refining as there is huge contrast in their volatilities.
- **Oligomerization:** Oligomer esters and corrosive were hydrolyzed utilizing reactive distillation innovation and results were steady with mechanical literature.

- **Transesterification:** Transesterification for blend and characterization of bio diesel from distinctive crude fabric such as palm oil, mustard oil etc has been investigated utilizing various homogeneous and heterogeneous catalysts.

CHAPTER 2: LITERATURE SURVEY

2.1. Historical Background:

Gasoline:

From around 1850 until 1900, gasoline was regarded as a worthless by-product of light fuel generation and was typically disposed of by burning. However, with the development and rising demand of the automobile, the demand for gasoline surged between 1900 and 1920. Thermal cracking defined as a process for breaking down heavier hydrocarbons into gasoline-range hydrocarbons, was introduced around 1913 to help meet this increased demand.

The need for gasoline grew significantly during World War I and continued to expand throughout the 1920s and 1930s. Before the 1920s, it was often sold at general stores, and hardware stores. The number of gasoline units in the United States rose dramatically from around 12,000 in 1921 to 143,000 by 1929.

The Clean Air Act (CAA) of 1970 established numerical limits for car exhaust emissions: 2.11 grams per kilometer of carbon monoxide and 0.25 grams per kilometer of hydrocarbons, with a observance deadline of 1975. Nitrogen oxide emissions were to be decreased to 0.25 grams per kilometer by 1976.

Gasoline Blending Agents and Additives:

Gasoline additives have been used commercially in the world since 1923 to enhance performance or to solve engine operating problems. Literally hundreds compounds have been used as gasoline blending agents or additives. The following discussion is limited to some of the most universally used and major additives and blending agents.

- **Lead Additives:** As vehicle engineers advanced engine control and efficiency, they encountered the problem of noisy combustion, commonly known as knocking. Engine knock was found to be associated with low-octane gasoline. Tetraethyl lead (TEL) was the first widely accepted gasoline additive for reducing engine knock.
  TEL, developed as an anti-knock agent in December 1921 by Thomas Midgley and Thomas Boyd of General Motors Research Corporation, was first marketed on February 1, 1923, in

Dayton, Ohio. Four months later, TEL-enhanced fuel was used by the top three finishers in the 1923 Indianapolis 500.

- **Methyl-Tert-Butyl Ether (MTBE):** MTBE was used as an octane booster for unleaded gasoline. In 1979, the Atlantic Richfield Company (ARCO) received EPA approval to add up to 7.0% MTBE to unleaded gasoline. Between 1980 and 1986, MTBE usage grew by about 40% annually.

- **Tert-Butyl Alcohol (TBA):** In 1979, the Atlantic Richfield Company (ARCO) received EPA approval to use TBA (tert-butyl alcohol) as an octane booster in unleaded gasoline at concentrations up to 7.0% by volume.

- **Methyl Cyclopentadienyl Manganese Tricarbonyl (MMT):** The invention of MMT, a trademark of the Ethyl Corporation, was announced in June 1957, along with results showing a 20% power increase in aircraft engines. MMT usage was stopped in Canada in 1997, but the ban was lifted in July 1998.

- **Other oxygenates- ETBE, TAME and TAEE:** Global demand of fuel ethers was 16.5 million tons in 2009, and consisted of 78% MTBE, 14% ETBE, and the remainder was TAME and TAEE. 26% of ethers were consumed in Europe and 25% in the Asia-Pacific. Fuel ethers are substantially used also in Latin America and the Middle East. (EFOA 2011). In Europe, MTBE and ETBE are dominating fuel ethers. ETBE and ethanol are increasing 28 their shares of gasoline pool following the bio fuel policies. In Europe, the demand for fuel ethers was about 6 million tons, of which ETBE consumption around 2.5 million tons (~ 1.6 Mtoe) in 2009. Substantial portion of ethanol is used as ETBE in Europe.

From 2012 onwards and till presently, the major work in the field of fuel oxygenate begin focus on determining the isomeric fuel ether oxygenates; ethyl tert-butyl ether (ETBE), di isopropyl ether (DIPE), and tert-amyl methyl ether (TAME), isolated from aqueous frameworks with a pervaporation layer module.

2.2. Previous Studies:

Molecular reactive distillation (MRD) is a specialized form of reactive distillation that specifically involves the use of molecular sieves as catalysts or co-catalysts within the distillation column. In a work reported the paper is a case study in the use of distillation simulation and process analysis ways to guide the selection process for an applicable toller, develop the operating parameters for the distillation crusade, and give day-to-day direction for the crusade to overcome unexpected timeline challenges caused by a detention in launch up lower than the anticipated column efficiency, a power outage, a pump seal failure, and under performance of a rented cooling water chiller. The factory outfit estimated for the isomerization and distillation process was re-evaluated for a semi-continuous distillation without response. The thing was to determine the minimal fixed reflux rate that would produce the maximum average rate of 97-98 ISOM-1 with the lowest batch cycle time. Making a theoretical computation for a column with the same periphery as in the factory and an infinite number of theoretical stages it was set up that the minimal influx rate is 6.17 and that a 6 day distillation cycle would produce a theoretical outside of 27,450 lbs of 98 ISOM-1. Assuming 24 hours for outfit launch-up and arrestment for each batch, the average hourly production rate is 163.4 pounds. The product demand in 2013 was projected to be 239,207 pounds at 98 chastity (234,423 pounds real ISOM-1). Therefore the number of operating days would be about 61, with the stylish theoretical product capability. It was clear that the equipment would not be available for the needed time. Evaluation of other distillation outfit in Cytec revealed analogous residency challenges. So attention shifted to distillation by an outside toll manufacturer. The use of computer simulations and process analysis tools to guide the distillation campaign were important reasons that the product and product quality targets were met. Continuous monitoring of the mass and quality of accumulated product handed signals that the column operating conditions demanded to be changed to insure that product rates would meet the campaign objects in the fixed quantum of time available for the campaign. These process engineering ways were used to successfully give original and mid-course corrections that crushed the following unlooked-for issues that contributed to reducing the effective number of operating hours of the crusade that is accumulation of the target volume of purified ISOM-1 was completed sufficiently in advance of the fixed termination date of the crusade to permit all of the fresh purchased feedstock to be successfully reused through the column to produce fresh product grade ISOM-1.[1]

At present, there is a lot of artificial interest in multi-purpose reactors with in situ product separation of reactants. Reactive distillation (RD) is considered to be one of the best in-situ product processing methods. The major advantage of RD technology in terms of capital cost reduction is that two process ways can be performed in one device. Product selectivity can get better because of quickly getting rid of waste or making more of the things that are needed. This lowers the chance of a series of reactions happening one after the other in the next step. To lower the cost of the building, make sure to use the column space efficiently and avoid having empty space. Biographies can either be used as a charger column or a packed reaching column.[8]

In this paper, the common prepare plan strategy and reenactment methodology for receptive refining (RD) are displayed based on the comes about. The test comes about gotten from the steady RD column in our past work were compared with the reenactment comes about anticipated by three harmony step models of diverse profundities utilizing the Aspen also computer program. Three sorts of harmony step models with distinctive complexities are created, parameterized and compared within the reenactments of this work. These models are based on arrange plan and utilize vapor-liquid balance suspicions on each organize demonstrate. Response division forms (RSPs) combine the response and partition unit operations into a single concurrent operation. It gives an critical synergistic impact and brings a few benefits. This response and partition emulsion in a single combined operation brings simplicity and novelty to the method within the preparing plot. The RD handle advancement prepare connected here can be isolated into four stages. Reenactments with an equilibrium-based demonstrate with generally response energy within the fluid stage are performed. For the response zone, the number of response stages is to begin with indicated as one and the number of response stages is expanded to a most extreme of 10. An introductory appraise of the catalyst volume is gotten from the heater plan. The response for RD accept that the response area could be a pressed bed reactor (PBR). With dependable thermodynamic information, practical working conditions and thorough Aspen Furthermore execution modeling , it is conceivable to reenact genuine plant operations. Realization of the show conditions and all recreations are performed utilizing the Aspen RADFRAC model plus a consistent state test system, which is based on a strict harmony step demonstrate to execute the work conditions . In these models, the non-ideality of the fluid stage is taken into consideration by the non-random two-liquid model demonstrate and the gas stage is expected to be perfect. In this paper, the plan angles of the RD mongrel for the synthesis of isoamyl acetic acid derivation were displayed through steady-state reenactments for an RD column. We found that there was truly great understanding between the comes about of Aspen plus database and reality columns. It ought to be famous that the outside resistance to mass exchange at the solid-liquid interface is at that point not taken into consideration. A comprehensive scale-based show is required to account for these impacts, which is past the scope of the show work. [14]

Reactive distillation, or combining chemical reaction and separation of distillation products in one unit, offers many unique advantages over conventional processes and other techniques. This study describes modeling of the reactive distillation of methyl acetate products by esterification. Methyl acetic acid derivation and water are created by a fluid stage response of acidic corrosive and methanol at a temperature of 298 K and a weight of 1 atm within the nearness of an corrosive catalyst (such as sulfuric corrosive or sulfonic corrosive and an particle trade gum). Receptive refining forms have been an region of interest over the past two years. The combination of response and partition in a single unit is an progress over old refining, where response and partition are performed in different units, which increments the capital taken a toll of the plant. Receptive refining columns work close stoichiometric nourish conditions, which limits reusing costs and increments column and change proficiency. This RADFRAC is included within the commercial steady-state test system Aspen Furthermore. It is based on a thorough balance step show for tackling the Work condition. This high temperature created by the receptive refining prepare within the response segment was found to be due to the exothermic response happening in this area of the column. Comparable tall temperatures have not been already watched in column profiles of customary prepare frameworks. This can be since in this case the column was utilized as it were for partition and not for concurrent response and division. [18]

Fluid Bio-fuels are picking up significance since of accessibility all through the year instead of biogas because during cold season it encompasses a draining supply. Some important sources of Biomass food include grains and crops that are high in starch, leftovers from farms and forests, organic matter, animal scraps such as fish oil and excrement, and crops grown specifically for energy like miscanthus[23] .Vitality requirement is developing quickly due to quick developing Industrialization and population growth. The supply of oil and its products is under great strain to meet the needs of people and industry. In any case, vegetable oil was not considered as a fuel at that time, as there was an inexhaustible supply of unrefined oil. [24][25][26]

CHAPTER 3: MODELING AND SIMULATION OF RDC

3.1. Modeling:

Modeling refers to the process of creating mathematical representations of physical systems to simulate their behaviour, predict outcomes, and optimize processes.

- **Purpose:** Modeling serves several purposes in chemical engineering which includes the understanding the behaviour of chemical processes and systems, predicts the performance of existing processes or systems under different conditions helps in designing new processes or systems,plays an important role in optimizing process parameters to improve efficiency, yield, and product quality.

- **Types of Models:**

1. **Mathematical Models:** These models describe the behavior of a system using mathematical equations based on principles such as mass balance, energy balance, and reaction kinetics. Mathematical models can be deterministic or stochastic, depending on whether they incorporate randomness.
2. **Empirical Models:** Empirical models are based on experimental data and statistical analysis rather than fundamental principles. They are often used when the underlying mechanisms of a system are complex or poorly understood.
3. **Physical Models:** Physical models are tangible representations of systems, such as scale models or prototypes, used for visualization, experimentation, and validation of mathematical models.

- **Components of a Model:**

1. **Variables:** Represent quantities that can change within the system, such as concentrations, temperatures, pressures, and flow rates.
2. **Equations:** Mathematical expressions that describe the relationships between variables based on fundamental principles, empirical correlations, or experimental data.
3. **Parameters:** Constants or coefficients in the equations that determine the behavior of the system. These parameters are often determined through experimentation or estimation.

- **Modeling Techniques:**

1. **First-Principles Modeling:** Based on fundamental physical and chemical principles, first-principles models describe the behavior of a system using mathematical equations derived from conservation laws and reaction kinetics.
2. **Empirical Modeling:** Empirical models are developed from experimental data using statistical techniques such as regression analysis or machine learning algorithms. These models may lack physical interpretation but can be useful for predicting system behavior when underlying mechanisms are complex or unknown.
3. **Hybrid Modeling:** Hybrid models combine elements of first-principles and empirical modeling to capture both the physics of the system and empirical correlations.

- **Model Validation and Verification:**

1. **Validation:** Comparing model predictions with experimental data to assess the model's accuracy and reliability. Validation ensures that the model accurately represents the behavior of the real system.
2. **Verification:** Checking that the model is implemented correctly and accurately represents the intended system.

3.2. Stream Connection Matrix Modeling:

In this the sluice network is represented as a matrix where each row and column correspond to a specific sluice member or reach. The values in the matrix represent the connectivity between these parts, generally in terms of inflow, deposition transport or nutrient transport. The matrix is frequently peopled grounded on factors similar as physical characteristics of the aqueducts, geomorphology, land use and hydrological data. This modeling fashion can be applied using colourful computational styles and models, similar as hydrodynamic models, hydraulic models, and statistical models.

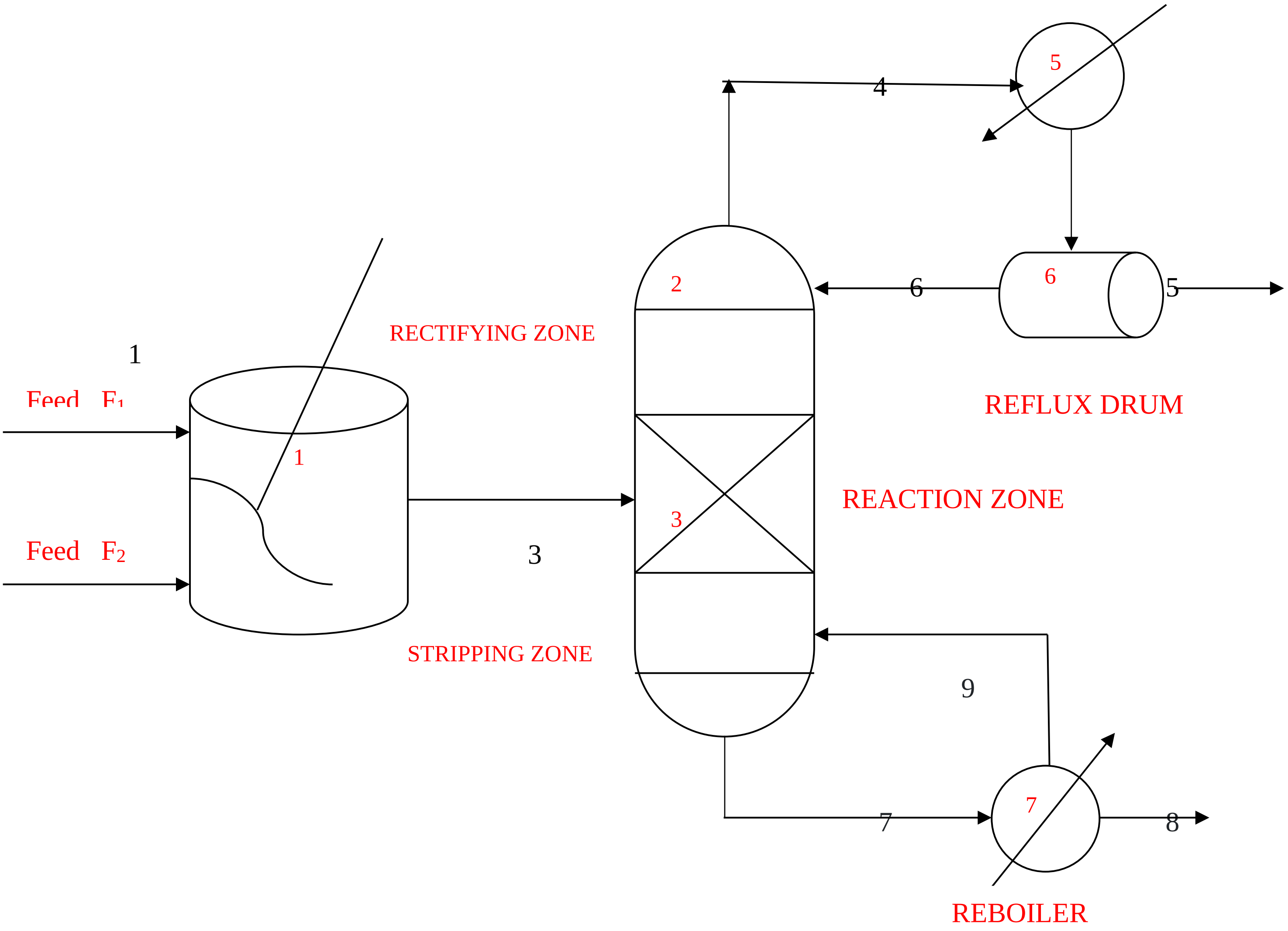

Fig.2. Schematic Diagram of Reactive Distillation

Table 1:Stream Connection Matrix Modeling of Reactive Distillation

Stream Number	From Unit Number	To Unit Number
1	1	3
2	1	3
3	1	3
4	2	5
5	6	0
6	6	2
7	4	7
8	7	0

9	7	4

3.2. Modeling of Reactive Distillation:

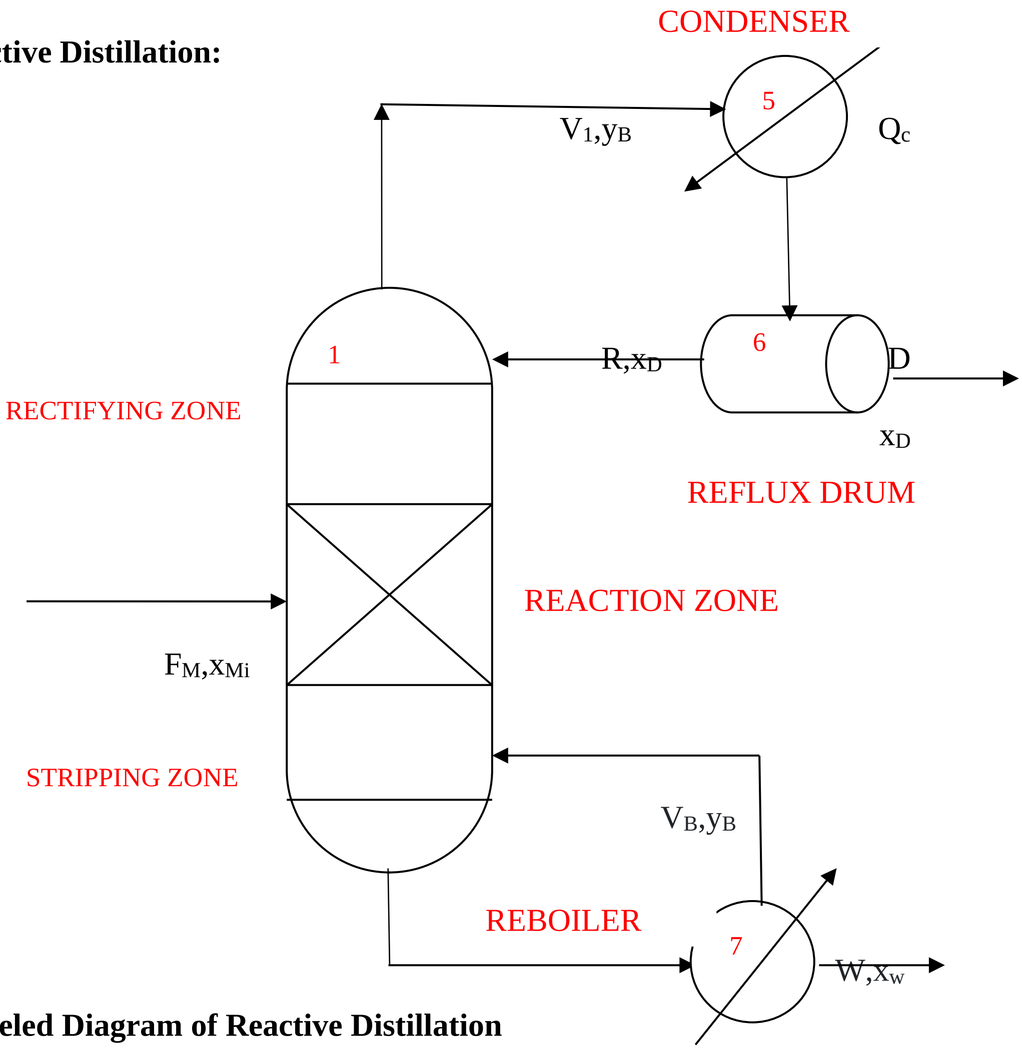

Fig.3. Modeled Diagram of Reactive Distillation

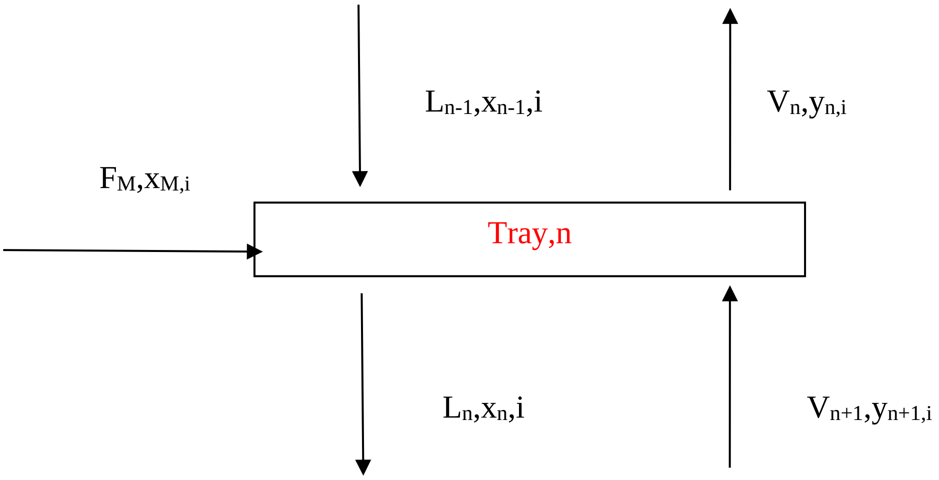

Fig.4. Schematic Diagram of nth tray

The following assumptions were made in order to write the balances over the system and to obtain modelled equations:

(1) Assume that every tray is an ideal stage.

(2) Take into account non-equal molar overflow.

(3) Model the liquid flow from each tray using a hydraulic time constant.

(4) Neglect the heat of mixing of water in acetic acid.

(5) Assume equilibrium driven reaction kinetics.

For Rectifying and Stripping Section:-

$d\,(x_{c,i}U_n)/dt = L_{n-1},x_{n-1} + V_{n+1},y_{n+1} - L_n - V_n$

For Reactive Tray:-

$d\,(x_nU_n)/dt = L_{n-1},x_{n-1} + V_{n+1},y_{n+1} - L_n - V_n + R_{nj}$

Feed Tray:-

$d\,(x_nU_n)/dt = L_{n-1},x_{n-1} + V_{n+1},y_{n+1} - L_n - V_n + R_{nj} + F_mx_m$

Net Reaction Rate:-

$R_{nj} = a_jU_n(k_{Fn}x_{ni} - k_{Bn}x_{MA})$

Reflux Drum:-

$d\,(x_DU_D)/dt = V_{NT}y_{NT},j - D(1+RR)x_{d,j}$

Column Base:-

$d\,(x_{wj}U_w)/dt = L_Nx_N - Wx_{w,j} - V_Sy_{wj}$

$V_n = V_{n-1} - (\lambda/\triangle H_v)\,R_{n,C}$

$L_n = L_{n-1} + (\lambda/\triangle H_v)\,R_{n,C}$

Reboiler Heat Duty:-

$Q_W = Wh_{w,i} + V_w\,H_{w,i} - L_N\,h_N$

Condenser Heat Duty:-

$QC = V_1H_1 - (R+D)h_D$

Energy Balance:-

$$V_{n+1} H_{n+1} + L_{n-1} h_{n-1} + F_n h_F - V_n H_n - L_n h_n - \lambda V_R R_{n,i} = \frac{d}{dt}(V_R H_R)$$

Fig.5. Laboratory Setup of Reactive Distillation

3.4.Simulation:

Simulation in chemical engineering involves using mathematical models to replicate the behaviour of real-world processes or systems over time.

- **Purpose:** Simulation is used to understand the dynamic behaviour of chemical processes and systems, predict how processes will perform under different operating conditions helps in optimizing the process design and control strategies and train operators and test new process concepts in a virtual environment.

- **Types of Simulation:**

1. Continuous Simulation: Models continuous processes where changes occur over time, such as fluid flow, heat transfer, and chemical reactions. Differential equations are typically used to describe system dynamics.

2. **Discrete Event Simulation:** Models systems where events occur at discrete points in time, such as manufacturing processes, supply chains, and queuing systems. Events trigger state changes in the system, and the simulation tracks these changes over time.
3. **Agent-Based Simulation:** Models complex systems by simulating the behavior and interactions of individual agents within the system. Agents have autonomous decision-making capabilities and interact with each other and their environment.

- **Simulation Software:** Chemical engineering simulation software packages provide tools for building, running, and analyzing simulations. Examples include Aspen Plus, MATLAB/Simulink, etc. These software packages offer libraries of pre-built unit operations, thermodynamic models, and reaction kinetics, as well as tools for optimization, sensitivity analysis, and visualization.

- **Simulation Process:**

1. **Model Development:** Develop mathematical models that represent the behavior of the system. This involves defining the system components, specifying equations or algorithms to describe their behavior, and selecting appropriate simulation techniques.
2. **Parameterization:** Assign values to model parameters based on experimental data, literature values, or estimates. Simulation Execution: Run the simulation using appropriate software tools. For continuous simulation, solve differential equations numerically over a specified time interval. For discrete event simulation, simulate events as they occur and update the system state accordingly.
3. **Analysis and Interpretation:** Analyze simulation results to understand system behavior, identify bottlenecks or inefficiencies, and evaluate the impact of different operating conditions or design choices.
4. **Validation and Verification:** Compare simulation results with experimental data or theoretical predictions to ensure that the model accurately represents the real-world system.

3.5. Laboratory Setup of Reactive Distillation:

We tried to make a column on the concept of Packed with Plate reactive distillation setup in order to get a better understanding of the process. The rectifying section and stripping section is designed on the concept of tray or plate column whereas the reactive section is designed on the concept of packed column. The reason for doing so is to get both the advantages of plate as well as packed column. The pressure drop is significantly less in packed column as compared to plate column. In the reactive section Amberlyst-15 solid catalyst is used. In a packed column it is always challenging to decide whether to use structured or random packing's, instead of just dumping the catalyst directly in the reactive section small packets of catalysts are used to avoid excess pressure build up in the reactive section.

Fig.6. Earthern pot with inbuilt heater for reboiler

Fig.7. Waste tea bags as catalyst packaging

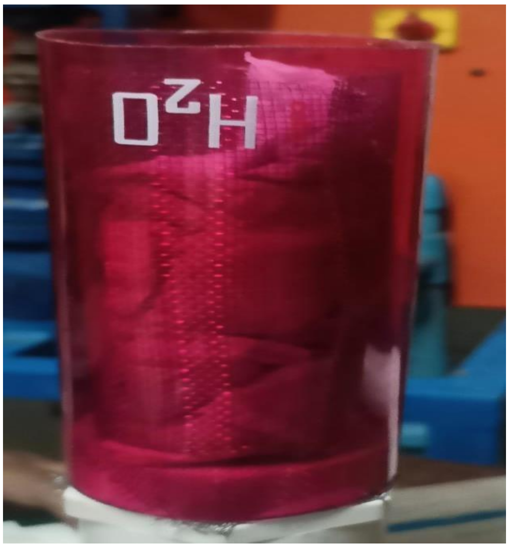

Fig.8. Waste PET bottle as Reactive Zone MOC

Fig.9. Waste PVC pipe for full distillation column

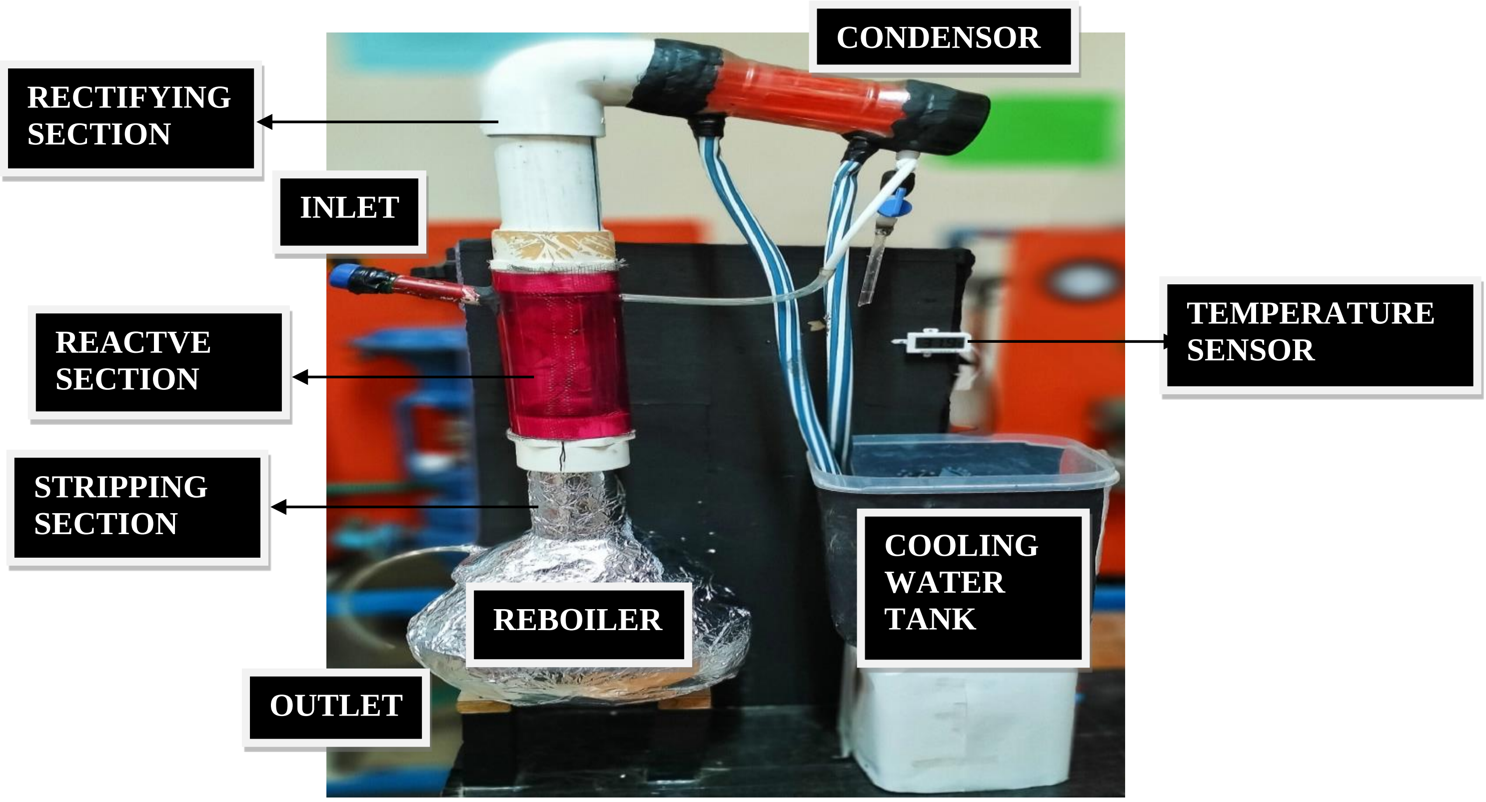

Fig.10. Pilot Plant Setup of Reactive Distillation

The number of stages used in the experimental setup was 10 (including the reboiler and condenser). Condenser used is a total vertical condenser. The reactive section is between 3-6 stages, the enriching section is between 1-2 stages and stripping section lies between 7-8 stages. Catalyst used is an acidic ion exchange catalyst (Amberlyst-15).

3.6. DWSIM(Simulation software):

DWSIM is a popular open-source chemical process simulator used for modeling, simulation, and optimization of chemical processes. DWSIM provides a wide range of tools for designing and analyzing chemical processes, including unit operations modeling, thermodynamics calculations, heat and mass balances, sensitivity analysis, and more.

The primary step in building a DWSIM flowsheet for the generation of TAEE includes the determination of the compounds such as ethanol,2-methyl-2-butanol,water and methyl tert-pentyl ether. Next, the NRTL(non-random two-liquid model) show is chosen as the property bundle and C5 unit framework is chosen.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1. Result of TAEE synthesis process in RDC:

The TAEE with loftiest chastity of 65% is attained at the bottom of the column while the top product contains much of the ethanol which can be further separated and reclaim to the column. Still we haven't shown the recycling process as in our real world factory this isn't possible experimentally.

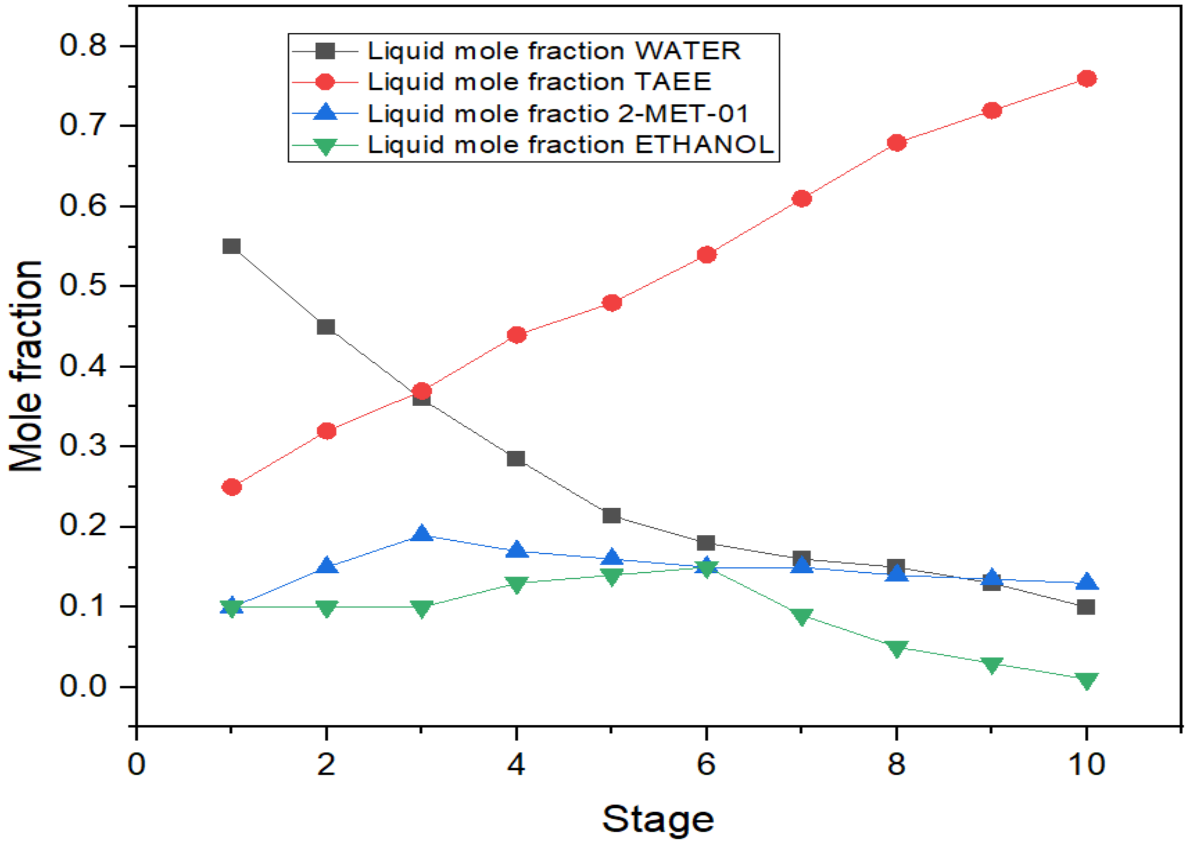

Fig.11. Concentration profile at each stage for reactive distillation column

Due to the exothermic reaction, a continuous increase in column temperature is observed from the top to the bottom of the column. Since there is also a reboiler at the bottom of the column, the highest temperature is measured at the final bottom of the column. The temperature chart is shown in Figure 12.

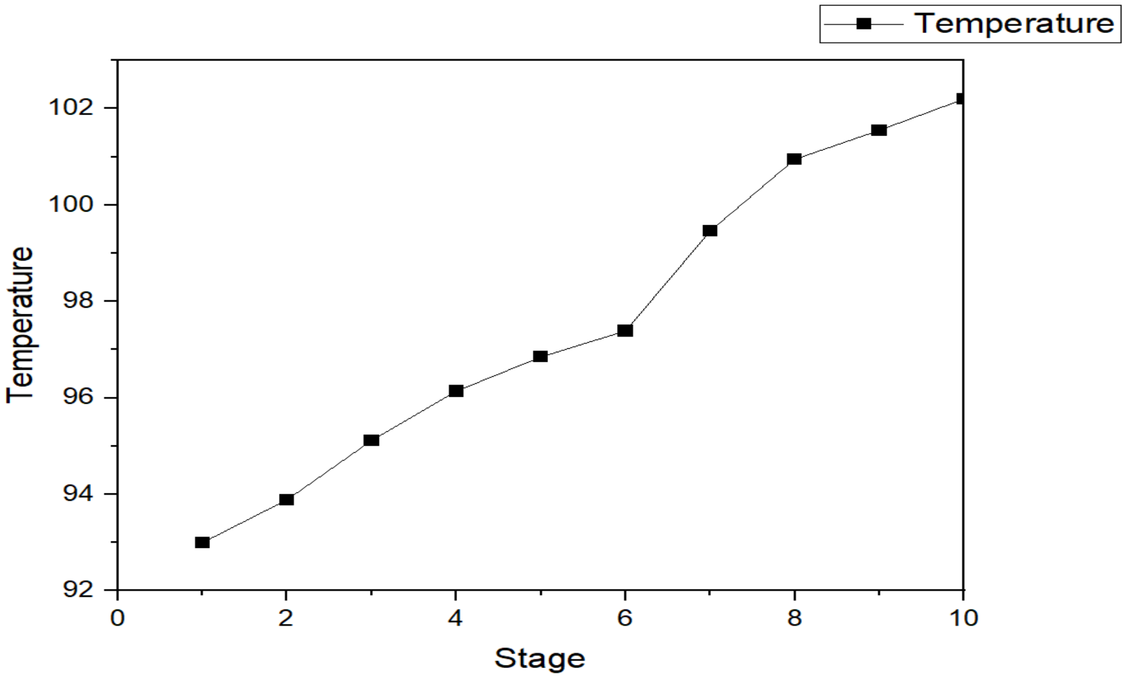

Fig.12. Temperature Profile for reactive distillation

4.2. Result of Optimization Using Sensitivity Analysis of TAEE:

For observing the loftiest value of TAEE chastity which can be achieved in our case study, we've applied perceptivity analysis which is a tool that gives the optimized value of variable subordinated to a given varying manipulated variable. In our case we've varied reboiler duty and influx rate and get the loftiest chastity of 65% at reboiler duty of 2 KW and a reflux rate of 4 are related. The attendant plots are shown below:

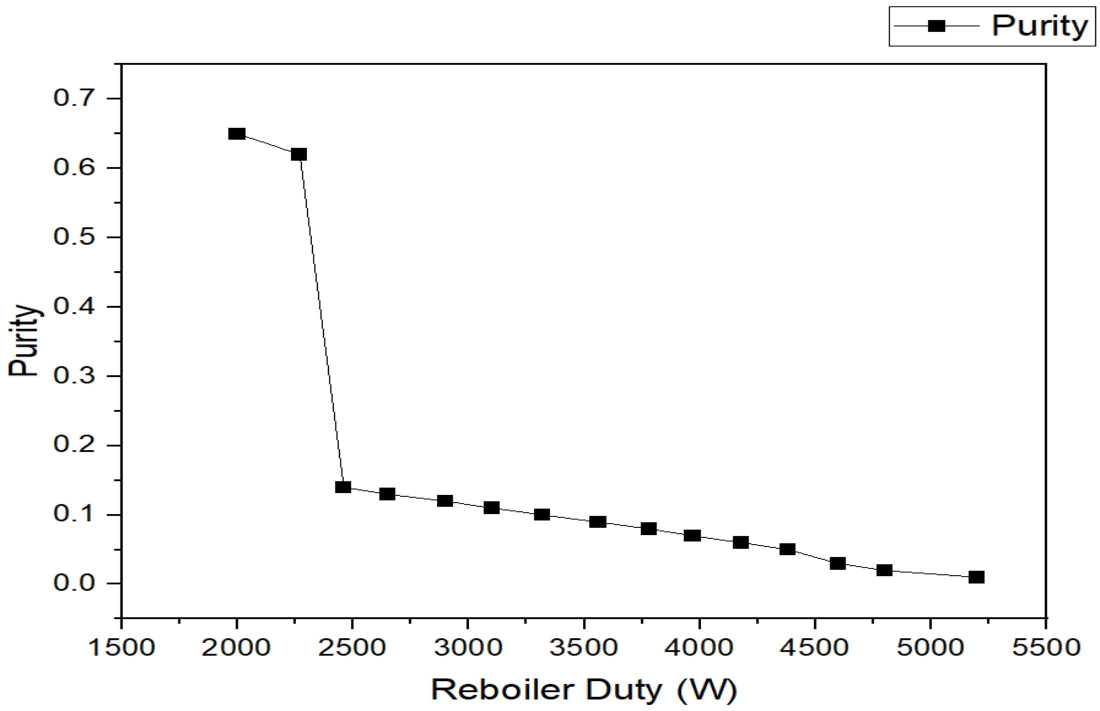

Fig.13. Plot of Sensitivity analysis for TAEE purity varying with Reboiler duty

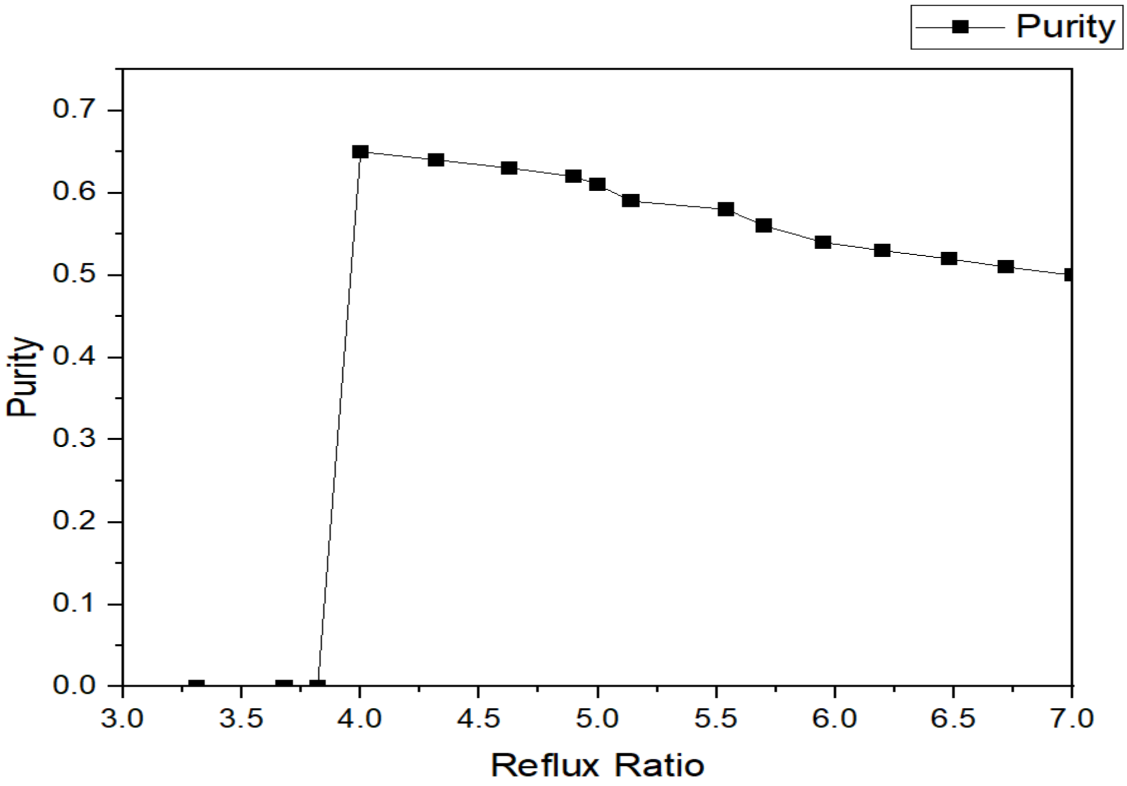

Fig.14. Plot of Sensitivity analysis for TAEE purity varying with Reflux Ratio

CHAPTER 5: CONCLUSION

The reactive distillation process experimentally explored in this study explores the combination of oxygenated biodiesel from used kitchen varnish and oxygenated energetic compounds from alcohol, yielding sustainable barrier to fossil fuels are being used less and less in order to create less waste and harm to the environment. Modeling and simulation also plays an important role while carrying out reactions on the laboratory as well as on the commercial basis.The reboiler's size and how much liquid goes into it.

5.1.Social relevancy:

➢ Reactive distillation:

The social relevance of reactive distillation lies in its potential to contribute to sustainability, energy efficiency, and environmental protection, thus impacting society in several ways:

- **Environmental Sustainability:** Reactive distillation can help reduce the environmental footprint of chemical processes by minimizing energy consumption, waste generation, and emissions. By integrating reaction and separation in a single unit, it reduces the need for multiple process steps, equipment, and energy-intensive separations, leading to lower greenhouse gas emissions and resource utilization.
- **Resource Conservation:** Reactive distillation enables the use of renewable feedstocks and facilitates the production of value-added chemicals from biomass or waste streams. This supports the transition towards a bio-based economy and reduces reliance on fossil fuels, contributing to resource conservation and sustainable development.
- **Product Quality and Safety:** Reactive distillation allows for precise control over reaction conditions, leading to higher product purity, consistency, and safety. This is particularly important in industries such as pharmaceuticals, where product quality directly impacts human health and safety.
- **Energy Efficiency:** By integrating reaction and separation processes, reactive distillation reduces energy losses associated with heat transfer, mixing, and vaporization. It enables energy-efficient processing by utilizing the heat released or absorbed during chemical reactions to drive separation, thereby reducing overall energy consumption and operational costs.

- **Economic Benefits:** Reactive distillation can improve the economics of chemical processes by reducing capital and operating costs, increasing process efficiency, and enabling the production of higher-value products. This can lead to job creation, economic growth, and improved competitiveness in the chemical industry.
- **Health and Safety:** Reactive distillation can enhance workplace safety by minimizing the handling and storage of hazardous chemicals and reducing the risk of accidents associated with multiple process steps and equipment. It also facilitates the production of cleaner and safer products, contributing to public health and well-being.

- **Fuel Oxygenates:**

Fuel oxygenates, such as ethanol and MTBE (methyl tert-butyl ether), have social relevance in several ways:

- **Air Quality Improvement:** Oxygenates help reduce tailpipe emissions of harmful pollutants, such as carbon monoxide and hydrocarbons, from vehicles. This leads to improved air quality, which benefits public health by reducing respiratory illnesses and overall pollution-related health issues.
- **Reduced Dependence on Fossil Fuels:** Many fuel oxygenates are derived from renewable sources, such as ethanol from corn or sugarcane. By incorporating these oxygenates into gasoline blends, societies can reduce their dependence on fossil fuels, contributing to energy security and sustainability goals.
- **Economic Opportunities:** The production and use of fuel oxygenates can create economic opportunities, particularly in agricultural sectors where feedstocks like corn and sugarcane are grown. This can stimulate rural economies and provide income opportunities for farmers and agricultural communities.
- **Engine Performance:** Oxygenates can enhance the octane rating of gasoline, improving engine performance and efficiency. This can lead to smoother-running engines and potentially longer engine lifespan, which benefits consumers and reduces maintenance costs.

5.2. Project Outcome:-

This project has helped me in the following ways:

1. It helped in gaining the more insights of the topic of the reactive distillation and how its working takes place.
2. I gained more insights about the modeling and simulation of the reactive distillation.
3. It helped me in gaining more knowledge of the new techniques about the modeling of the reactive distillation that involves process matrix method, incidency matrix method modeling,etc.
4. The simulation part helped me in knowing about the various property packages and how the changing in the value of a particular property leads to the change in the value of the mole fractions and subsequently other properties.
5. Fuel oxygenates also have the potent to replace and have the tendency to replace the fossil fuels such as petroleum and diesel.
6. It also helped me in knowing about the synthesis process involved in the manufacturing of the fuel oxygenates and how the catalyst packaging plays an important role.

Overall this project has helped me a lot in applying my knowledge of the chemical process calculations, thermodynamics and has helped me in gaining practical and theoretical of the reactive distillation and the synthesis of the fuel oxygenates.

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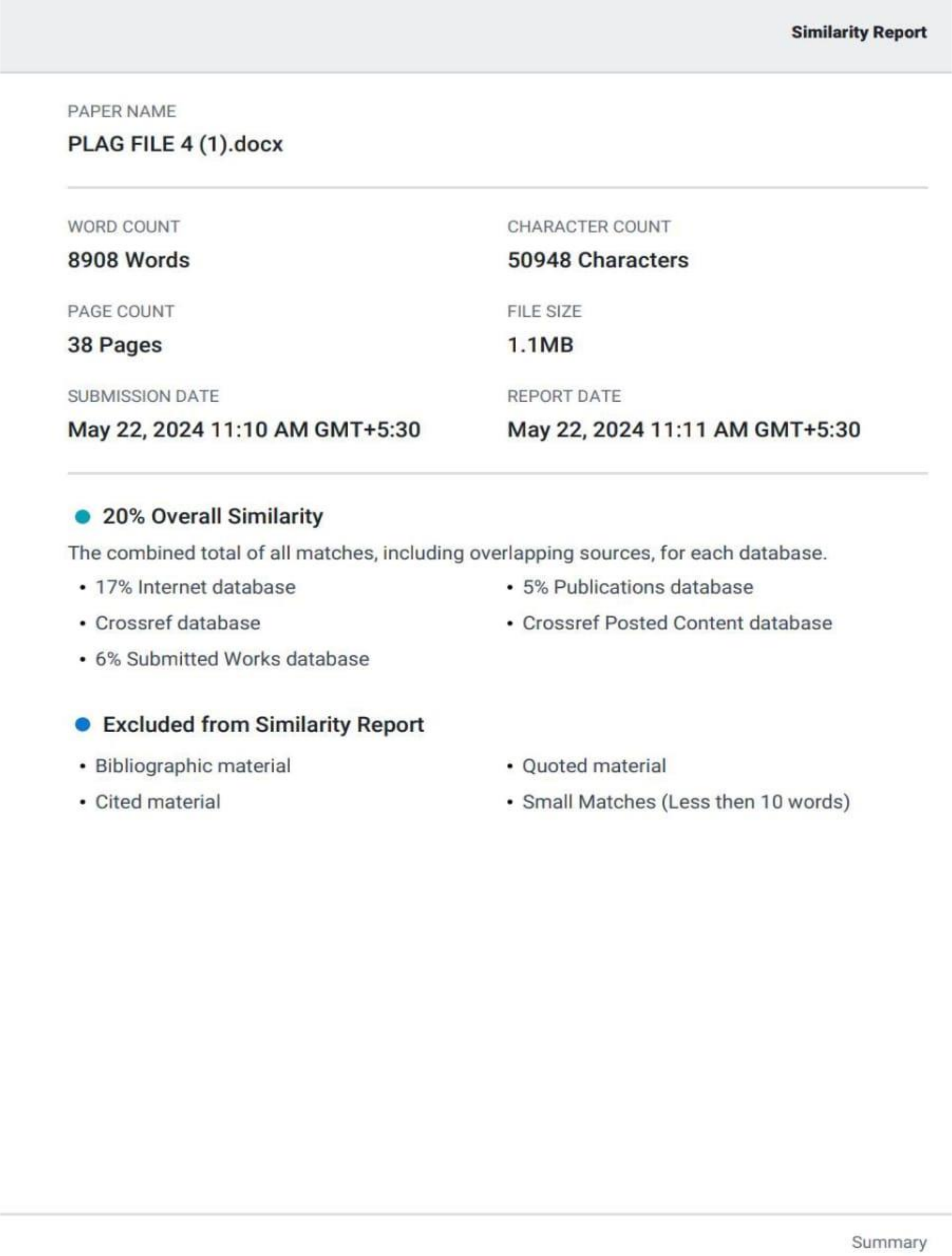

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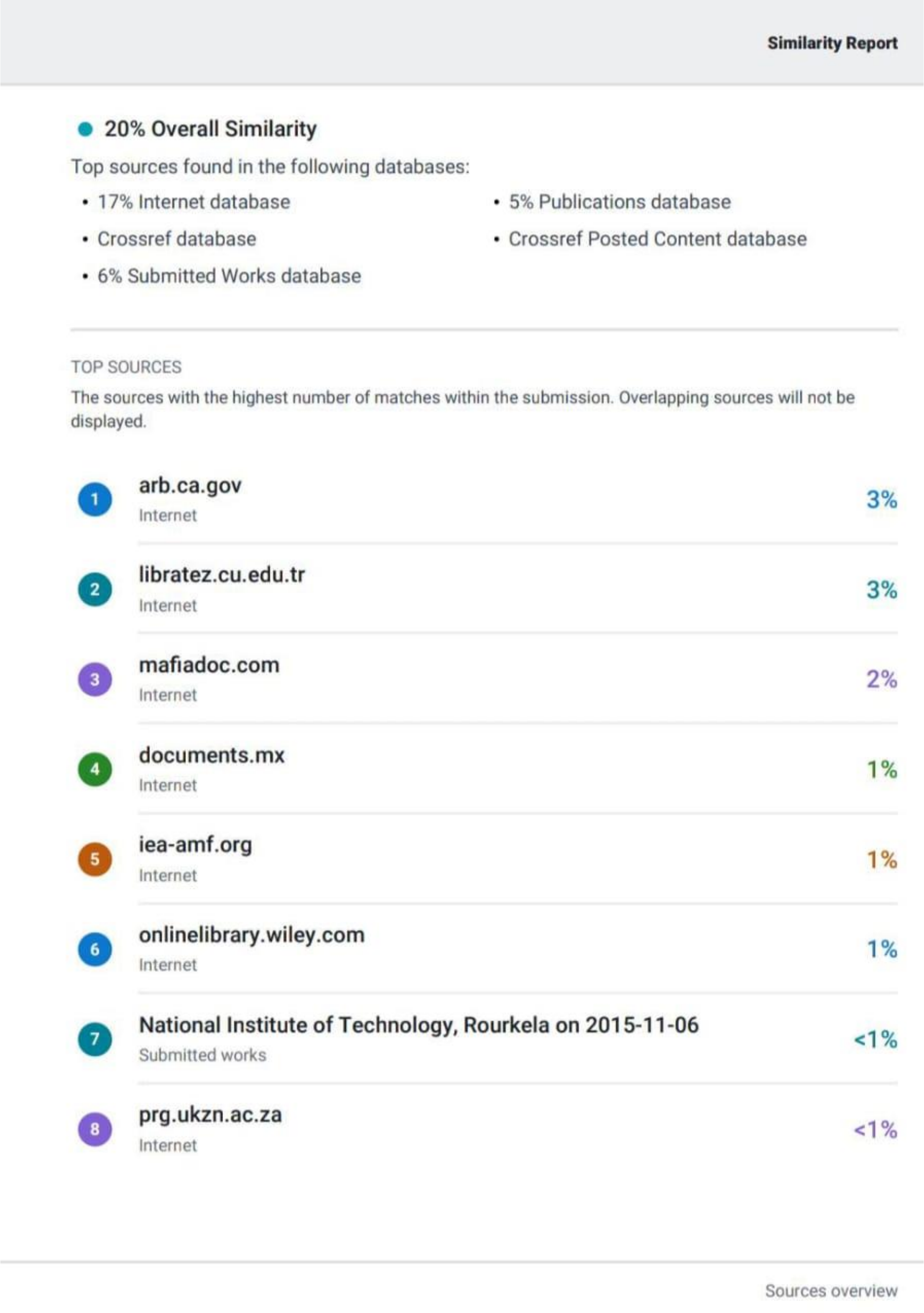

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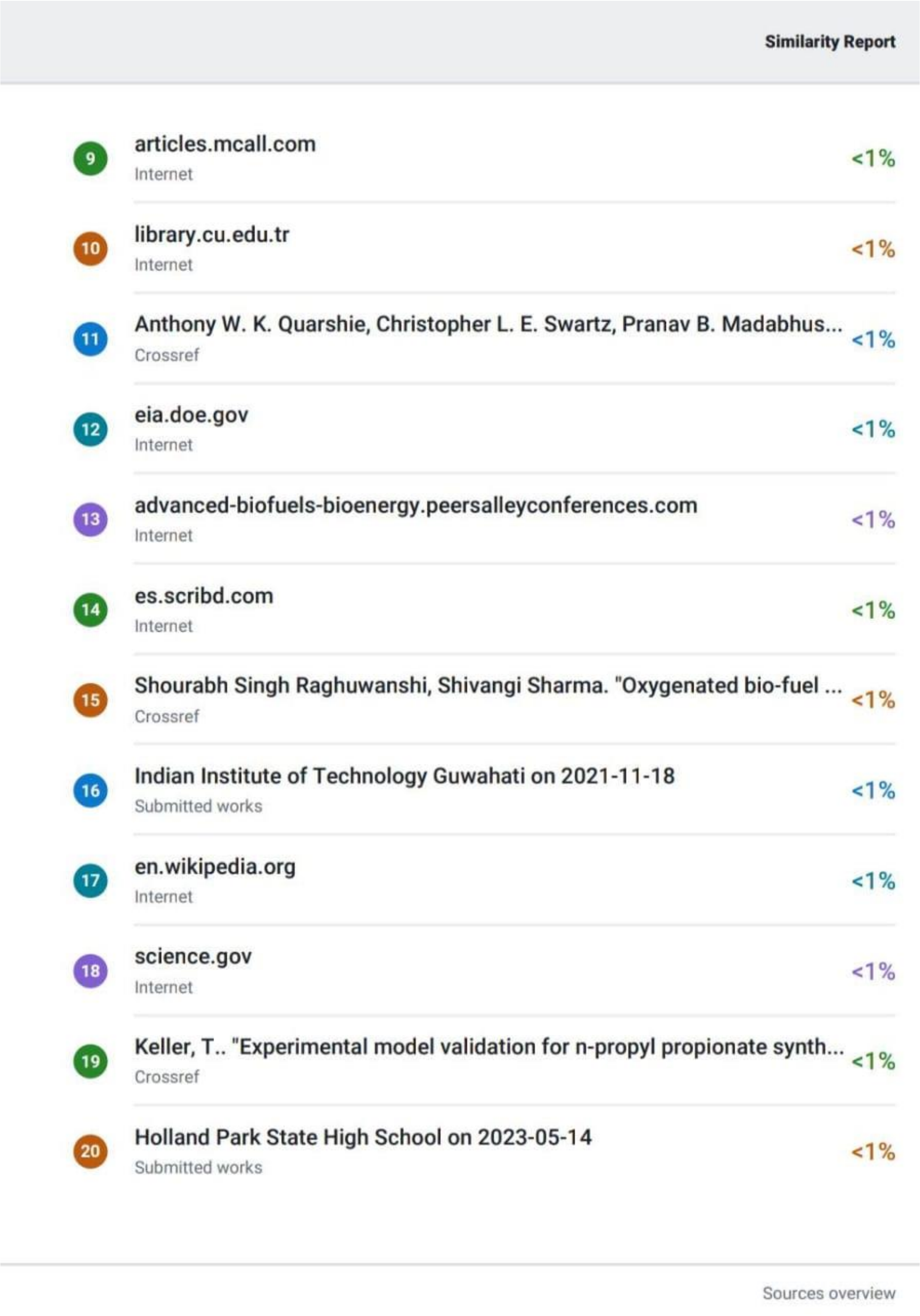

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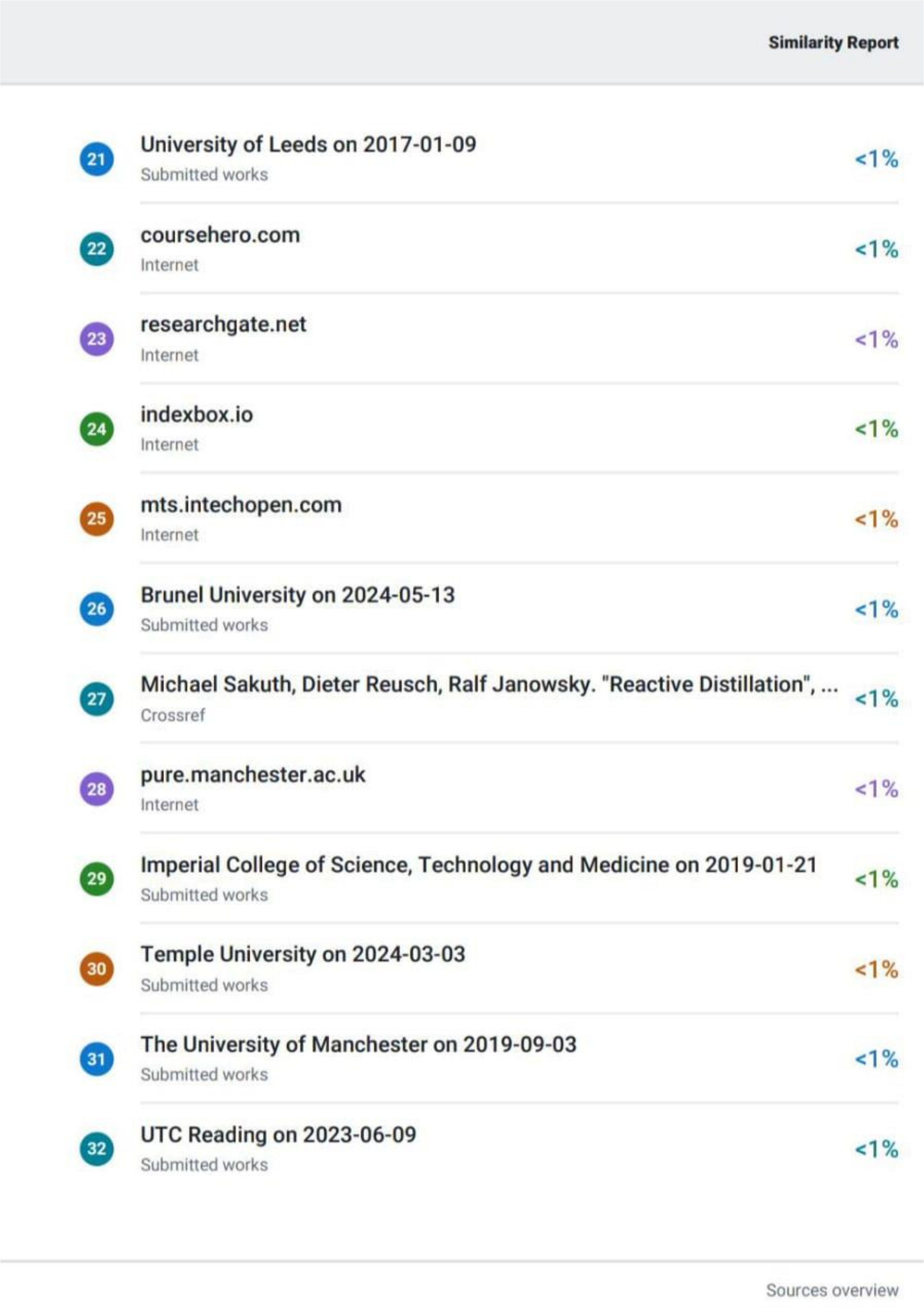

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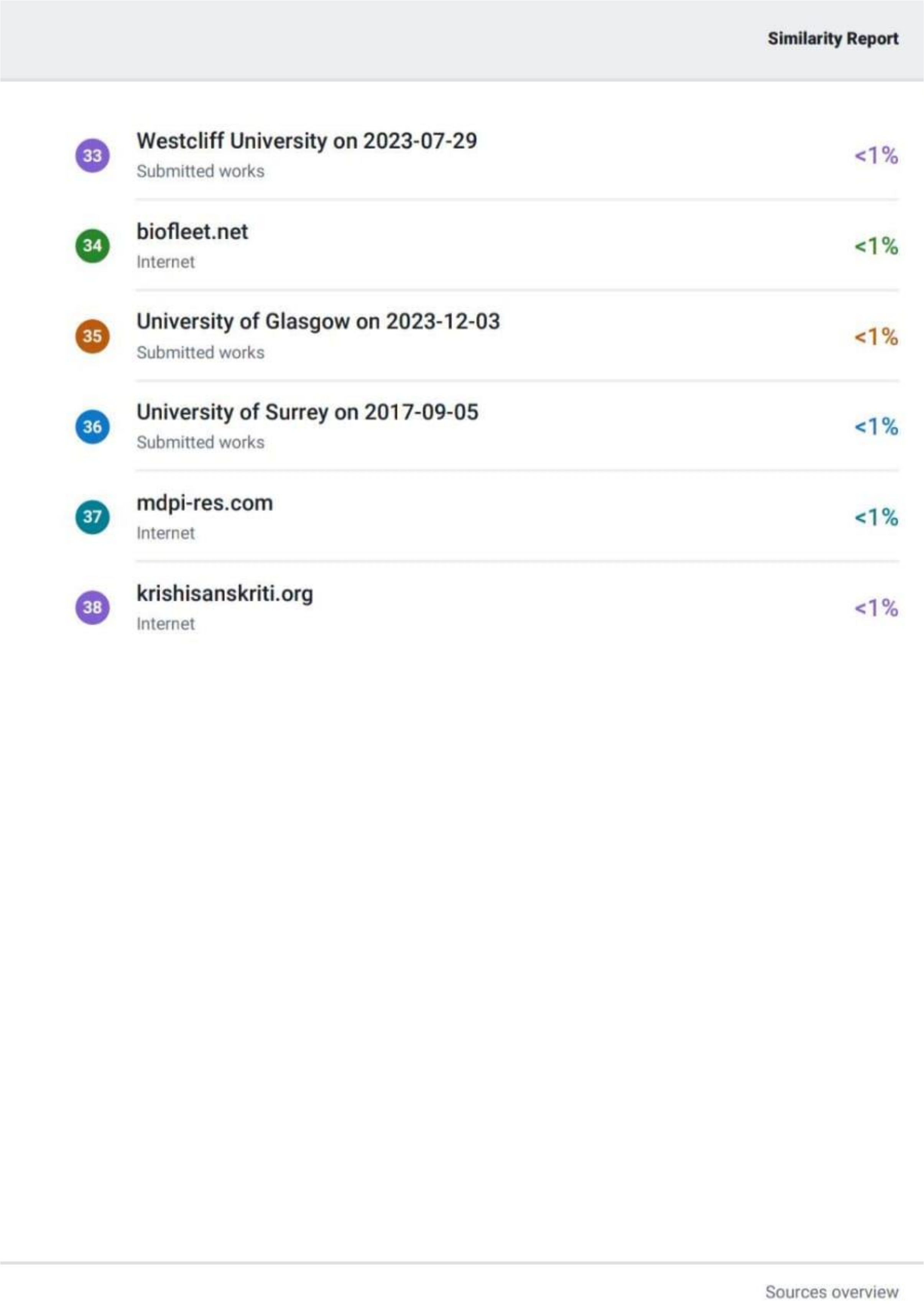

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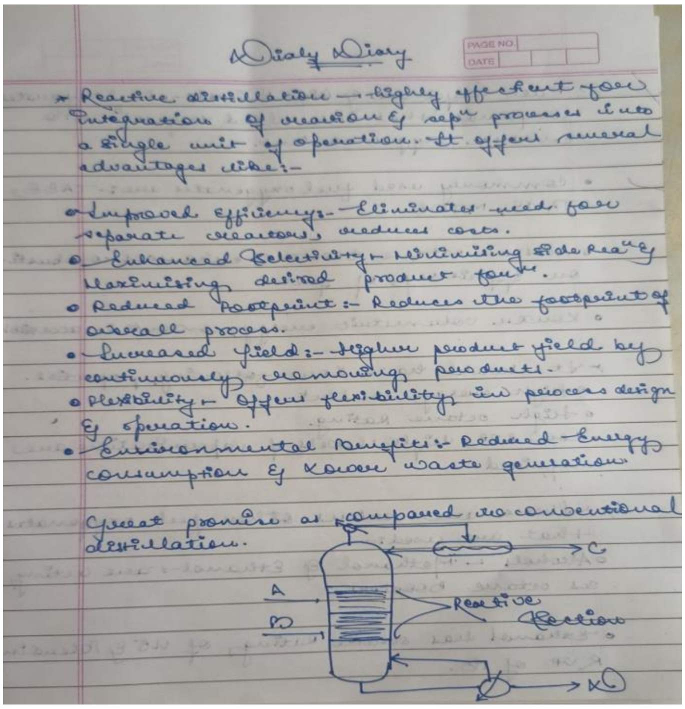
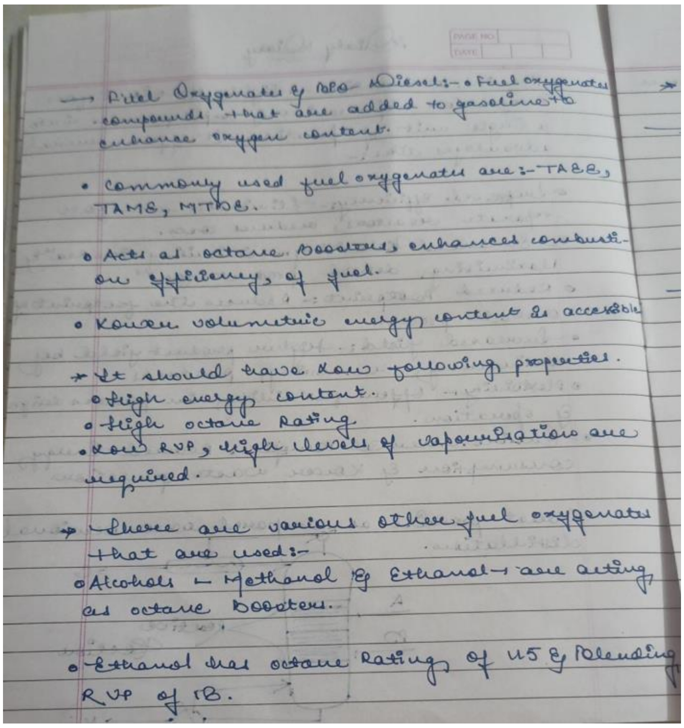


Dialy Diary

- Reactive distillation — highly efficient for integration of reaction & sep^{n} processes into a single unit of operation. It offers several advantages like:-

- Improved Efficiency:- Eliminates need for separate reactors, reduces costs.
- Enhanced Selectivity:- Minimising side Rea^{n} & Maximising desired product form^{n}.
- Reduced Footprint:- Reduces the footprint of overall process.
- Increased Yield:- Higher product yield by continuously removing products.
- Flexibility:- Offers flexibility in process design & operation.
- Environmental Benefits:- Reduced Energy consumption & lower waste generation.

Great promise as compared to conventional distillation.



→ Fuel Oxygenates & Bio Diesel:- Fuel oxygenates compounds that are added to gasoline to enhance oxygen content.

- Commonly used fuel oxygenates are:- TAEE, TAME, MTBE.

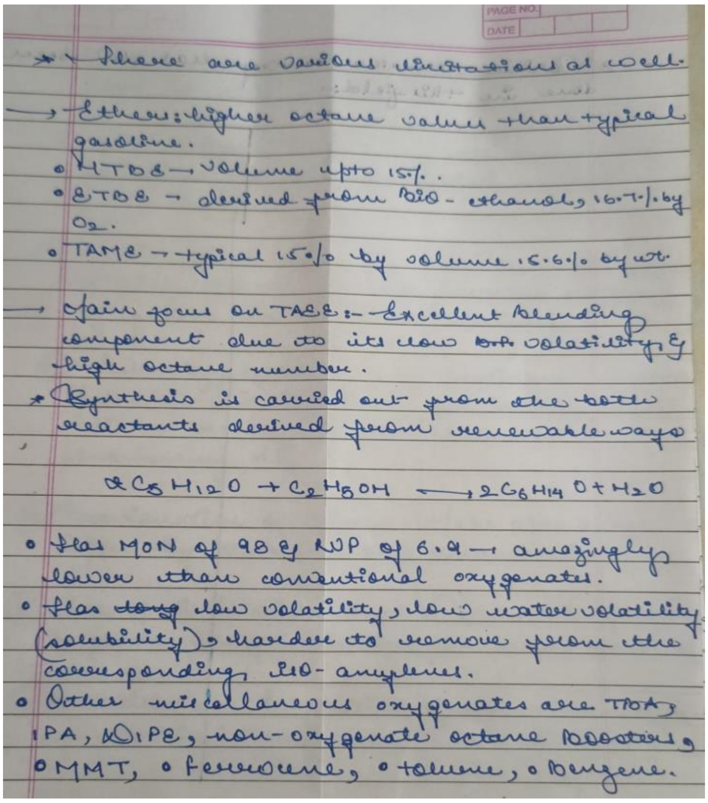
- Acts as octane boosters, enhances combustion efficiency of fuel.

- Lower volumetric energy content is accessible

* It should have the following properties.
- High energy content.
- High octane Rating.
- Low RVP, high levels of vaporisation are required.

→ There are various other fuel oxygenates that are used:-
- Alcohols - Methanol & Ethanol - are acting as octane boosters.

- Ethanol has octane Rating of 115 & Blending RVP of 18.



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* There are various limitations as well.

→ Ethers: higher octane values than typical gasoline.

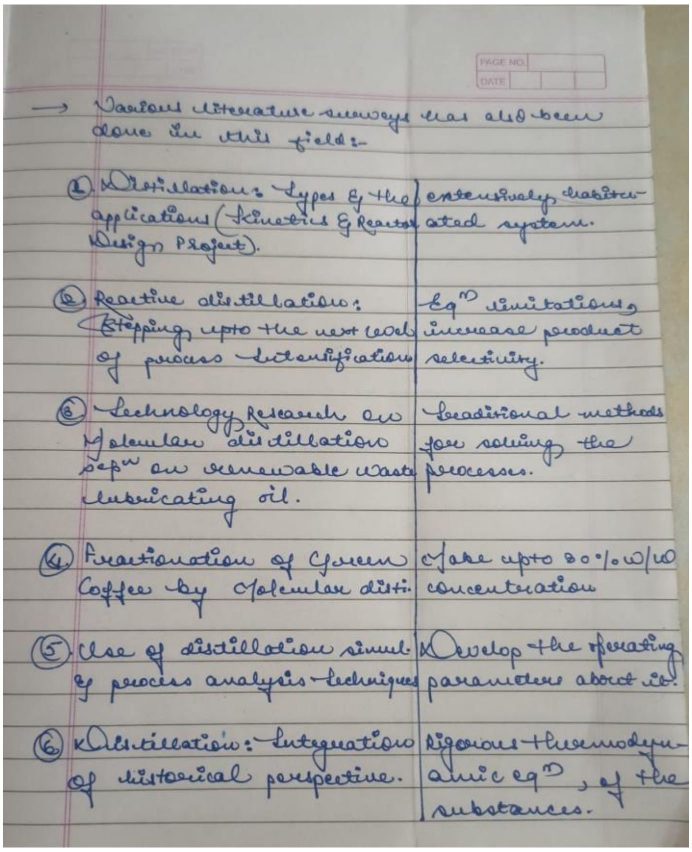
- MTBE → volume upto 15%.
- ETBE → derived from bio-ethanol, 16.7% by O_2.
- TAME → typical 15% by volume 15.6% by wt.

→ Main focus on TAEE:- Excellent blending component due to its low b.p. volatility & high octane number.

* Synthesis is carried out from the both reactants derived from renewable ways

$$2C_5H_{12}O + C_2H_5OH \longrightarrow 2C_6H_{14}O + H_2O$$

- Has MON of 98 & RVP of 6.9 → amazingly lower than conventional oxygenates.
- Has ~~long~~ low volatility, low water volatility (solubility), harder to remove from the corresponding iso-amylenes.
- Other miscellaneous oxygenates are TBA, IPA, DIPE, non-oxygenate octane boosters, ◦ MMT, ◦ ferrocene, ◦ toluene, ◦ benzene.



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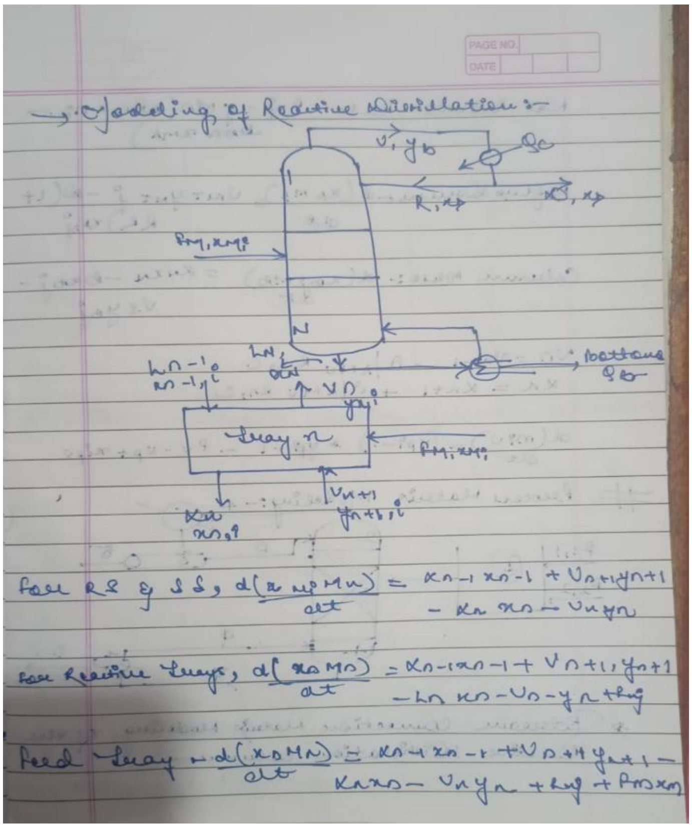
→ Various literature surveys has also been done in this field:-

① Distillation: Types & the applications (Kinetics & Reactor Design Project).	extensively sophisticated system.
② Reactive distillation: Stepping upto the next level of process intensification	Eq^n limitations, increase product selectivity.
③ Technology Research on Molecular distillation sep^n on renewable waste lubricating oil.	traditional methods for solving the processes.
④ Fractionation of Green Coffee by Molecular disti.	Make upto 80% w/w concentration
⑤ Use of distillation simul. & process analysis techniques	Develop the operating parameters about it.
⑥ Distillation: Integration of historical perspective.	Rigorous thermodynamic eq^n, of the substances.

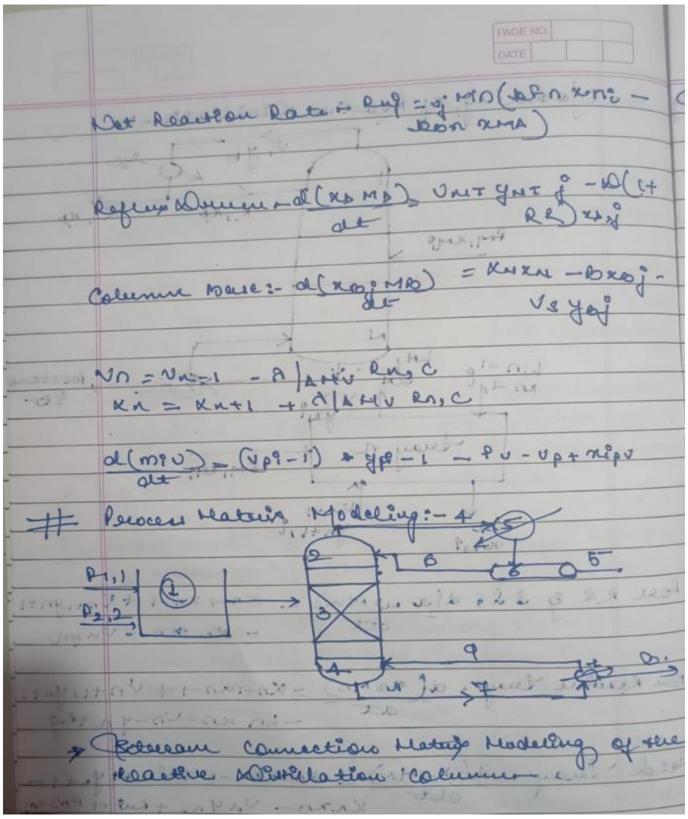


→ Modeling of Reactive Distillation :-

for RS & SS, $\frac{d(x_{n,i} M_n)}{dt} = L_{n-1} x_{n-1} + V_{n+1} y_{n+1} - L_n x_n - V_n y_n$

for Reactive trays, $\frac{d(x_n M_n)}{dt} = L_{n-1} x_{n-1} + V_{n+1} y_{n+1} - L_n x_n - V_n - y_n + R_{nj}$

Feed tray – $\frac{d(x_n M_n)}{dt} = L_{n-1} x_{n-1} + V_{n+1} y_{n+1} - L_n x_n - V_n y_n + R_{nj} + F_m x_m$



Net Reaction Rate :- $R_{nj} = \nu_j M_n (k_{f,n} x_{n,i} - k_{b,n} x_{MA})$

Reflux Drum – $\frac{d(x_D M_D)}{dt} = V_{NT} y_{NT,j} - D(1+RR) x_{D,j}$

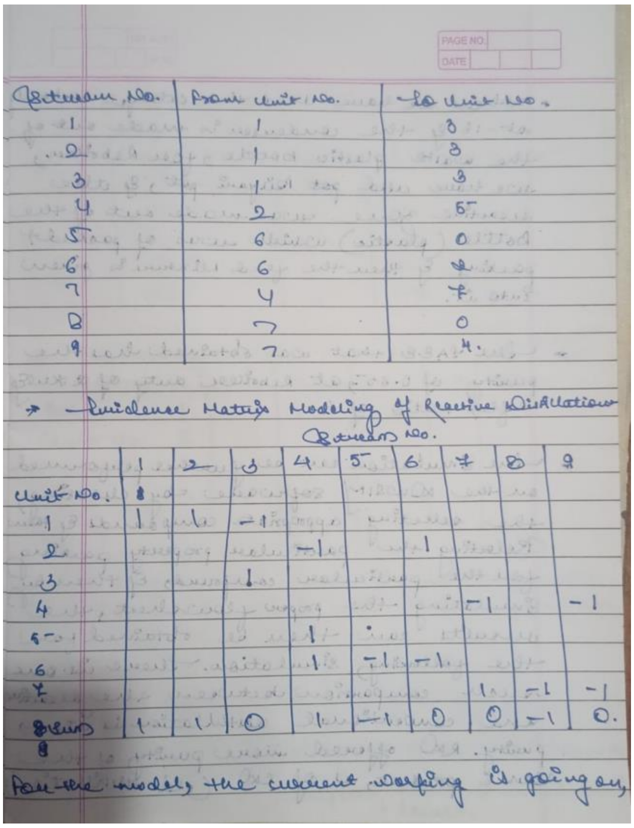
Column Base :- $\frac{d(x_{B,j} M_B)}{dt} = L_N x_N - B x_{B,j} - V_s y_{B,j}$

$V_n = V_{n-1} - \lambda|\Delta H_v R_{n,C}$
$L_n = L_{n+1} + \lambda|\Delta H_v R_{n,C}$

$\frac{d(m_i v)}{dt} = (v p_{i-1}) + y p_{i-1} - f v - v p + x_i p v$

Process Matrix Modeling :-

→ Stream Connection Matrix Modeling of the Reactive Distillation Column.

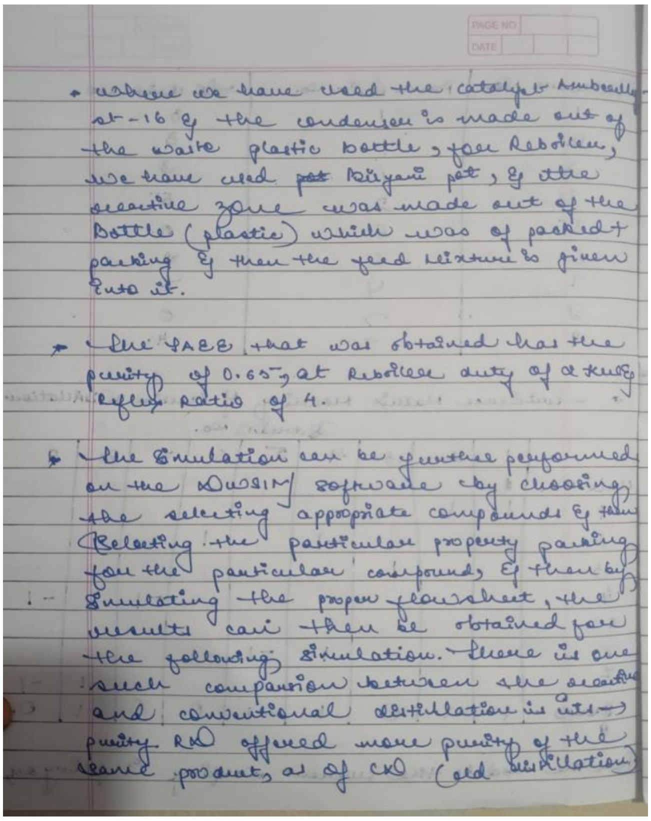


Stream No.	From Unit No.	To Unit No.
1	1	3
2	1	3
3	1	3
4	2	5
5	6	0
6	6	2
7	4	7
8	7	0
9	7	4.

* Incidence Matrix Modeling of Reactive Distillation

	Stream No.								
	1	2	3	4	5	6	7	8	9
Unit No.									
1	1	1	-1						
2				-1		1			
3			1						
4							-1		-1
5				1					
6				1	-1	-1			
7							1	-1	-1
Sum 8	1	1	0	1	-1	0	0	-1	0.

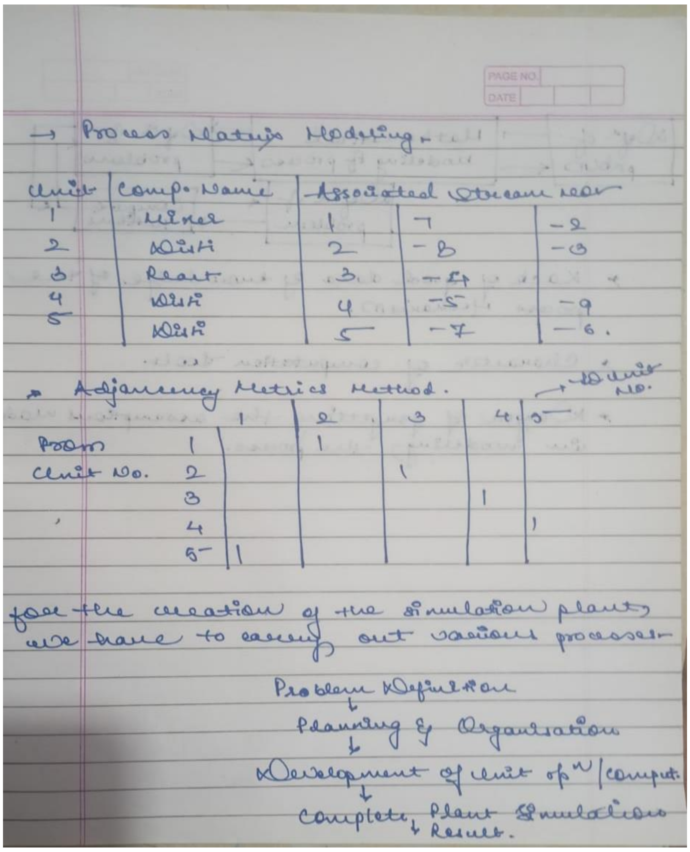
For the model, the current working is going on,



- where we have used the catalyst Amberlyst-16 & the condenser is made out of the waste plastic bottle, for Reboiler, we have used ~~pot~~ Biryani pot, & the reactive zone was made out of the Bottle (plastic) which was of packed + packing & then the feed mixture is given into it.

* The TAEE that was obtained has the purity of 0.65, at Reboiler duty of a kW & reflux ratio of 4.

* The simulation can be further performed on the DWSIM software by choosing the selecting appropriate compounds & then selecting the particular property package for the particular compounds & then by simulating the proper flowsheet, the results can then be obtained for the following simulation. There is one such comparison between the reactive and conventional distillation in its → purity. RD offered more purity of the same product, as of CD (old distillation)



→ Process Matrix Modelling.

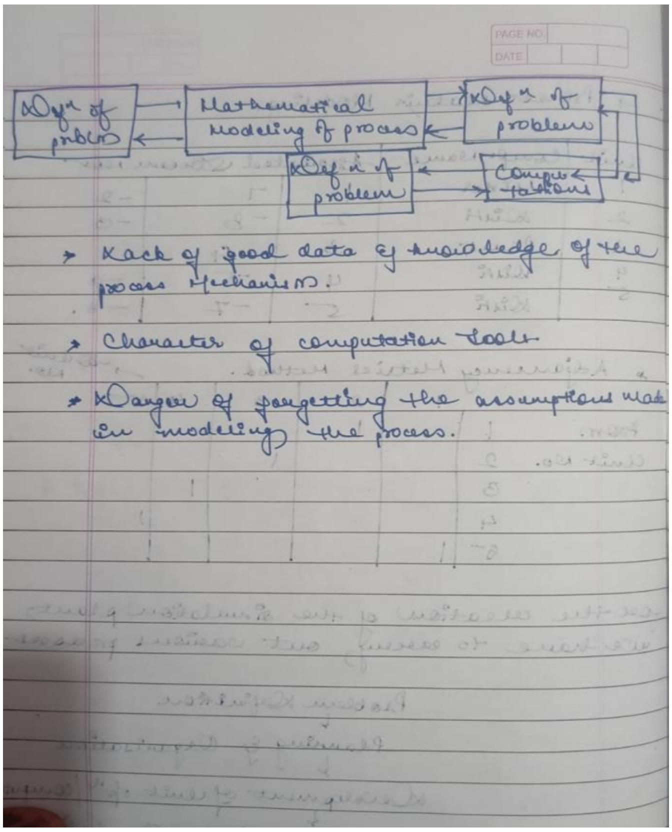
Unit	Comp. Name	Associated Stream No.		
1	Mixer	1	7	-2
2	Distl	2	-8	-3
3	React	3	-4	
4	Distl	4	-5	-9
5	Distl	5	-7	-6.

* Adjacency Metrics Method.

From Unit No.	To Unit No. 1	2	3	4	5
1		1			
2			1		
3				1	
4					1
5	1				

for the creation of the simulation plant, we have to carry out various processes

Problem Definition
↓
Planning & Organisation
↓
Development of unit opn/comput.
↓
Complete, Plant Simulation
↓ Result.



* Lack of good data & knowledge of the process Mechanism.
* Character of computation tools.
* Danger of forgetting the assumptions made in modeling the process.

CERTIFICATE

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Author(s): Deerghaa Gupta (Madhav Institute of Technology & Science, Gwalior, India)*

Paper ID:
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M Pandit

Dr. Manjaree Pandit
Coordinator, ISCMCTR - 2024

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