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Fischer Tropsch Synthesis Wastewater Treatment Study using DW SIM

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Abstract: ***This project focuses on utilising DWSIM to treat wastewater from the Fischer-Tropsch process. A well-known technique for transforming synthesis gas, a combination of carbon monoxide and hydrogen, into liquid hydrocarbons is the Fischer-Tropsch process. However, this procedure generates wastewater, which, if not adequately treated, contains a variety of chemicals that can be detrimental to aquatic life. To eliminate these contaminants and meet regulatory standards, the Fischer-Tropsch process necessitates water treatment. The most often employed therapeutic modalities are physical, pharmacological, and biological therapies. To maintain the sustainability and environmental friendliness of the Fischer-Tropsch process, efficient and effective water treatment is essential. The Fischer-Tropsch process can continue to be an effective way to produce liquid hydrocarbons while minimising its adverse effects on aquatic habitats with the proper water treatment. As a result, the goal of this research is to examine the treatment process, determine the chemical oxygen demand (COD) level of Fischer-Tropsch water obtained by distillation, reduce its concentration, and prepare the water for neutralisation.***

Keywords: ***Wastewater treatment, Fischer-Tropsch Process, Synthesis gas, Liquid hydrocarbons, Chemical contaminants, Aquatic life, Physical therapy, Pharmacological therapy, Biological therapy, Regulatory standards, Sustainability, Environmental friendliness, Chemical oxygen demand (COD), Distillation, Neutralization.***

I. INTRODUCTION

A. Discovery of the Fisher-Tropsch Process:

Franz Fischer and Hans Tropsch, two German chemists, created the Fischer-Tropsch (FT) procedure in 1925. They were seeking a method to convert coal into liquid fuels while working at the Kaiser Wilhelm Institute in Berlin.

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Using metal catalysts, they developed a procedure to convert synthesis gas —a mixture of carbon monoxide and hydrogen —into liquid hydrocarbons. The Fischer-Tropsch method, as it came to be known, was a crucial technique for producing liquid fuels during World War II, when Germany was cut off from conventional oil supplies.

II. REACTION MECHANISM:

A sequence of chemical processes is used in the Fischer-Tropsch process to create a range of hydrocarbons, preferably with the formula (C_nH_{2n+2}). Alkanes are made through the following more advantageous reactions.

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$$

Where n is typically 10–20. The formation of methane (n = 1) is unwanted.

A series of chemical processes known as the Fischer-Tropsch process transform syngas, a combination of hydrogen and carbon monoxide, into liquid hydrocarbons. At pressures of one to several tens of atmospheres and temperatures of 150–300 °C (30–572 °F), these reactions often take place in the presence of metal catalysts.

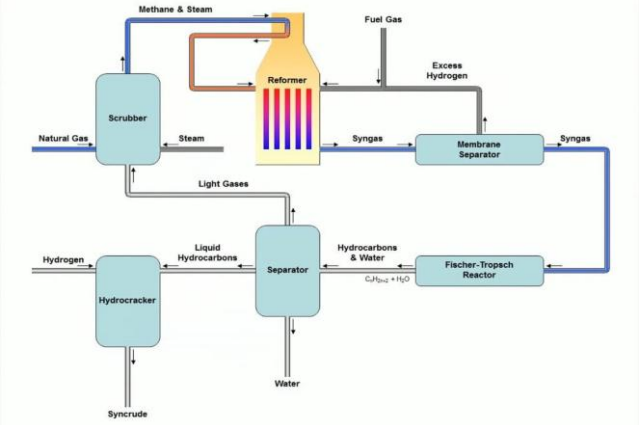

Fig. 1: Fischer-Tropsch (FT) Process

The Fischer-Tropsch (FT) process involves several steps:

1. Feedstock preparation: Before gasification, the carbon-based feedstock, such as coal, natural gas, or biomass, must be prepared.
2. Gasification: The feedstock is then gasified to produce synthesis gas, also known as syngas, a mixture of carbon monoxide and hydrogen. Several techniques, such as steam generation or oxygen gasification, can be employed to achieve this goal.
3. Syngas cleaning: The syngas is then cleansed to remove particles, heavy metals, sulfur, nitrogen compounds, and other contaminants. This is necessary to maintain the catalyst's activity and prevent catalyst poisoning.

4. Fischer-Tropsch reaction: The cleaned syngas is next passed at high pressure and temperature over a metal catalyst, usually cobalt, iron, or ruthenium. The conversion of the synthesis gas into liquid hydrocarbons, predominantly paraffins and olefins, is facilitated by the metal catalyst through a sequence of reactions.
5. The unreacted syngas and other byproducts, including water and carbon dioxide, are subsequently separated from the liquid hydrocarbons in step 5.
6. Product enhancement: The liquid hydrocarbons produced by the Fischer-Tropsch method are frequently unsuitable for use as fuels due to their low quality. As a result, the hydrocarbons must undergo further processing to be upgraded into more valuable products, such as gasoline, diesel, or jet fuel.
7. Wastewater treatment: By eliminating impurities, water generated throughout the FT process, including that from the syngas cleaning and product separation operations, is made suitable for reuse or disposal.
8. Product refinement: The finished item is refined to the required standards for its intended application.

To optimize product quality and reduce waste formation, each stage of the FT process requires rigorous monitoring and control.

A. Applications of the Fisher-Tropsch Process

The Fischer-Tropsch method is widely used in the manufacturing of synthetic fuels, notably diesel fuel and jet fuel. This is due to the process's ability to create high-quality, sulfur-free fuels with attributes comparable to those of traditional petroleum-based fuels.

Other applications for the process include the manufacturing of waxes, lubricants, and other compounds. Furthermore, the Fischer-Tropsch method has been utilised to produce synthetic natural gas, which can be used as a substitute for natural gas in various applications.

Overall, the Fischer-Tropsch method has been employed in a wide range of commercial applications, most notably the manufacture of synthetic fuels and chemicals.

III. WATER

Water is a colourless, odourless, and tasteless liquid that is essential for all known forms of life. It is the most common substance on Earth and covers approximately 71% of the planet's surface. Water is composed oftwo hydrogen atoms and one oxygen atom, giving it the chemical formula H2O. It exists in three states: solid (ice), liquid (water), and gas (water vapour). Water is essential for various bodily functions, including digestion, circulation, and maintaining body temperature. It is also used for multiple purposes, including agriculture, industry, and transportation.

Selected Physical Properties of Water	
Molar Mass	18.0151 grams per mole
Melting Point	0.00 °C
Boiling Point	100.00 °C
Maximum Density (at 3.98 °C)	1.0000 grams per cubic centimetre
Density (25 °C)	0.99701 grams per cubic centimetre
Vapor Pressure (25 °C)	23.75 torr
heat of fusion (0 °C)	6.010 kilojoules per mole
heat of vaporization (100 °C)	40.65 kilojoules per mole
heat of formation (25 °C)	−285.85 kilojoules per mole
entropy of vaporization (25 °C)	118.8 joules per °C mole
viscosity	0.8903 centipoise
surface tension (25 °C)	71.97 dynes per centimetre

A. What is Chemical Oxygen Demand (COD)?

The amount of dissolved oxygen required in water to oxidise chemical organic compounds, such as petroleum, is known as the chemical oxygen demand (COD). COD is a measure of the short-term influence of wastewater effluents on the oxygen levels of receiving waters.

B. Why Measure Chemical Oxygen Demand (COD)?

When treated wastewater is released into the environment, it can bring organic pollutants into receiving waterways. High levels of COD in wastewater indicate the presence of organic matter that may deplete dissolved oxygen in the water, resulting in significant environmental and regulatory consequences. Oxygen demand is a crucial parameter for determining the impact and, ultimately, limiting the quantity of organic pollutants in water.

C. Industrial uses of water:

Water is used in manufacturing and other sectors throughout the production process to create items or to cool the equipment used in product creation. Wastewater and industrial water are byproducts of industrial or commercial activity. Water is essential for nearly every step of manufacturing across a wide range of industries, from the food we eat to the products we purchase. The wastewater that results must be appropriately controlled.

Some industrial water applications include:

- **Manufacturing processes**: Water is utilised in various manufacturing processes, including cleaning, cooling, and lubrication. It is also employed as a solvent for numerous compounds and in chemical processes.
- **Energy generation**: Water is utilised to generate energy in thermal power plants, primarily through hydropower and steam turbines.
- **Cleaning and sanitation**: Water is utilised in various sectors, including food and beverage manufacturing, pharmaceuticals, and healthcare, for cleaning and sanitation purposes.
- **Agriculture**: Water is employed in the agricultural sector for irrigating as well as for livestock watering.
- **Waste management**: Water can be utilized in waste disposal operations such as sewage treatment and industrial wastewater treatment.
- **Product quality**: Water is frequently used to make high-quality products in sectors such as textiles, paper, and electronics.
- **Sustainability**: Due to the scarcity of water, companies are increasingly focusing on lowering water usage and developing water management practices to ensure long-term sustainability.

IV. INDUSTRIAL WATER TREATMENT

Water has several industrial applications. Raw water entering an industrial plant frequently requires treatment to fulfil stringent quality standards. Meanwhile, used water must be treated before it can be reused or disposed of.

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In a nutshell, an industrial water treatment system processes water to make it more suitable for specific applications, such as consumption, production, or disposal. Standard industrial water treatment systems typically include:

- Raw water treatment systems
- Cooling tower treatment
- Wastewater treatment systems

A. Raw Water Treatment Systems:

Raw water treatment systems are used to pre-treat and optimise source water, often to enhance production efficiency and improve process performance for specific applications. Raw water treatment typically removes suspended and colloidal particles, iron, bacteria, and hardness. Pre-treating cooling tower, boiler feed water, process water, production water, and drinking water are examples. Raw water treatment is frequently concerned with protecting downstream equipment against scaling, fouling, corrosion, and other types of damage or premature wear caused by pollutants in the source water.

B. Cooling Tower Treatment:

Cooling tower water treatment systems are used to prevent damage to cooling tower components caused by pollutants in feed water, circulation water, and/or blowdown water. Chlorides, hardness, iron, biological materials, silica, TDS, and/or TSS are examples of pollutants.

C. Wastewater Treatment Systems:

A wastewater treatment system is used in the industrial water context to convert waste streams into effluent that can be reused within the operation or safely discharged into the environment. The complexity of the treatment system will be primarily determined by the compliance laws affecting the facility and the composition of the waste stream. However, in many activities, the following technologies are commonly used: clarity, disinfection, softening, and distribution.

D. Industrial Water Quality Requirements:

The standards for industrial water quality vary significantly based on the use, locality, and local regulations. Water required for food and beverage processing, for example, differs from the water needed for oil and gas extraction and treatment. Even within these divisions, water quality varies across different food categories, such as dairy and confectionery, as well as beverages, including soft drinks and alcoholic beverages. It is a challenging mix of quality criteria when combined with local rules and worldwide. Water in the food sector, on the other hand, should fulfil local criteria for safe drinking water or the World Health Organization (WHO) Guidelines for Drinking-water Quality.

Technologies used to treat industrial Wastewater:

There are several industrial water solutions available, and the decision will be influenced by various criteria, including the quality of the raw water in the region, regional legislation governing the facility, the type of product being processed, and the required water purity, among others. For example, the solutions needed to achieve ultrapure water for semiconductor manufacturing will differ significantly from those required to treat wastewater from pulp and paper manufacturing. Water solutions used for municipal water treatment, such as membranes, are frequently employed for industrial purposes. Furthermore, due to the broader range of contaminants, concentrations, and temporal variability in industrial effluents, industrial water treatment options tend to be more diversified than municipal alternatives. Here are some standard technologies used for the treatment of industrial Wastewater:

- **Physical Treatment**: Sedimentation, filtration, and screening are physical treatment methods used to remove suspended solids, oil and grease, and other big particles from wastewater. These techniques can be employed alone or in conjunction with different forms of therapy.
- **Chemical Treatment**: Chemical treatment techniques utilize chemicals to remove or *neutralize pollutants in wastewater.* Coagulation and flocculation are two standard chemical treatment methods in which chemicals are introduced to wastewater to generate flocs that can be readily removed.
- **Biological Treatment**: Microorganisms are used in biological treatment methods to break down organic materials in wastewater. Activated sludge treatment, trickling filters, and biological nutrient removal are all standard biological treatment techniques.
- **Membrane Filtration**: Membrane filtration methods, such as reverse osmosis, ultrafiltration, and nanofiltration, remove pollutants from wastewater by using a semi-permeable membrane. These methods are capable of pulling a broad variety of contaminants, including dissolved solids, bacteria, and viruses.
- **Advanced oxidation processes**: Advanced oxidation methods, such as ozonation and UV treatment, remove pollutants from wastewater through chemical or physical interactions. These technologies have the potential to be beneficial in eliminating persistent organic pollutants and other contaminants that are challenging to remove using current methods.
- **Zero liquid discharge**: The zero liquid discharge (ZLD) technique eliminates all pollutants from wastewater, leaving only a solid residue that can be disposed of properly. Evaporation and crystallization are two ZLD methods that can be costly but effective for treating high-concentration wastewater streams.

V. ABOUT DW-SIM SOFTWARE

DWSIM is a CAPE-OPEN-compliant open-source chemical process simulator. It is compatible with Windows, Linux, and Mac OS. It enables us to do experiments and analyze data using sophisticated models and processes. DWSIM is based on the Microsoft .NET and Mono platforms, and it features a graphical user interface (GUI), sophisticated thermodynamic calculations, reaction support, and capabilities for petroleum characterisation and

hypothetical component creation.

With the Thermodynamic Models and Unit Operations listed below, DWSIM can model steady-state, vapour-liquid, vapour-liquid-liquid, solid-liquid, and aqueous electrolyte equilibrium processes.

- Thermodynamic models: Cool Prop, Peng–Robinson equation of state, Peng–Robinson-Stryjek-Vera (PRSV2), Soave–Redlich–Kwong, Lee-Kesler, Lee-Kesler-Plöcker, UNIFAC(-LL), Modified UNIFAC (Dortmund), Modified UNIFAC (NIST), UNIQUAC, NRTL, Chao-Seader, Grayson-Streed, Extended UNIQUAC, Raoult's Law, IAPWS-IF97 Steam Tables, IAPWS-08 Seawater, Black-Oil and Sour Water.
- Unit operations: CAPE-OPEN Socket, Spreadsheet, Custom (Iron Python Script), Mixer, Splitter, Separator, Pump, Compressor, Expander, Heater, Cooler, Valve, Pipe Segment, Shortcut Column, Heat exchanger, Reactors (Conversion, PFR, CSTR, Equilibrium and Gibbs), Distillation column, Simple, Refluxed and Reboiled Absorbers, Component Separator, Solids Separator, Continuous Cake Filter and Orifice plate.
- Utilities: Binary Data Regression, Phase Envelope, Natural Gas Hydrates, Pure Component Properties, True Critical Point, PSV Sizing, Vessel Sizing, Spreadsheet and Petroleum Cold Flow Properties.
- Tools: Hypothetical Component Generator, Bulk C7+/Distillation Curves Petroleum Characterization, Petroleum Assay Manager, Reactions Manager and Compound Creator.
- Process Analysis and Optimization: Sensitivity Analysis Utility, Multivariate Optimizer with bound constraints.
- Extras: Support for Runtime Python Scripts, Plugins and CAPE-OPEN Flowsheet Monitoring Objects.

A. DWSIM Environment

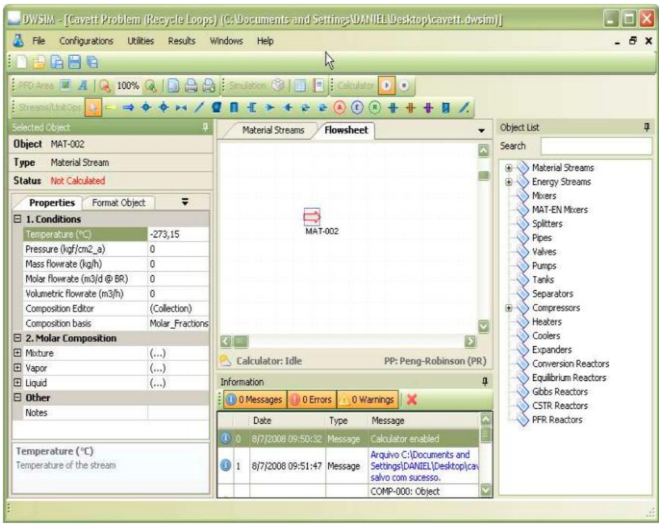

Fig. 2: Template Module

At the initial stage, we received a dialogue box containing multiple categories and options to choose from, based on our process parameters.

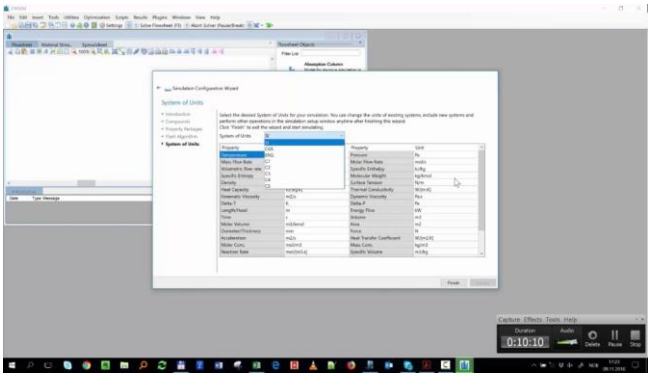

Fig. 3: Properties Tab

Here, we can find the Components tab, where we specify the required feed components by entering their IDs or inserting components from the DWSIM library by clicking the Find button.

Example: When searching for the Component Water in DWSIM, we obtain multiple options, such as seawater and heavy water.

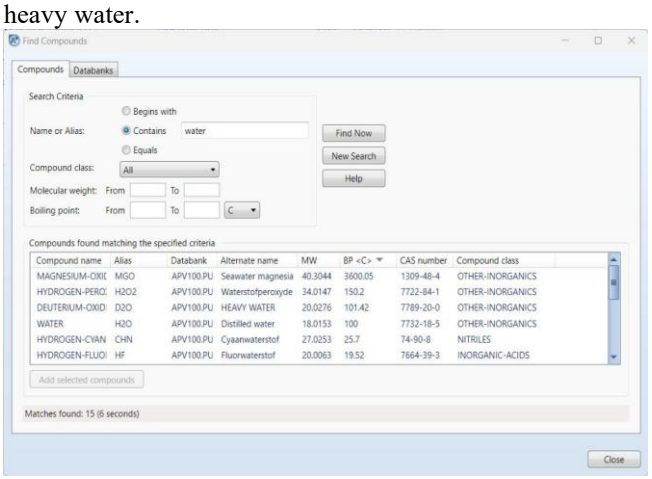

Fig. 4: Showing us the Multiple Components

We can add multiple components by clicking on 'Add Selected Components.' Upon completion of the selection, click 'Close.' On the top bar, we can see options like Next, Run, Reset, etc., which help the simulation run forward or backwards.

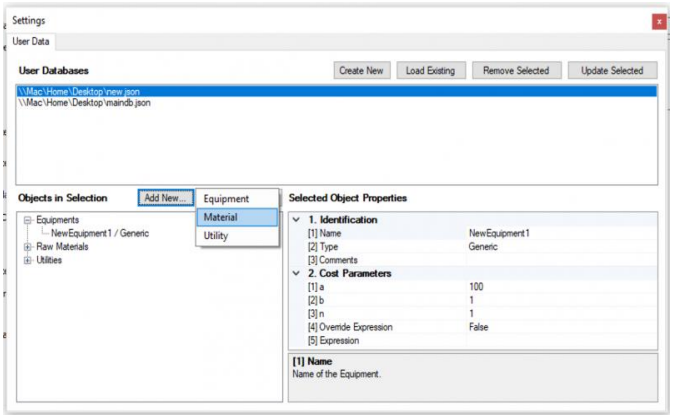

Fig. 5: Method tab

B. Simulation Tab:

In the model palette, the DWSIM has multiple designs for various components.

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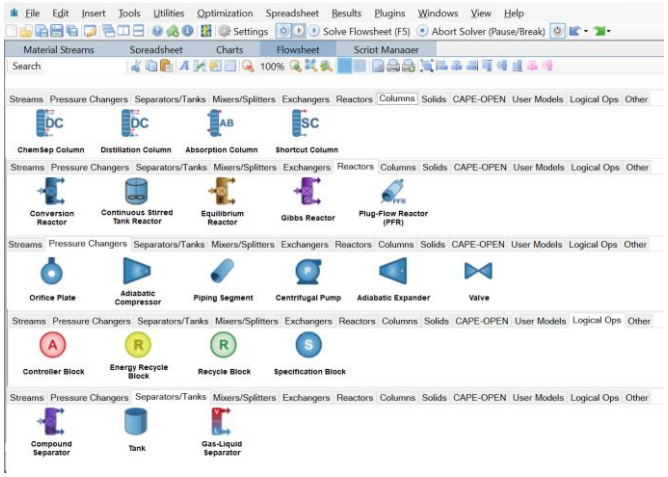

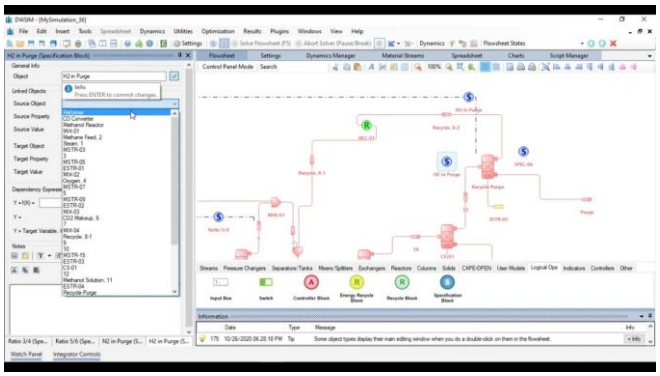

Fig. 6 & 7: Shows the Model Pallet in the DWSIM & the Simulation

VI. LITERATURE REVIEW

The Fisher-Tropsch process, according to the literature [1] is a chemical reaction that transforms carbon monoxide and hydrogen gas into liquid hydrocarbons. Water, which is produced as a byproduct of the interaction between carbon monoxide and hydrogen, has a significant impact on the environmental sustainability of the process. Water in the Fischer-Tropsch process can lead to the formation of undesirable byproducts, including alcohols, ethers, and carboxylic acids. These byproducts can diminish the output of desirable hydrocarbon products while also increasing the chemical oxygen demand (COD) of the process's wastewater. COD is a measure of the amount of oxygen required to oxidise the organic matter in sewage. The greater the COD level, the more organic matter there is in the Wastewater, which may cause a reduction in dissolved oxygen in the receiving water body. This, in turn, can hurt aquatic life and ecosystems. Operational parameters and the type of catalyst utilised heavily influence the COD levels in wastewater produced by the Fisher-Tropsch process. Higher temperatures and more extended reaction periods can lead to higher COD levels in wastewater. Furthermore, the use of specific catalysts, such as cobalt and ruthenium, which can create VOC contaminants, may increase the COD levels in wastewater.

A. The Main Problem for this Study

The literature [2-12] describes an investigation of the real process in a Malaysian industrial facility. The Fischer-Tropsch reaction generates a large volume of water, which exceeds the amount of hydrocarbon produced. The reaction produces two (2) phases: vapour and liquid. This process produced byproducts, including water vapour and alcohol, for the C5 to C25 portion, and the aqueous stream contains corrosive contaminants. To avoid environmental issues, the produced water cannot be utilized or discarded without suitable treatment. The components of Fischer-Tropsch water, such as alcohol, aldehydes, hydrocarbons, and ketones, do not behave well. These compounds are, in fact, more volatile than water. As a result, a distillation column is required to remove non-acidic chemicals from the reaction water, such as alcohols, aldehydes, and ketones.

Chemical	Chemical Group	Smell	pH	Corrosivity	COD Rate	Uses
Water	Inorganic	Odorless	7	Non-corrosive	Low	Various industrial, domestic, and agricultural applications
Carbon Dioxide	Inorganic	Odorless	5.5-7.5	Non-corrosive	Low	Carbonation of beverages, fire extinguishers, and oil recovery, and more
Propionic Acid	Carboxylic Acid	Pungent, rancid	2.85	Corrosive	High	Food preservatives, flavouring agents, herbicide, and more
N-Valeric Acid	Carboxylic Acid	Pungent, rancid, sweaty	4.82	Corrosive	High	Flavouring agent, perfumes, and more
N-Hexanoic Acid	Carboxylic Acid	Rancid, cheese-like	4.82	Corrosive	High	Flavouring agent, food preservative, and more
N-Butyric Acid	Carboxylic Acid	Pungent, rancid, cheesy	4.82	Corrosive	High	Flavouring agent, food preservative, and more
Formic Acid	Carboxylic Acid	Pungent, acidic	2.2	Corrosive	High	Textile and leather processing, coagulant in the rubber industry, and more
Acetic Acid	Carboxylic Acid	Pungent, vinegar-like	2.4	Corrosive	High	Food preservative, pickling agent, and more

Valeraldehyde	Aldehyde	Pungent, fruity, floral	7.2	Non-corrosive	High	Perfumes, flavours, and more
N-Propionaldehyd e	Aldehyde	Pungent, fruity, nutty	8.8	Non-corrosive	High	Perfumes, flavours, and more
N-Butyraldehyde	Aldehyde	Pungent, fruity, nutty	7.2	Non-corrosive	High	Flavouring agent, perfumes, and more
Acetaldehyde	Aldehyde	Pungent, fruity, floral	7	Non-corrosive	High	Chemical intermediate, food flavouring, and more
Methyl-n-propyl-ketone	Ketone	Pungent, minty, fruity	7	Non-corrosive	High	Solvent for lacquers, paints, and varnishes, and more
Methyl-ethyl-ketone	Ketone	Sweet, fruity, acetone-like	7	Non-corrosive	High	Solvent for paints, adhesives, and coatings, and more
Acetone	Ketone	Sweet, fruity, acetone-like	7	Non-corrosive	Low	Solvent for paints, adhesives, coatings, and more
2-Hexanone	Ketone	Sweet, fruity, acetone-like	7	Non-corrosive	High	Solvent for resins, waxes, and coatings, and more
1-Propanol	Alcohol	Mild, sweet, alcoholic	7.2	Non-corrosive	High	Solvent for paints, coatings, inks, and more

Chemical	Chemical Group	Smell	pH	Corrosivity	COD Rate	Uses
Methanol	Alcohol	Pungent, alcoholic, somewhat sweet	7	Non-corrosive	High	Solvent for fuels, antifreeze, and formaldehyde production, and more
Isopropyl Alcohol	Alcohol	Mild, sweet,alcoholic	7	Non-corrosive	High	Solvent for cleaning agents, hand sanitizers, and more
Ethanol	Alcohol	Pungent, alcoholic, somewhat sweet	7.2	Non-corrosive	High	Solvent for perfumes,medicines, and fuels, and more
N-Butanol	Alcohol	Sweet, fruity, somewhat pungent	7.2	Non-corrosive	High	Solvent for paints, coatings, and resins, and more
1-Pentanol	Alcohol	Sweet, slightlyfloral	7.2	Non-corrosive	High	Solvent for perfumes, flavours, and cleaning agents, and more
1-Hexanol	Alcohol	Sweet, slightlyfloral	7.2	Non-corrosive	High	Solvent for flavours, perfumes, and disinfectants, and more

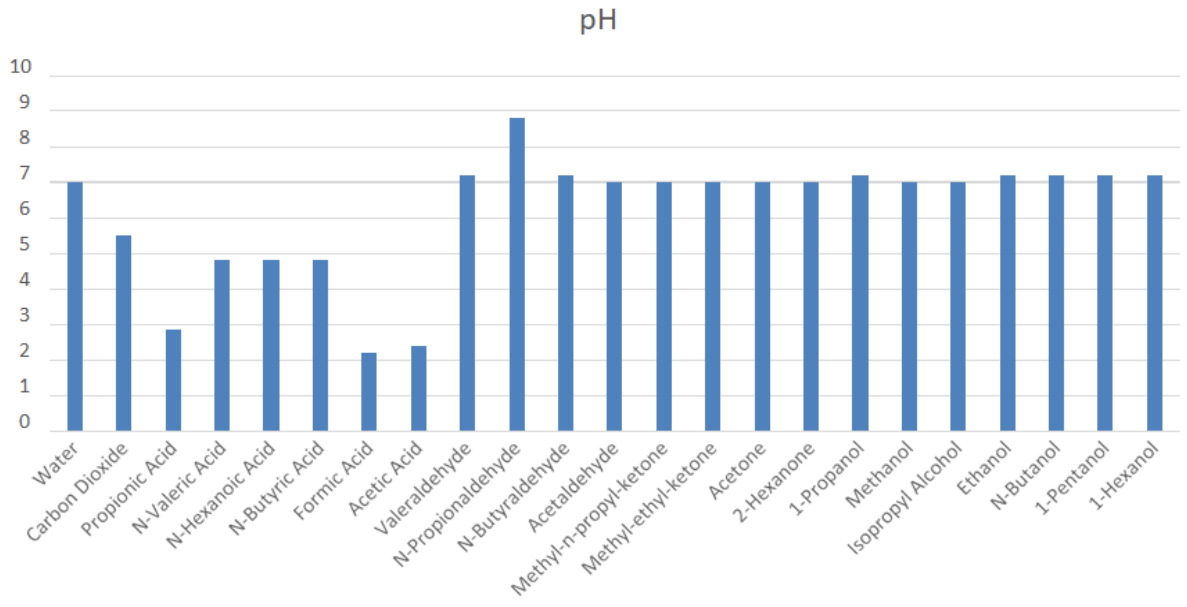

Fig. 8: This tabulated data has been made as per the References

According to the data, we can see that we need to remove or reduce the corrosive carboxylic acids and also eliminate aldehydes, alcohols, and ketones, which impact the COD values of water. This must be done to enable water to be reused or recycled in the process plants, as these factors affect the state andconditions of the system.

VII. MATERIALS AND METHODS

The analysis software we used was DWSIM V10 for process simulation and optimization which is perfectly suitable for Chemical industry.

A. Feed Components:

Component ID	Type	Component Name	Alias
WATER	Conventional	WATER	H2O
CARBO-01	Conventional	CARBON-DIOXIDE	CO2
PROPI-01	Conventional	PROPIONIC-ACID	C3H6O2-1
N-VAL-01	Conventional	N-VALERIC-ACID	C5H10O2-1
N-HEX-01	Conventional	N-HEXANOIC-ACID	C6H12O2-D5
N-BUT-01	Conventional	N-BUTYRIC-ACID	C4H8O2-1
FORMI-01	Conventional	FORMIC-ACID	CH2O2
ACETI-01	Conventional	ACETIC-ACID	C2H4O2-1
VALER-01	Conventional	VALERALDEHYDE	C5H10O-1
N-PRO-01	Conventional	N-PROPIONALDEHYDE	C3H6O-3
N-BUT-02	Conventional	N-BUTYRALDEHYDE	C4H8O-1
ACETA-01	Conventional	ACETALDEHYDE	C2H4O-1
METHY-01	Conventional	METHYL-N-PROPYL-KETONE	C5H10O-2
METHY-02	Conventional	METHYL-ETHYL-KETONE	C4H8O-3
ACETO-01	Conventional	ACETONE	C3H6O-1
2-HEX-01	Conventional	2-HEXANONE	C6H12O-D3
1-PRO-01	Conventional	1-PROPANOL	C3H8O-1
METHA-01	Conventional	METHANOL	CH4O
ISOPR-01	Conventional	ISOPROPYL-ALCOHOL	C3H8O-2
ETHAN-01	Conventional	ETHANOL	C2H6O-2
N-BUT-03	Conventional	N-BUTANOL	C4H10O-1
1-PEN-01	Conventional	1-PENTANOL	C5H12O-1
1-HEX-01	Conventional	1-HEXANOL	C6H14O-1

B. Method Selection

According to the components in the water, there are only two suitable methods that help in simulation. The methods are:

- NRTL
- UNIQUAC HOC

C. NRTL method (Non-Random Two-Liquid)

The NRTL (Non-Random Two-Liquid) approach is a thermodynamic model used to calculate the activity coefficients of mixture components. It is frequently used to simulate the behavior of non-ideal organic chemical combinations. Renon and Prausnitz developed the NRTL approach in 1968, which is based on the premise that deviations from optimal behaviour in a mixture are caused by interactions between molecules of different components. The NRTL approach considers the size, shape, and polarity of molecules.

In the chemical and process industries, the NRTL approach has numerous applications. Among the most popular applications of the NRTL approaches are:

1. **Design and Optimisation of Distillation Columns:** The NRTL technique is used to compute the activity coefficients of mixture components, which are essential parameters in the construction and optimisation of distillation columns. The NRTL approach facilitates the optimisation of distillation operations and reduces energy usage by accurately predicting the behaviour of mixtures.
2. **Solvent Selection in Extraction Processes**: The NRTL technique is employed in extraction operations to determine the optimal solvent for a specific application. The NRTL approach can help optimise the extraction process and maximise yields by accurately predicting the behaviour of mixtures.
3. **Design of Chemical Processes**: The NRTL approach is utilised in chemical process design to predict mixture behaviour and optimise process parameters. This can help minimise the time and expense of process development while also increasing the overall efficiency of chemical processes.
4. **Prediction of Thermodynamic Properties**: The NRTL approach can predict various thermodynamic parameters, including activity coefficients, vapour-liquid equilibrium, and liquid-liquid equilibrium. This data is essential for the design and optimization of many chemical processes.

Overall, the NRTL technique is an effective tool for predicting the behaviour of non-ideal mixtures in various chemical and industrial applications. Its simplicity and precision make it a popular option among chemical engineers and scientists.

D. UNIQUAC HOC Method

The UNIQUAC HOC (Hierarchy of Orders of Contribution) method is an extension of the UNIQUAC (Universal Quasi-Chemical) model for predicting the activity coefficients of components in a mixture. The UNIQUAC HOC method is beneficial for mixtures containing highly asymmetric and associating components, such as alcohols, organic acids, and water.

The UNIQUAC model is a group contribution method that uses the interaction parameters between groupsof molecules to calculate activity coefficients. The UNIQUAC HOC model extends this concept by incorporating a hierarchy of orders of contribution to the interaction parameters. The hierarchy is based on the degree of association of the components in the mixture, with higher orders of contribution accounting for stronger associations. The UNIQUAC HOC model consists of two main steps:

1. **Calculation of the Interaction Parameters**: The interaction parameters between the groups of molecules are calculated based on experimental data. The interaction parameters are then organized into a hierarchy of orders of contribution based on the degree of association of the components.
2. **Calculation of the Activity Coefficients**: The activity coefficients of the components in the mixture are calculated using the interaction parameters and the UNIQUAC equation. The UNIQUAC HOC model considers the hierarchy of order of contribution in calculating activity coefficients, thereby enhancing the model's accuracy for mixtures containing highly asymmetric and associating components.

The UNIQUAC HOC method has been demonstrated to provide significantly improved accuracy compared to the original UNIQUAC model for mixtures containing highly asymmetric and associating components. It is widely used in the chemical and process industries for designing and optimising processes involving such mixtures.

E. Input Constraints

Temperature (°C)	**100**
Pressure (bar)	1.3
Input feed Mass flow rate (Kg/hr)	100000
Number of stages	20
Feed stage	5
Reflux ratio	5
Distillate to feed mole ratio	0.9
Condenser pressure [bar]	1.1
Reboiler pressure [bar]	1.4

F. Feed Inputs in Terms of Mass Fractions

WATER	0.98833
CARBO-01	0.0002
PROPI-01	1.00E-05
N-VAL-01	3.00E-05
N-HEX-01	1.00E-05
N-BUT-01	2.00E-05
FORMI-01	0.0001
ACETI-01	0.0008
VALER-01	0.0006
N-PRO-01	0.0003
N-BUT-02	0.0003
ACETA-01	0.0008
METHY-01	0.0001
METHY-02	0.0003
ACETO-01	0.001
2-HEX-01	3.00E-05
1-PRO-01	0.0012
METHA-01	0.005
ISOPR-01	0.0001
ETHAN-01	4.00E-05
N-BUT-03	0.00055
1-PEN-01	0.00017
1-HEX-01	1.00E-05

G. Process

1. Open the simulation and select a black simulation with metric units.
2. Ensure the Properties tab is open.
3. In the setup, select 'Wastewater' and click 'Next'.
4. Add all components by their component ID or manually locate them.
5. Select the base method as NRTL and click Next.
6. Next, click on the simulation tab and design the flowsheet.
7. Add a feed line, mixer and Distillation column (DISTL) and connect

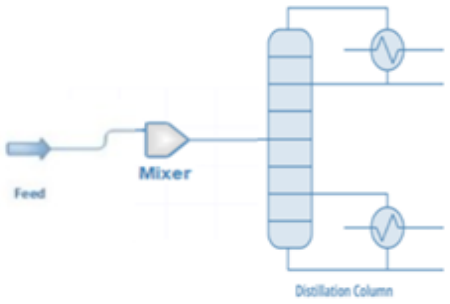

Fig. 9: A Feed Line, Mixer, and Distillation Column

8. Now enter the feed components (Inputs) by their mole fractions as mentioned above.
9. Now, in the distillation column, enter the number of stages, feed stage, and reflux ratio, as well as the distillate-to-feed mole ratio and condenser and reboiler pressures.
10. Add the property as Chemical Oxygen Demand (COD) in display options.
11. Run the simulation and check for status.
12. As the simulation runs successfully, we can view the results on the left as a stream summary.
13. Check the water and COD mixture in terms of fractions.

Material					
Stream Name	**Units**	**FEED**	**UP**	**WASTE H20**	
Description					
From				B1	B1
To		B1			
Stream Class			CONVEN	CONVEN	CONVEN
Maximum Relative Error					
Cost Flow	$/hr				
MIXED Sub stream					
Phase		Liquid Phase	Liquid Phase	Liquid Phase	
Temperature	C	100	95.0612	109.351	
Pressure	bar	1.3	1.2	1.4	
Molar Enthalpy	kcal/mol	-66.8297	-66.7988	-66.7029	
Mass Enthalpy	kcal/kg	-3684.1	-3631.66	-3699.26	
Molar Entropy	cal/mol-K	-34.8837	-35.2796	-34.3696	
Mass Entropy	cal/gm-K	-1.92302	-1.91805	-1.9061	
Molar Density	kmol/cum	50.4613	49.7067	50.3675	
Mass Density	kg/cum	915.369	914.28	908.197	
Enthalpy Flow	Gcal/hr	-368.41	-110.472	-257.398	
Average MW		18.14	18.3935	18.0314	
Mass Flows	kg/hr	100000	30419.2	69580.8	
Mass Fractions					
WATER		0.98833	0.964597	0.998705	
Volume Flow	cum/hr	109.246	33.2712	76.6143	
COD Chemical oxygen demand for the mixture	fraction	0.0213103	0.0671229	0.00128209	

As we can see, a large volume of water is lost since it was supplied as the top fraction, and the COD levels of the top fraction are higher than those of the bottom fraction. To reflux water from the top to the distillation column, we must include a Separator and Pump in the design flow sheet and link the top portion of the distillation column to the Separator.

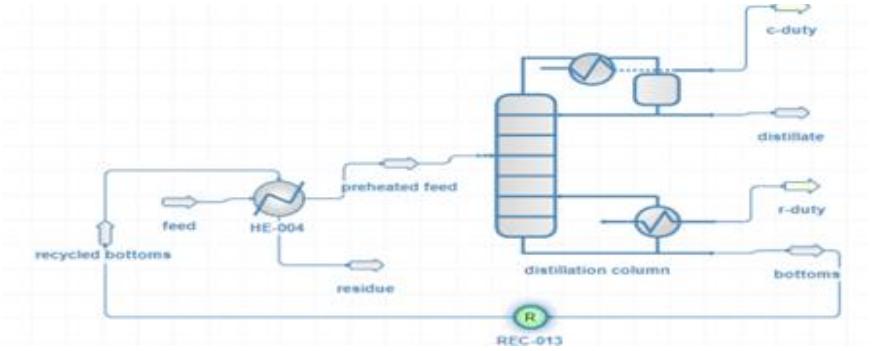

Fig. 10: Shows a Portion of the Distillation Column to the Separator

In the Separator, the temperature is set to 95 degrees and the pressure is 1.1 bar. Now apply pressure of 1.2 bar to the pump and connect the bottoms of the separator to the pump. From the pump, recycle it back to the mixer. Now, run the simulation and check the results. Rerun the simulation for both methods and compare them.

VIII. DISTILLATION COLUMN OUTPUT DATA

Name	B1
Property method	NRTL
Henry's component list ID	
Electrolyte chemistry ID	
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Number of stages	20
Feed stage	5
Reflux ratio	4
Distillate to feed mole ratio	0.3
Condenser pressure [bar]	1.2
Reboiler pressure [bar]	1.4
Condenser duty [Gcal/hr]	113.2665
Reboiler duty [Gcal/hr]	114.1513
Feed stage temperature [C]	105.7479
Top stage temperature [C]	92.69132
Bottom stage temperature [C]	109.3474
Feed quality	-0.005056
Total feed stream CO2e flow [kg/hr]	22.20964
Total product stream CO2e flow [kg/hr]	22.20964
Net stream CO2e production [kg/hr]	0

Name	B1
Property method	UNIQUAC
Henry's component list ID	
Electrolyte chemistry ID	
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Number of stages	20
Feed stage	5
Reflux ratio	4
Distillate to feed mole ratio	0.3
Condenser pressure [bar]	1.2
Reboiler pressure [bar]	1.4
Condenser duty [Gcal/hr]	112.507402
Reboiler duty [Gcal/hr]	113.358721
Feed stage temperature [C]	105.73984
Top stage temperature [C]	92.5858671
Bottom stage temperature [C]	109.349059
Feed quality	-0.006054286
Total feed stream CO2e flow [kg/hr]	21.2292929
Total product stream CO2e flow [kg/hr]	21.2292929
Net stream CO2e production [kg/hr]	0

IX. NRTL Method

Material						
Stream Name	Units	FEED	UP	WASTEH20	SEPUP	SEPDOWN
Mass Fractions						
WATER		0.98833	0.903811	0.999231	0.545745	0.924445
CARBO-01		0.0002	0.000470026	0	0.0083198	1.77E-05
PROPI-01		1.00E-05	6.09E-05	9.30E-06	3.86E-05	6.22E-05
N-VAL-01		3.00E-05	2.49E-07	3.07E-05	3.23E-08	2.62E-07
N-HEX-01		1.00E-05	0.000650203	4.55E-06	0.00023021	0.00067441
N-BUT-01		2.00E-05	0.000328764	1.55E-05	0.00020344	0.00033599
FORMI-01		0.0001	0.000164065	9.97E-05	0.00011114	0.00016712
ACETI-01		0.0008	0.0109139	0.00060876	0.00856472	0.0110493
VALER-01		0.0006	0.00198678	0	0.0249594	0.00066294
N-PRO-01		0.0003	0.000905237	0	0.0124797	0.00023824
N-BUT-02		0.0003	0.00132048	0	0.0124797	0.00067741
ACETA-01		0.0008	0.00239216	0	0.0332792	0.00061224
METHY-01		0.0001	0.000311436	0	0.0041599	8.97E-05
METHY-02		0.0003	0.00113352	0	0.0124797	0.00047967
ACETO-01		0.001	0.00458499	0	0.0415989	0.00245199
2-HEX-01		3.00E-05	8.47E-05	0	0.00124797	1.76E-05
1-PRO-01		0.0012	0.00812116	0	0.0499186	0.0057125
METHA-01		0.005	0.0579389	1.84E-14	0.207994	0.0492918
ISOPR-01		0.0001	0.000542265	0	0.00415989	0.00033379
ETHAN-01		4.00E-05	0.000340899	0	0.00166395	0.00026466
N-BUT-03		0.00055	0.00307311	0	0.0228794	0.00193174
1-PEN-01		0.00017	0.000814333	0	0.0070718	0.00045374
1-HEX-01		1.00E-05	5.12E-05	0	0.00041599	3.02E-05
Volume Flow	cum/hr	109.246	48.7936	107.455	2731.6	46.0857
Chemical oxygen demand for mixture	fraction	0.0213103	0.161036	0.00079823	0.854075	0.121099

H. UNIQUAC HOC Method

Material					
Stream Name	Units	FEED	UP	WASTEH20	SEPDOWN
Mass Fractions					
WATER		0.98833	0.909874	0.999056	0.930598
CARBO-01		0.0002	0.000483465	0	2.96E-05
PROPI-01		1.00E-05	1.33E-05	1.01E-05	1.37E-05
N-VAL-01		3.00E-05	0.00149772	3.72E-07	0.00151216
N-HEX-01		1.00E-05	0.00036925	6.01E-11	0.000366297
N-BUT-01		2.00E-05	0.000504378	1.16E-05	0.000512455
FORMI-01		0.0001	1.44E-06	0.000102425	1.50E-06
ACETI-01		0.0008	1.19E-05	0.000819406	1.24E-05
VALER-01		0.0006	0.00167945	0	0.000330944
N-PRO-01		0.0003	0.000879146	0	0.000207146
N-BUT-02		0.0003	0.0010451	0	0.000382594
ACETA-01		0.0008	0.00446049	3.50E-14	0.0027895
METHY-01		0.0001	0.000369374	0	0.00014974
METHY-02		0.0003	0.00110202	0	0.000442773
ACETO-01		0.001	0.00553577	0	0.00344477
2-HEX-01		3.00E-05	0.000105087	0	3.89E-05
1-PRO-01		0.0012	0.00801943	0	0.00558897
METHA-01		0.005	0.05917	4.26E-14	0.050516
ISOPR-01		0.0001	0.000484831	0	0.0002718
ETHAN-01		4.00E-05	0.000345372	0	0.000268821
N-BUT-03		0.00055	0.00314623	0	0.002002
1-PEN-01		0.00017	0.000855097	0	0.000494714
1-HEX-01		1.00E-05	4.70E-05	0	2.56E-05
Volume Flow	cum/hr	109.246	48.6799	107.489	45.9148
Chemical oxygen demand for mixture	fraction	0.0213103	0.158251	0.00094602	0.118219

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X. RESULT

		Initial Stage		final stage	
Stream Name	**Units**	**FEED**	**WASTEH20**	**FEED**	**WASTEH20**
Temperature	C	100	109.351	100	109.341
Pressure	bar	1.3	1.4	1.3	1.4
Molar Enthalpy	kcal/mol	-66.8297	-66.7029	-66.8423	-66.6959
Mass Enthalpy	kcal/kg	-3684.1	-3699.26	-3684.8	-3700.2
Molar Entropy	cal/mol-K	-34.8837	-34.3696	-34.9202	-34.369
Mass Entropy	cal/gm-K	-1.92302	-1.9061	-1.92503	-1.90675
Molar Density	kmol/cum	50.4613	50.3675	50.4613	50.3885
Mass Density	kg/cum	915.369	908.197	915.369	908.249
Enthalpy Flow	Gcal/hr	-368.41	-257.398	-368.48	-361.125
Average MW		18.14	18.0314	18.14	18.0249
Mass Flows	kg/hr	100000	69580.8	100000	97596.1
Mass Fractions					
WATER		0.98833	0.998705	0.98833	0.999231
Volume Flow	cum/hr	109.246	76.6143	109.246	107.455
COD Chemical oxygen demand for the mixture	fraction	0.0213103	0.00128209	0.02131	0.000798231

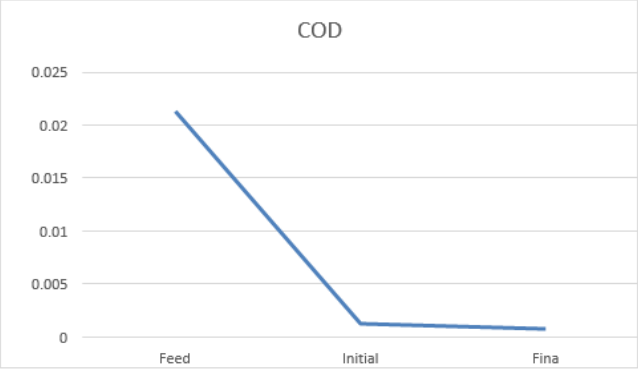

Fig. 11: Graph Showing the COD Results

The elimination of aldehydes, ketones, and alcohols that might alter COD values has been performed according to the simulation findings, and a substantial difference is evident throughout. The NRTL technique yields a higher Mass Fraction than the UNIQUAC HOC model, with a minimally significant difference. However, we may observe a higher COD in NRTL than in UNIQUAC HOC.

XI. CONCLUSION

Indian standards for effluent quality must optimise the COD levels in the wastewater produced by the Fischer-Tropsch process before being released into the environment. As a result, post-treatment of the treated water is necessary. DW SIM is being used in this instance to examine the COD readings within various components of the wastewater treatment system. Wastewater can be utilised for industrial purposes after post-treatment. We employed the NRTL approach to produce a large volume of water, as per this analysis. The neutralisation device receives the wastewater and adjusts its pH. Now, industrial processes can safely utilise wastewater, which is also beneficial for the environment.

AIM AND OBJECTIVE

The objective of our study is to analyze water treatment in the Fisher-Tropsch process and eradicate volatile contaminating chemicals. The Volatile Organic Compound (VOC) significantly contributes to the Chemical Oxygen Demand (COD) of Wastewater. This investigation aims to utilise the distillation column and DWSIM modelling software to minimise the COD of water and remove contaminants from it.

DECLARATION STATEMENT

Funding	No, did not receive funds from any resources.
Conflicts of Interest	No conflicts of interest to the best of our knowledge.
Ethical Approval and Consent to Participate	No, the article does not require ethical approval or consent to participate, as it presents evidence that is not subject to interpretation.
Availability of Data and Material/ Data Access Statement	In this research work, the authors used publicly available data from various e-commerce websites.
Authors Contributions	All authors contributed equally to the article.

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