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INTEGRATED PYROLYSIS–HDN CONVERSION OF WASTE PLASTICS TO MARINE DIESEL: A COMPREHENSIVE REVIEW

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ABSTRACT

The global increase in polymer consumption and ineffective waste management have made the accumulation of plastic waste a serious environmental and energy concern. This paper provides a thorough examination of developments in the combined pyrolysis and hydrodenitrogenation (HDN) methods for turning mixed waste plastics into marine fuel. It investigates the physicochemical characteristics of pyrolytic oils, the thermochemical processes of plastic pyrolysis, and the HDN upgrading that follows to satisfy marine fuel regulations. In addition, frameworks for life-cycle assessment (LCA) and techno-economic assessment (TEA) are examined in order to assess how sustainable such processes are. The assessment highlights important research gaps in areas such as hydrogen sourcing, catalyst deactivation, and the absence of integrated process simulation for the generation of marine diesel. There are suggestions for using green hydrogen technologies, creating inexpensive catalysts, and fine-tuning parameters. The results show that pyrolysis–HDN integration can be a good way to meet the goals of the circular economy and decarbonize marine transportation fuels.

Keywords: Plastic Waste, Pyrolysis, Hydrodenitrogenation, Marine Diesel.

1. INTRODUCTION

The rapid rise in plastic consumption has caused growing alarm around the world because of its long-lasting effects on the environment. Less than 10% of the 400 million tons of plastic produced annually in 2023 were successfully recycled [1]. Plastic pollution and energy insecurity are made worse in Nigeria and other developing nations by a lack of proper waste management infrastructure. One possible path toward resource recovery and pollution reduction is the thermochemical conversion of waste plastics into fuels, such as pyrolysis [2], [3].

However, the high content of heteroatoms, such as nitrogen, sulfur, and oxygen compounds, which cause instability and corrosivity, limits the direct use of pyrolysis oil [4]. Catalytic hydrotreatment, especially hydrodenitrogenation (HDN), is necessary to upgrade the oil quality to meet International Maritime Organization (IMO) specifications for marine diesel [5, 6]. This paper explores the latest developments in pyrolysis and HDN processes, concentrating on their integration for sustainable marine diesel production, and assesses the techno-economic and environmental viability of such approaches.

2. PLASTIC WASTE AND MANAGEMENT STRATEGIES

Globally, the production of plastic garbage still exceeds the capacity for recycling. Flooding, greenhouse gas emissions, and oceanic microplastic contamination are only a few of the detrimental ecological and social effects of improper disposal [7]. Energy inefficiency and polymer incompatibility are the main drawbacks of traditional management techniques such landfilling, incineration, and mechanical recycling [8]. A sustainable substitute that can transform diverse plastic streams into useful chemicals and fuels is chemical recycling, most especially pyrolysis [9].

Effective waste valorization in Nigeria is hampered by a lack of segregation infrastructure and lax enforcement of waste regulations [10]. Pyrolysis might therefore be included into circular economy frameworks to meet national carbon reduction goals while improving waste recovery and energy diversification.

3. PYROLYSIS OF MIXED WASTE PLASTICS

Pyrolysis is a thermal breakdown process that yields char, gas, and oil without the presence of oxygen. Temperature (usually 400–550 °C), heating rate, and residence time are important factors that affect the process [11]. Lighter hydrocarbon yields are the result of cracking, which is encouraged by high temperatures and quick heating [12].

By employing metal oxides (Ni, Co, Fe-based catalysts) or zeolites (HZSM-5, USY), catalytic pyrolysis enhances selectivity for diesel-range hydrocarbons and inhibits the production of char [13]. When it comes to heat transfer and product dispersion, reactor types including fixed-bed, fluidized-bed, and auger reactors offer clear benefits [14]. For example, better oil yields and consistent temperature control are made possible using fluidized-bed reactors [15].

As a result of the different rates of polymer breakdown, mixed plastic feedstocks add another layer of complication. PVC produces chlorinated chemicals that need to be neutralized, polystyrene (PS) produces aromatics, while polyethylene (PE) and polypropylene (PP) mostly produce aliphatic hydrocarbons [16], [17]. Predicting ideal operating conditions is made easier with process optimization using Design Expert or Aspen HYSYS simulations.

4. CHARACTERISTICS AND LIMITATIONS OF PYROLYTIC OILS

With traces of oxygenates, nitrogen, and sulfur compounds, pyrolytic oils usually have a complex mixture of aliphatic, aromatic, and olefinic hydrocarbons [18]. These heteroatoms lead to corrosivity, instability, and poor ignition quality. Pyrolysis oils have higher density, higher overall acid numbers, and lower cetane numbers than traditional marine diesel [19].

Therefore, hydrotreating procedures are necessary to enhance the pyrolytic oils' chemical and combustion characteristics. Such oils do not fulfill MARPOL Annex VI sulfur limitations (<0.5 wt%) in the absence of HDN and hydrodesulfurization (HDS) [20], [21]. The key elements affecting oil quality are compiled in Table 1.

Table 1: The key elements affecting oil quality

Parameter	Typical Condition	Product Effect	Reference
Temperature	400–550 °C	High liquid yield	[22]
Heating rate	>50 °C/min	Improved oil fraction	[23]
Residence time	<2 s	More liquids, fewer gases	[24]
Reactor design	Fluidized-bed	Uniform distribution	[25]
Catalyst type	Zeolite-based	Enhanced selectivity	[26]

5. HYDRODENITROGENATION PROCESS FOR UPGRADING

A hydrogen-aided catalytic process called hydrodenitrogenation (HDN) eliminates nitrogen-containing substances from hydrocarbon feedstocks, including amines and nitriles [27]. It functions at high hydrogen pressures (up to 10 MPa) and temperatures (between 300 and 450 °C). Process variables, feedstock type, and catalyst composition all affect total efficiency.

Because of their stability and activity, Ni–Mo/Al_2O_3 and Co–Mo/Al_2O_3 catalysts are used extensively [28]. Heterocycles are usually hydrogenated in reaction pathways, which are then followed by the breaking of C–N bonds to produce hydrocarbons and ammonia [29]. In order to enhance dispersion and withstand deactivation, recent research has investigated modified catalysts employing supports such as ZrO_2, TiO_2, and mesoporous silica [30], [31]. Catalyst deactivation processes include coke deposition, sintering, and poisoning by sulfur and nitrogen species [32].

When HDN and pyrolysis are combined, upgrading and purifying can occur simultaneously, producing fuels that satisfy marine diesel requirements. The advantages for the environment are greater when hydrogen is produced from renewable resources.

6. TECHNO-ECONOMIC AND ENVIRONMENTAL ASSESSMENT

Life-cycle assessment (LCA) and techno-economic analysis (TEA) are essential instruments for assessing the viability of a process. TEA calculates operational expenses (OPEX), capital expenditures (CAPEX), and profitability metrics like internal rate of return (IRR) and net present value (NPV) [33]. According to studies, the factors that most affect project viability are catalyst life, feedstock cost, and hydrogen price [34].

Energy efficiency, resource usage, and greenhouse gas (GHG) emissions are all revealed by environmental analysis using life cycle assessment (LCA). When pyrolysis is combined with HDN, life-cycle emissions can be reduced by as much as 60% when compared to diesel obtained from fossil fuels, especially when renewable energy or green hydrogen is utilized [35]. In poor nations like Nigeria, the energy intensity of hydrogen production is still a problem [36].

7. FUTURE RESEARCH DIRECTIONS

Although considerable progress has been made, several challenges persist. Future research should emphasize:

- Development of low-cost and coke-r esistant catalysts for HDN;
- Exploration of renewable hydrogen sources (e.g., solar-electrolytic systems);
- Integration of simulation tools (Aspen Plus, HYSYS, Design Expert) to optimize process performance;
- Establishment of pilot-scale demonstration plants using real-world waste streams;
- Policy frameworks that incentivize waste-to-fuel technologies within circular economy models [37]–[39].

8. CONCLUSION

A technically viable and environmentally friendly method of turning mixed waste plastics into premium marine fuel is the combination of pyrolysis and hydrodenitrogenation. Researchers can find cost-effective routes that support global decarbonization goals by combining process optimization with techno-economic and life-cycle studies. The transition to circular plastic economy systems will be accelerated by additional innovation in catalyst design, large-scale deployment, and renewable hydrogen generation.

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