IJARSCT

International Journal of Advanced Research in Science, Communication and Technology

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

ISSN: 2581-9429

Volume 5, Issue 1, August 2025

Impact Factor: 7.67

Microreactor Technology for Hydrotreatment of Biofuels: A Review

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Abstract: *Population growth, industrial expansion, and growing urbanization are all contributing to the rapid alteration of the global energy landscape. The International Energy Agency (IEA) projects that by 2040, the world's energy consumption will have increased by more than 25%, putting tremendous strain on the world's supply of fossil fuels and posing major questions about energy security and environmental sustainability. The over reliance on fuels generated from petroleum is a major contributor to air pollution, climate change, and greenhouse gas (GHG) emissions. As a result, a shift to cleaner, greener, and more sustainable energy sources is desperately needed. Out of all the options, biofuels have become a vital part of the worldwide movement to decarbonize the energy sector, especially the markets for industrial and transportation fuels.*

Keywords: *International Energy Agency*

I. INTRODUCTION

1.1 Overview

Population growth, industrial expansion, and growing urbanization are all contributing to the rapid alteration of the global energy landscape. The International Energy Agency (IEA) projects that by 2040, the world's energy consumption will have increased by more than 25%, putting tremendous strain on the world's supply of fossil fuels and posing major questions about energy security and environmental sustainability. The over reliance on fuels generated from petroleum is a major contributor to air pollution, climate change, and greenhouse gas (GHG) emissions. As a result, a shift to cleaner, greener, and more sustainable energy sources is desperately needed. Out of all the options, biofuels have become a vital part of the worldwide movement to decarbonize the energy sector, especially the markets for industrial and transportation fuels.

1.2 Biofuels and its need for Hydrotreatment:

Biofuels are renewable sources of energy derived from processing of plants, biomass, etc. These include ethanol, biodiesel, pyrolysis oil, Biogas which can be used to get energy. Their applications include blending in transportation fuel, electricity generation, cooking and other industrial applications [1]. Although biofuels have many applications in energy sector, they cannot be used directly as a transportation fuel. In order to use them as direct transportation fuel, the biofuel needs to be treated through some pathways, including steam reforming, which is followed by Fischer-Tropsch synthesis, and catalytic cracking over zeolites. However, recently, there has been a lot of interest in the hydro-deoxygenation (HDO) of pyrolysis oil [2]. Hydrotreatment or HDO of biofuels is done in order to make the biofuel an alternative to conventional transportation fuel which can be directly used in vehicles [3]. Hydrotreatment of biofuels is achieved by introducing hydrogen gas in a reactor along with biofuel with specific reaction parameters [4]. This process modifies the physical and chemical properties of biofuels by changing its density, cetane number, viscosity, oxygen content, sulfur content, thermal stability, etc [5].

1.3 Microreactors:

The above process can be achieved through various types of reactors and the requirement of catalyst for every reactor. The most common types of reactors are batch reactor, continuous reactor, autoclave reactor, packed bed reactor and

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microchannel reactor (microreactor). Microreactors refer to systems with a characteristic length in the micrometre range. Systems in this size allow handling small quantities of reagents and samples, with reduced residence time, better control of chemical species concentration, high heat and mass transfers, and high surface/volume ratio. These characteristics led to the application of these microdevices in several areas, such as biological systems, energy, liquid-liquid extraction, food, agricultural sectors, pharmaceuticals, flow chemistry, microreactors, and biodiesel synthesis. Microreactors are devices that have interconnected microchannels, in which small amounts of reagents are manipulated and react for a certain period of time [6].

The objective of this paper is to review the existing process of hydrotreatment of biomass derived biofuel to transportation fuel using microreactor technology. In this process, the biomass derived biofuel is fed into the microchannels of microreactors along with hydrogen gas in presence of a catalyst and respective reaction parameters to get the desired product.

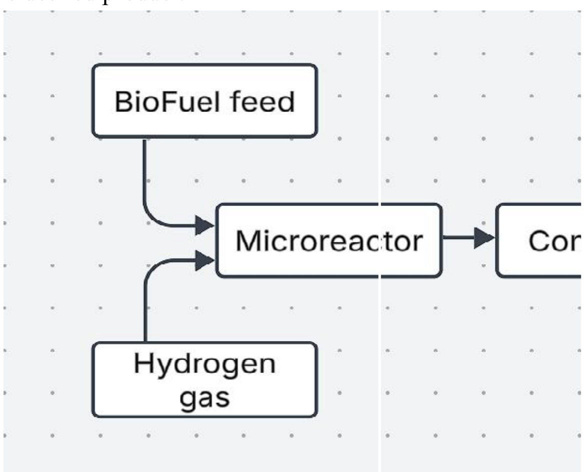

Figure 1. Basic block diagram for the process of Hydro-deoxygenation.

II. BIOFUELS AND ITS TYPES

Biofuel is a type of fuel derived from biomass which can be produced in short period of time unlike traditional fuels. They can be made from plants, agricultural waste or industrial biowaste. Biofuels can be used in various applications like transportation, electricity generation, heating, etc. Biofuels are classified on the basis of feedstock, production methods and whether the biofuel is in liquid, solid or gaseous state. The various types of biofuels are as follows,

2.1 Types of Biofuels:

1. Bioethanol: Bio-ethanol obtained from agricultural materials and agro- wastes offers a sustainable alternative to conventional energy sources and is also low cost and readily available. The utilization of agricultural waste for bio-ethanol production also does not disturb the consumer food supply as it is based on waste-to-energy concept. The production of bioethanol mainly involves the fermentation of starch and sugars such as corn or sugarcane. The obtained product can be used as an additive in convention fuel [7].

2. Biodiesel: Biodiesel is defined as the renewable fuel made from natural sources like vegetable oil, waste cooking oil, biomass or animal fats. Biomass is readily available resource on earth. Thus, converting biomass to biodiesel is a good alternative to replace conventional diesel. Biodiesel is fatty acid methyl ester (FAME) produced using chemical trans-esterification process. The properties of biodiesel depend on the raw material and the techniques used for conversion [8].

3. Pyrolysis oil: Pyrolysis oil is produced using thermal degradation of organic material like plastic in the absence of oxygen. In this process, long carbon chains are broken down into useful fraction. Typically, solid char, pyrolysis oil and

DOI: 10.48175/IJARSCT-28669

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pyrolysis gas are produced from the organic material. As plastic cannot be recycled or takes very long to degrade, plastic pyrolysis is a good way to reduce plastic and convert it into valuable product [9].

4. Biogas: Biogas technology employs the use of microorganisms to break down organic feedstocks, mainly composed of livestock manure, crop residues, debarked wood and other perishable crops, and wet organic wastes from the food processing industries. In addition to producing electricity, this procedure minimizes greenhouse gas emissions and waste. Therefore, it is clear that biogas plays a significant role in giving developing nations that lack adequate infrastructure access to sustainable energy for direct use in cooking and electricity generation. As a result, biogas has two benefits: it prevents the effects of waste products while producing electricity through the appropriate use of renewable resources [10].

5. Bio Syngas: Bio syngas, also known as synthesis gas from biomass, is a mixture of carbon monoxide (CO), hydrogen (H2), and other gaseous components. It is produced by partial gasification of biomass at high temperature. This syngas produced by biomass gasification is cleaner and efficient as compared to those of direct combustion [11].

6. Bio Hydrogen: Among the potential substitutes for fossil fuels, hydrogen has been identified for its potential to be a carbon-free energy carrier. As an innovative energy carrier, hydrogen can perform a vital role in environmental decarbonization, when sustainably produced. Biomass- based hydrogen production has garnered a lot of attention lately since it can significantly lower greenhouse gas emissions. Examples of biomass that can be utilized as feedstock to generate energy include energy crops, industrial and municipal trash, and agricultural residues. One of the various ways to generate energy is by converting biomass feedstocks into power or heat; other processes can transform biomass into secondary energy sources and energy carriers like hydrogen. The primary methods for producing hydrogen from biomass as a feedstock are thermochemical and biological processes. The output of hydrogen is usually larger and the thermochemical pathway is substantially faster than biological processes. On the other hand, biological conversion methods are often regarded as more reliable and advanced technologically. Gasification, pyrolysis, and hydrothermal liquefaction (HTL) are examples of thermochemical process [12].

7. Biomass Pellets: Solid biomass can act as a biofuel in its original form but is heterogenous in nature due to its origin, harvesting and handling procedures. All these variable results in high moisture content and/or unfavorable weight to volume ratio. This can be overcome by processing the solid biomass into biomass pellets. Pellets are densified version of solid biomass with more homogeneity, less moisture and higher energy density. Due to these properties, these pellets can be used in large and small power plants and also individual boiler rooms [13].

III. NEED FOR HYDROGENATION OF BIO FUELS

As the global demand for sustainable energy sources grows, biofuels have emerged as a promising alternative to fossil fuels. However, raw biofuels, especially those derived from biomass such as vegetable oils and animal fats, often suffer from poor fuel properties that limit their direct use in conventional engines. To improve the quality of biofuels, hydrogenation a catalytic process involving the addition of hydrogen is widely employed. This process significantly enhances the chemical stability, combustion characteristics, and compatibility of biofuels with existing infrastructure.

3.1 Limitations of Raw Biofuels:

Raw biofuels, such as vegetable oils or bio-oils produced via pyrolysis or liquefaction, typically contain a variety of oxygenated compounds (e.g., carboxylic acids, aldehydes, ketones, esters, and phenols). These compounds are undesirable for several reasons:

- High oxygen content reduces the energy density and causes incomplete combustion [14].
- High viscosity makes pumping and atomization inefficient in internal combustion engines [15].
- Poor thermal and oxidative stability leads to gum formation and carbon deposits [16].
- Corrosiveness due to acidic compounds damages engine parts and pipelines [17].

These shortcomings necessitate further upgrading of biofuels, among which hydrogenation stands out as a key refining method.

3.2 Role of Hydrogenation:

Hydrogenation refers to the addition of hydrogen (H_2) to the chemical structure of bio-oil components in the presence of a suitable catalyst and under elevated temperature and pressure. The primary objectives of hydrogenation in biofuel processing include:

A. Hydrodeoxygenation (HDO)

HDO removes oxygen from oxygenated compounds by converting them into hydrocarbons and water. This improves the calorific value, stability, and hydrophobicity of the fuel [18].

B. Hydrodesulfurization (HDS)

Hydrogenation helps eliminate sulfur- and nitrogen-based impurities, producing cleaner-burning fuels with low emissions [19].

C. Saturation of Double Bonds

In triglycerides and fatty acids, unsaturated bonds are hydrogenated to saturated bonds. This process:
• Increases oxidative stability
• Prevents polymerization and gum formation
• Reduces NOx emissions due to more complete combustion [20]

D. Cracking and Isomerization

Under more severe conditions, hydrogenation can lead to hydrocracking, breaking large molecules into smaller, more volatile compounds suitable for use as gasoline, diesel, or jet fuel. Isomerization also improves cold flow properties [21].

• Summary of Parameter Changes

Parameter	Before Hydrogenation	After Hydrogenation
Oxygen Content	High (due to esters, alcohols)	Low (converted to hydrocarbons)
Saturation Level	Unsaturated (double bonds)	Saturated (single bonds)
Cetane Number	Lower	Higher
Density	Higher	Lower
Viscosity	Higher	Lower
Cold Flow Properties	Poorer (higher cloud/pour points)	Better (lower cloud/pour points)
Oxidative Stability	Lower	Higher
Thermal Stability	Lower	Higher
NOx Emissions	Higher	Lower
Particulate Matter Emissions	Higher	Lower
sulphur Content	Higher (if not desulfurized)	Lower (if desulfurized)
Energy Density	Lower	Higher

Table 1

IV. CATALYST FOR HYDROTREATMENT OF BIOFUELS

Hydrotreatment is one of the crucial steps in converting biofuels into renewable transportation fuel such as green diesel. Biomass feed ranging from vegetable oils and animal fats to pyrolysis oils are typically rich in oxygenated compounds, which contribute to low heating value, corrosiveness, and chemical instability [22]. To produce stable and high-quality fuels, the oxygen in bio-oils must be removed through reactions like hydrodeoxygenation (HDO), hydrocracking, hydrogenation, and isomerization. These transformations are catalytically driven and require the presence of hydrogen

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ISSN: 2581-9429 Volume 5, Issue 1, August 2025 Impact Factor: 7.67

under elevated temperatures (250–400 °C) and pressures (30–130 bar) [23]. Catalysts play a vital role in enhancing the efficiency, selectivity, and viability of these reactions. Without catalysts, hydrotreatment would demand prohibitively high energy inputs and yield undesirable by-products [24]. Sulfided catalysts such as NiMo/Al2O3 and CoMo/Al2O3 are commonly used in petroleum refining and adapted for bio-oil processing due to their cost-effectiveness and robust activity [25]

Below is the list of various catalysts used to perform hydrotreatment of different types of biofuels in different types of reactors. These experiments were performed by researchers using different process parameters to support their experiments.

Sr No.	Catalyst	Reactor	Reference
1	NiMo/Al_2O_3	Batch Reactor	[26]
2	NiCu/Al-MCM-41	Batch Autoclave Reactor	[27]
3	Pd/C	Catalytic Packed Bed Reactor	[28]
4	NiCu/Al_2O_3	Batch Reactor	[29]
5	Pt/C	Batch Reactor	[30]
6	Ru/C	Batch Reactor	[31]
7	NiCu/TiO_2	Batch Reactor	[32]
8	NiMoS	Packed Bed Reactor	[33]
9	CoMo/Al_2O_3	Packed Bed Reactor	[34]

V. DESIGN OF MICRO-CHANNEL REACTOR

The design calculations will present the designing of microchannel reactor to hydrotreat the biodiesel based on already known facts and assumptions as not much research has been conducted on this topic.

This design will be done to calculate the volume of hydrogen gas required to hydrotreat 10 LPH of Biodiesel (methyl oleate- a common type of FAME found in biodiesel) with 300oC Temperature and 100 bar pressure of both biodiesel feed and hydrogen gas. Based on these calculations, a micro-channel reactor design will be carried out with packed bed NiMo/Al2O3 catalyst. The MOC of the reactor is plate type stainless steel with grade 316. LPSH of biodiesel is assumed to be 1 per hour.

Given Data

Biodiesel flowrate = 10 L/hr Density of biodiesel = 0.88 g/mL
Molecular weight of biodiesel (methyl oleate) = 296 g/mol
Hydrogen requirement = 3 mol H_2 per mol of biodiesel
Reactor operating conditions: 300°C (573 K), 100 bar (98.7 atm)
LPSH = 1/hr
MOC = SS 316
Catalyst = NiMo/Al2O3

5.1 Volume of Hydrogen required to perform hydrotreatment:

a) Converting biodiesel volume to mass:
Mass = 10,000 mL/hr × 0.88 g/mL = 8800 g/hr

b) Converting mass to number of moles of biodiesel:
Moles of biodiesel = 8800 g/hr ÷ 296 g/mol = 29.73 mol/hr

c) Calculate moles of hydrogen required:
H_2 required = 29.73 mol/hr × 3 = 89.2 mol/hr

d) Use the ideal gas law to calculate volume at 100 bar and 300°C:
$PV = nRT$
Therefore, $V = (nRT)/P$
$R = 0.0821$ L·atm/mol·K, $T = 573$ K, $P = 98.7$ atm
$V = (89.2 \times 0.0821 \times 573) / 98.7 = 42.4$ L/hr $\approx$ 43 L/hr
The Volume of hydrogen gas required to perform hydrotreatment of biodiesel is approximately 43L/hr.

5.2 Design of reactor

a. Catalyst Volume Required:
Liquid Hourly Space Velocity (LHSV) = 1 h^{-1}
Biodiesel volumetric flowrate = 0.01 m^3/h
Catalyst volume required = Q liquid / LHSV
= 0.01/1
= 0.01 m^3

b. Channel Volume and Number of Channels:
Cross-sectional area of one cylindrical channel:
$A = (\pi/4) \times d^2$
$= (\pi/4) \times (0.005)^2$
$= 1.9635 \times 10^{-5}\ m^2$

Volume per channel (assuming 1 m length):
Volume of single channel = A × L
$= 1.9635 \times 10^{-5} \times 1$
$= 1.9635 \times 10^{-5}\ m^3$

Number of channels required:
N = Volume of catalyst / Volume of single channel
$= 0.01 / 1.9635 \times 10^{-5}$
$= 509 \approx 510$ channels

c. Plate Thickness Calculation
To calculate the minimum plate thickness to withstand 100 bar pressure: Using ASME flat plate design:
$t = \sqrt{(P \times a^2 / (K \times \sigma))}$ + corrosion allowance

Assumptions:
- Plate span (a) = 20 mm = 0.02 m
- Design pressure (P) = 10 MPa
- Allowable stress (σ) = 100 MPa
- K (constant) = 0.3
- Corrosion allowance = 1 mm

$t = \sqrt{((10^7 \times 0.02^2) / (0.3 \times 10^8))} + 0.001$
$= \sqrt{(1.333 \times 10^{-4})} + 0.001$
$= 0.01155 + 0.001$
$= 0.0126$ m = 12.6 mm

DOI: 10.48175/IJARSCT-28669

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Parameter	Value
Biodiesel feedrate	10 LPH
Hydrogen gas flowrate	43 LPH
Total flowrate	0.053 m³/h
Operating temperature	300°C (573 K)
Operating pressure	100 bar (10 MPa)
Catalyst volume	0.01 m³ (10 liters)
Channel diameter	5 mm
Channel length	1 meter
Number of channels	510
Plate thickness (minimum)	12.6 mm
Material of construction	SS 316
Corrosion allowance	1 mm
Safety factor used	3

VI. ADVANTAGES AND LIMITATIONS

Microreactor technology is gaining traction as a game-changing approach for the hydrotreatment of biofuels, especially biodiesel. Known for its ability to improve reaction efficiency and operational safety, this technology offers a modern alternative to traditional large-scale reactors. However, like any emerging technology, it comes with both significant advantages and a few challenges. Below is a clear look at the key benefits and drawbacks of microreactor technology in this context.

6.1 Advantages

1) Faster Reaction Times
Thanks to their high surface-area-to-volume ratio, microreactors significantly speed up reaction times reducing processes that typically take hours to just minutes [35].

2) Improved Process Efficiency
Enhanced heat and mass transfer leads to higher conversion rates and selectivity, ultimately lowering the amount of raw materials needed and reducing waste [36].

3) Lower Energy Consumption
With superior heat transfer capabilities, microreactors use less energy, making the entire process more economical and environmentally friendly [36].

4) Enhanced Safety
Because microreactors operate on a much smaller scale, the risks of runaway reactions or other hazardous situations are significantly reduced [36].

6.2 Limitations:

1) Technical Complexity
Designing and operating microreactors requires specialized expertise and equipment, which can make implementation more challenging than conventional systems [37].

2) Scalability Challenges
While microreactors perform exceptionally well at lab or pilot scale, scaling them up to industrial levels while maintaining consistency and performance remains a key hurdle [37].

3) High Initial Costs

The development and deployment of microreactor systems involve considerable upfront investment, which may deter some companies from adopting the technology [37].

VII. RECENT ADVANCES AND FUTURE PROSPECTS

Recent advancements in micro-channel reactor technology for the hydrotreatment of biofuels have brought significant improvements in efficiency, cost-effectiveness, and fuel quality. These reactors stand out due to their high surface-area-to-volume ratio, which greatly enhances both heat and mass transfer. This design feature allows for better mixing and faster reaction rates, making micro-channel reactors highly suitable for the complex processes involved in biofuel production. With the integration of advanced catalysts and innovative reactor designs, these systems are becoming even more effective in meeting the growing demands of cleaner and more sustainable fuels.

7.1 Enhanced Heat and Mass Transfer:

Thanks to their compact structure and large surface-area-to-volume ratio, micro- channel reactors offer exceptional heat and mass transfer capabilities. This enables faster, more efficient chemical reactions, ultimately boosting productivity in biofuel processing. Moreover, the use of structured catalyst systems such as metallic monolith supports further reduces resistance to mass transfer and improves heat conductivity, optimizing the reactor's overall performance [38].

7.2 Catalyst and Reactor Design Innovations:

Innovative catalyst formulations, when evenly coated on metallic surfaces, allow for the production of hydrocarbons with narrower carbon chain distributions. This means more of the desired gasoline and diesel-range products are produced, minimizing the need for further downstream processing [38].

Additionally, the use of microfilaments and microspheres within the reactor promotes turbulent flow and improves mixing critical factors for effective biofuel hydrotreatment.

7.3 Economic and Environmental Benefits:

Micro-channel reactors can achieve up to 15 times the productivity of conventional systems, which translates to major economic advantages [38]. On top of that, these reactors are more energy-efficient, leading to lower operating costs and reduced environmental impact. The ability to produce high-quality biofuels with minimal energy input supports the goals of sustainable energy development [37].

Despite these impressive benefits, challenges remain particularly in scaling up micro-channel reactors for large-scale industrial applications and optimizing their configurations for different biofuel feedstocks. Continued research and development are essential to address these hurdles, improve catalyst performance, and fine-tune reactor designs. With ongoing innovation, micro- channel reactor technology holds great promise for the future of efficient and eco-friendly biofuel production.

VIII. CONCLUSION

The hydrotreatment of biofuels using microreactor technology represents a transformative step toward cleaner, more efficient, and more sustainable fuel production. Unlike traditional large-scale reactors, microreactors offer precise reaction control, faster processing times, and improved safety due to their compact design and enhanced heat and mass transfer capabilities. The integration of advanced catalysts—such as NiMo/Al_2O_3, NiCu-based systems, and supported noble metals—has further improved conversion efficiency, selectivity, and fuel properties, enabling the production of transportation-ready fuels with higher cetane numbers, better cold flow properties, and lower oxygen content.

From an environmental perspective, microreactor-based hydrotreatment significantly reduces energy consumption, minimizes waste generation, and supports decarbonization targets by upgrading renewable feedstocks such as biodiesel, pyrolysis oil, and microalgal-derived oils. Economically, these systems can achieve much higher productivity per unit volume compared to conventional designs, making them attractive for decentralized and modular fuel production facilities.

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ISSN: 2581-9429 Volume 5, Issue 1, August 2025 Impact Factor: 7.67

However, the path to large-scale industrial implementation is not without obstacles. Scaling microreactor systems through numbering-up requires careful engineering to ensure consistent performance across multiple units, while the initial capital investment remains a barrier for widespread adoption. Material innovations, cost-optimized fabrication methods, and robust reactor designs will be essential to overcome these challenges.

Looking forward, the synergy between microreactor technology, renewable hydrogen production, and integrated biorefinery systems offers a compelling vision for the future of sustainable fuels. With continued research and development, microreactors could evolve from specialized laboratory tools to mainstream industrial systems, playing a central role in the global transition toward cleaner energy and reduced reliance on fossil fuels.

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