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Editorial

Experimental spray characterization of pyrolysis oil-diesel blend by effervescent atomization using high speed imaging

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Abstract: The utilization of plastic in everyday life has significantly increased due to its affordability, durability, versatility, lightweight, and hardness. However, the non-biodegradable nature of plastic has led to environmental pollution. Hence, this research focused on converting plastic waste into useful renewable energy through an environmentally friendly process. Specifically, the decomposition of polypropylene waste from PPE kits, which contains a high proportion of polypropylene plastic, was investigated. Proximate, ultimate and TGA analyses were conducted to understand the chemical composition and the decomposition temperature of polypropylene. The activation energy and kinetic parameters of decomposition were calculated using three different methods: Kissinger-Akahira-Sunose (KAS), Ozawa-Flynn-Wall (OFW), and Starink model, yielding values in the range of 175 to 190 kJ/mol. The pyrolysis of polypropylene resulted in an oil yield of 31.1 percentage. The collected oil was analyzed using FTIR Spectroscopy. Furthermore, blending of pyrolyzed oil with diesel was carried out and assessed for fuel properties, which were compared to diesel properties. To characterize the spray of the biodiesel blend, an effervescent atomizer was fabricated, and stability variables were extracted from flow visualization using a high-speed camera. Therefore, it was concluded the decomposition of polypropylene plastic waste offers an opportunity to extract pyrolyzed oil, which can be blended with diesel for combustion by achieving fine sprays using an atomizer. This study can be further extended to investigate the development of new kind of atomizers to disintegrate the pyrolytic blend diesel oil. This study will also assist to examine breakup morphology and spray characterization using high speed imaging techniques.

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Nomenclature

Symbols	Meaning	Units
E_a	Activation energy	[kJ/mol]
k	Rate constant	–
α	Conversion ratio	–
R	Universal gas constant	[J/mol.K]
T	Temperature	[K]
A_e	Pre-exponential factor	–
β	Heating rate	[kg/m^3]
ω	Rotor rotational speed	[rad/s]
ΔH	Change in enthalpy	[kJ/mol]
ΔG	Gibbs energy change	[J/mol.K]
ΔS	Entropy change	[J/mol.K]
K_b	Boltzmann constant	[J/K]
h	Planck constant	[J.s]
V_a	Air velocity	[m/s]
V_f	Fuel velocity	[m/s]

1. Introduction

Over the past few decades, the global population growth and the desire for enhanced living standards have resulted in a significant surge in plastic consumption [1]. Since their invention, plastics have become extensively integrated into daily life due to their attractive characteristics like lightweight, strength, and cost-effectiveness. They play a significant role in enhancing comfort and convenience, but their resistance to natural degradation also contributes to substantial environmental concerns and waste management challenges [2]. Polypropylene has emerged as a notable component of plastic waste in household refuse in recent times. Its effective reuse has gained significant importance in response to the rising need for resource recycling and environmental conservation [3]. Polypropylene (PP) is a versatile engineering plastic known for its remarkable chemical resistance, high purity, low water absorption, and effective electrical insulation properties. Due to these favorable attributes, PP is extensively employed as a packaging material for various consumer goods, internal cases, and electronic product containers. The global production of PP has witnessed substantial growth in recent years, resulting in an annual waste generation of over more than 50 million tons worldwide [4].

Waste polypropylene (PP) poses challenges in terms of biological degradation and tends to transform into microplastics, posing risks to human health. The COVID-19 pandemic's surge in mask and PPE kits usage further contributed to the accumulation of PP waste in the environment [5]. The worldwide attention towards waste management and utilization has sparked a global concern. Currently, there is a strong emphasis on converting waste into useful energy resources, which has led to a collective effort in seeking efficient and effective methods to achieve this conversion [6]. Thermal decomposition, also known as pyrolysis, offers a potential method to handle this waste effectively. Pyrolysis and gasification processes hold promise as viable routes for converting waste, such as polypropylene, into valuable fuel or chemical feedstock while ensuring appropriate treatment and utilization [3, 7, 8]. Studies found that Pyrolysis is an efficient method known for producing liquid fuel through a thermochemical conversion process. This process involves applying heat within the temperature range of 250–650 °C under an inert atmosphere, resulting in the generation of liquid, gaseous, and solid fuels. The product composition depends on various factors, such as the catalyst, pyrolysis temperature, starting material, and the type of pyrolysis system used. These products can serve as fuel blending components or additives for valuable chemical production, making them potential replacements for some fossil fuel products [9–13].

To gain a comprehensive understanding of the pyrolysis process of PP, conducting Kinetic analysis and exploring its Thermodynamic behavior through multi-heating rate thermogravimetric analysis (TGA) is crucial. Utilizing a model-free kinetic analysis can help estimate the activation energy (Ea) at various conversion levels, even when the specific reaction model is not known. Many studies have focused on investigating the pyrolysis kinetics of plastic wastes, often relying on the assumption that the reaction can be described by an nth order reaction model [14–19]. Furthermore, the pyrolyzed oil obtained from polypropylene can be blended with diesel to enhance combustion efficiency by generating fine sprays through the utilization of an atomizer. Several investigations have indicated the feasibility of blending pyrolysis oil derived from polypropylene with diesel fuel. This blending approach presents a potential method to utilize waste plastic effectively and mitigate its environmental impact [20]. It is possible to achieve a fine spray of polypropylene pyrolysis oil blended with diesel by utilizing an atomizer. The recent study reveals that effervescent atomizers exhibit the capability to produce fine sprays of liquid with a more uniform distribution of droplet sizes. Additionally, the effervescent atomizer demonstrates the ability to create a stable liquid jet with a well-defined breakup length, which is crucial for achieving a fine spray of liquid. Moreover, this atomization technique shows promise in atomizing high-viscosity feed liquids, even with large exit orifices, resulting in narrower droplet sizes at very low injection pressure [21–23].

A combustion analysis was conducted on various biodiesel blends under two compression ratios of 16 and 17.5. Their findings emphasize that the 15% biodiesel blend exhibited superior engine performance compared to other blends [24]. The investigation of energy recovery from animal waste fat, focusing on blending sheep fat and diesel fuel with nanoparticles to enhance combustion efficiency and reduce emissions. The study demonstrated that blends such as B20+ZnO 100 and B20+ZnO 50 outperformed other combinations [25]. The influence of different catalysts in the pyrolytic process of waste soya-bean was examined by Umit et al., [26] and concluded that a blend containing 25% diesel and 75% IO-II catalyst yielded better biodiesel suitable for CI combustion. Vellaiyan [27] endeavored to improve the physiochemical properties of pyrolytic oil derived from medical plastic waste, finding that specific reaction conditions generated a higher yield of waste plastic oil with exceptional properties. They also utilized response surface methodology (RSM) to optimize combustion efficiency, observing a yield rate of 43.93% for waste pyrolytic oil with the strongest C-H bond [28]. Vellaiyan [29] investigated methods to maximize the yield rate of waste plastic oil through pyrolysis process optimization and fuel modifications. Their study concluded that the WPO10W emulsion significantly enhanced combustion efficiency while drastically reducing NOx, HC, and CO emission.

Effervescent atomizers find extensive use in various industries, with many experimental studies conducted across fields such as gas turbines, internal combustion engines, boilers, and industrial processes. In gas turbine combustors, these atomizers efficiently break down fuel for combustion, resulting in improved fuel-air mixing and combustion efficiency. Likewise, in internal-combustion engines, they enhance fuel atomization and combustion performance, contributing to enhanced engine efficiency and reduced emissions [29]. The objectives of this study were to develop a suitable pyrolysis technique for the degradation of polypropylene waste and to analyze its thermodynamic properties and kinetics, particularly by estimating the activation energy of the pyrolysis reaction through Iso-conversional, Kissinger-Akahira-Sunose, Ozawa-Flynn-Wall, and Starink models from non-isothermal thermogravimetric data. Additionally, the research aimed to blend the pyrolyzed oil of PP with diesel and investigate its spray characteristics using an effervescent atomizer to gain insights into the atomization process of synthetic fuels.

2. Materials and Methods

2.1. Sample collection and pre-treatment

PPE kits (Personal Protective Equipment) containing polypropylene were purchased and then left to dry for 5 days to remove moisture. Subsequently, the kits were cut into smaller pieces using a knife and converted into particles with a size range of 950-1500 μm.

Table 1. Proximate and ultimate properties of polypropylene.

Proximate analysis	Amount (wt.%)	Ultimate Analysis	Amount (wt.%)
Moisture	3.45	Carbon	83.78
Volatile	94.07	Hydrogen	15.24
Ash	1.79	Sulfur	0.20
Fixed Carbon	0.69	Oxygen	0.78

2.2. Physicochemical characterization of polypropylene plastic

The Polypropylene sample undergoes proximate and ultimate analysis following ASTM standards (E872, D-1102, and E871-8), and the results are presented in Table 1. A high volatile content in the polypropylene feedstock (94.07%) suggests that there is a significant potential for energy and matter recovery during thermal cracking, leading to a high yield of products. The ultimate analysis of Polypropylene indicates its suitability as a feedstock for the pyrolysis process due to its high carbon content. The presence of oxygen, sulfur, chlorine, and nitrogen may be attributed to additives introduced during polymer processing [30].

2.3. Thermal analysis (TGA)

TGA is the preferred technique to understand the thermochemical decomposition of Polypropylene plastic materials over a range of temperatures and heating rates. The experiments were conducted at temperatures between 20°C and 700°C with heating rates of 5, 10, 15, and 20°C per minute. Weight measurements were taken for each trial, and the results from TGA were used to calculate kinetic and thermodynamic parameters using various iso-conversional model-free methods.

2.4. Kinetic Analysis

The kinetic factors, which consist of apparent activation energy (E_a) and reaction model ($f(\alpha)$), are essential parameters that are determined using model-free iso-conversional methods [31]. There are many methods that are frequently utilized for establishing the activation energy of polypropylene through chemical kinetic study; however, based on the Arrhenius equation, there are several ways to estimate the activation energy. The most accurate approach, though, is the one developed by Kissinger-Akahira-Sunose (KAS), Starink, and Ozawa-Flynn-Wall (OFW) model [32]. The thermal degradation mechanism of polypropylene is assumed to be a multi-step kinetic process, but it can be effectively approximated as a single-step reaction. The pyrolysis reaction, which converts the polypropylene substrate into yield, can be represented by the following relation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \tag{1}$$

where $\frac{d\alpha}{dt}$ and $f(\alpha)$ represent rate of conversion and function of physical and chemical properties respectively. The conversion ratio (α) is characterized as follows:

$$\alpha = \frac{W_o - W_t}{W_o - W_f}, \tag{2}$$

where W_o, W_t, and W_f represent initial mass, mass at a specific time, and the mass at the end of the decomposition process. These variables can be determined by conducting Thermogravimetric Analysis. The rate of reaction $k(T)$ is calculated using the Arrhenius equation:

$$k(T) = Ae^{\frac{-E_a}{RT}}, \tag{3}$$

where Ae is the pre-exponential factor, E_a is the activation energy (in kJ/mol), R is the universal gas constant, and T signifies the absolute reaction temperature measured in Kelvin. Substituting the obtained expression for $k(T)$ and considering a constant linear heating rate denoted by $\beta = \frac{dT}{dt}$:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{\frac{-E_a}{RT}} f(\alpha). \tag{4}$$

Writing the Equation (3) as an integral equation:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T} e^{\frac{-E_a}{RT}} dT = \frac{AE_a T^2}{\beta} e^{\frac{-E_a}{RT}}, \tag{5}$$

where: $\int_0^\alpha \frac{d\alpha}{f(\alpha)}$ is $g(\alpha)$. The solution to the mentioned equation can be determined either through numerical computation or by approximating $g(\alpha)$ using a specific equation, such as the Kissinger-Akahira-Sunose model:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{g(\alpha)}\right) - \frac{E_a}{RT}, \tag{6}$$

from the slope of $\ln\left(\frac{\beta}{T^2}\right)$ plotted against $\frac{1}{T}$, E_a can be calculated. The expression for the Starink iso-conversional model is given as follows:

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = \text{Constant} - 10008\left[\frac{E_a}{RT}\right], \tag{7}$$

and the $\ln\left(\frac{\beta}{T^{1.92}}\right)$ plotted against $\frac{1}{T}$ used to determine E_a. Similarly, the Ozawa-Flynn-Wall iso-conversional model is represented as:

$$\ln \beta = \ln\left(\frac{A}{Rg(\alpha)}\right) - 5.331 - 1.052\left[\frac{E_a}{RT}\right]. \tag{8}$$

The value of apparent activation energy E_a can be determined by calculating the slope of $-1.052\left[\frac{E_a}{RT}\right]$ from the plot of $\ln(\beta)$ against $\frac{1}{T}$.

2.5. Evaluation of Thermodynamic Parameters

The determination of thermodynamic parameters plays a crucial role in assessing the effectiveness of the pyrolysis process, which contains the enthalpy change (ΔH), Gibbs energy change (ΔG), and entropy change (ΔS), were calculated by the following Equations (9) to (11), respectively [33].

$$\Delta H = E_a - RT, \tag{9}$$

$$\Delta G = E_a + RT \ln \left[\frac{K_b T}{hAe}\right], \tag{10}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}, \tag{11}$$

where, pre-exponential factor (Ae) was taken from the Kissinger method, (T) denotes the maximum peak decomposition temperature measured in Kelvin, (K_b) corresponds to the Boltzmann constant, and (h) signifies the Planck constant (6.626×10^{-34} Js).

2.6. Pyrolysis of Polypropylene PPE kits

In the laboratory-scale pyrolysis experiment, around 900 grams of chopped PPE kits polypropylene waste was subjected to thermal decomposition at temperatures ranging from 450 to 650 °C for over 1 hour. The process took place in a closed reactor chamber, ensuring the absence of oxygen. The pyrolysis process was carried out at four different heating rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min. The resulting pyrolysis oil was collected in a beaker, and its volume was approximately 350 ml. The calculated yield percentage of the pyrolysis oil of PP was found to be 31.11%. Furthermore, the pyrolyzed oil PP was analyzed using FTIR spectroscopy to identify its chemical composition, functional groups, and chemical bonds.

2.7. Polypropylene Pyrolysis Oil-Diesel Blend and its Fuel Properties

In the search for an eco-friendly alternative to fossil fuels, the blending of polypropylene pyrolysis oil with diesel was conducted, combining 10% polypropylene pyrolysis oil with 90% diesel. Extensive studies have revealed that a blend of 10% to 30% plastic pyrolysis oil with diesel exhibits optimal engine performance characteristics [20,34]. The fuel properties of the blended polypropylene pyrolysis oil with diesel were evaluated and compared with the properties of diesel fuel. The summarized data in Table 2 indicates that the blend exhibits similar properties to diesel.

2.8. Design & Fabrication of Effervescent Atomizer

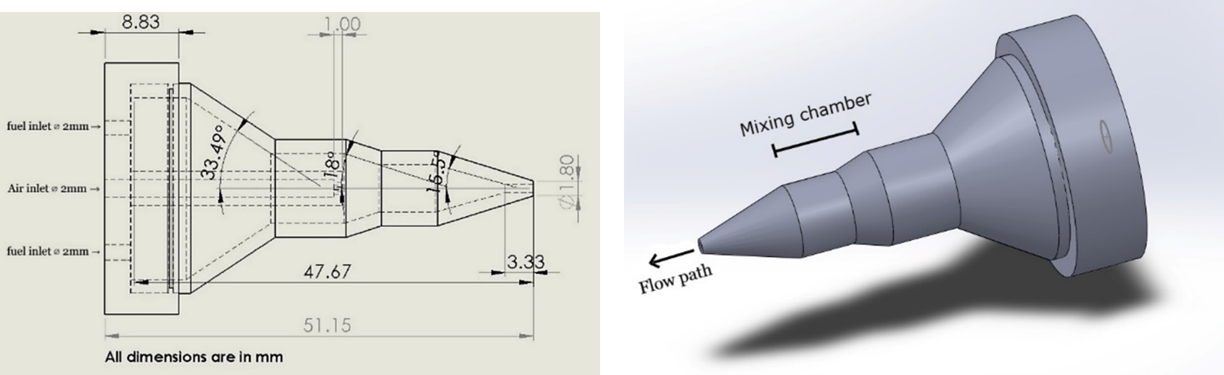
The design and fabrication of the present effervescent atomizer are based on an inside-out system from the literature [21,23,35]. The system has been further improved by using coflowing air instead of a perpendicular air injection configuration. Figure 1(a) illustrates the technical drawing of the effervescent atomizer. The diameter of exits and inlet orifice are 2 and 1mm, respectively. The angle of the exit cone is set at 15.5 degrees, in Figure 1(b) three-dimensional solid model of effervescent atomizer, air injection configuration with 0.5 mm holes has been utilized. The outer casing's convergence facilitates efficient mixing of individual liquid jets as they enter the mixing chamber, creating a bubbly two-phase flow. The atomizer was fabricated using 3D printing and special attention was given to achieving a smooth surface finish inside the atomizer using PLA material.

2.9. Test Conditions and Experimental Setup for Flow Visualization

In Figure 2 illustrates the experimental set-up that includes a fuel line and an airline, the flow valve's assistance allows the biodiesel mixture in the flow tank to pass through the atomizer. A mini compressor with gauge pressure injects air into the atomizer. A hypodermic needle with an outer diameter of 450 μm was employed as a stagnation port for air velocity measurement. It was connected to a U-tube manometer containing distilled water as the gauge fluid. The atomization was captured by high-speed camera with

Table 2. Fuel Property Comparison of Blended PP Pyrolysis Oil and Diesel.

Parameters	Polypropylene pyrolysis oil diesel blend	Diesel
Flash Point (°C)	54	52-92
Fire point (°C)	62	55-100
Density (g/cc)	0.82	0.835-0.88
Kinematic viscosity (centistokes)	2.61	2-4.5
Dynamic viscosity (centipoise)	3.18	2.5-5



(a) Front-view two-dimensional sketch. **(b)** Solid model in three dimensions.

Figure 1. Effervescent atomizer.

the help of diffuser light in the background. A 37 W LED source with 105 on/off cycles per second was utilized in flow visualization tests to produce a homogeneous background light. High-speed camera was operated at an exposure duration of 40 μs and an image capture rate of 5,000 fps (Photron Fastcam Mini UX50, West Wycombe, UK) and resolution is 1280 x 96 pixels in line with that in Figure 2. The picture was taken with a 50 mm Nikon lens at a 1:12 aperture. The interference caused by background noise was avoided with sufficient attention. The required qualitative information from the images was then extracted using the software program PHOTRON FASTCAM VIEWER and IMAGEJ [23].

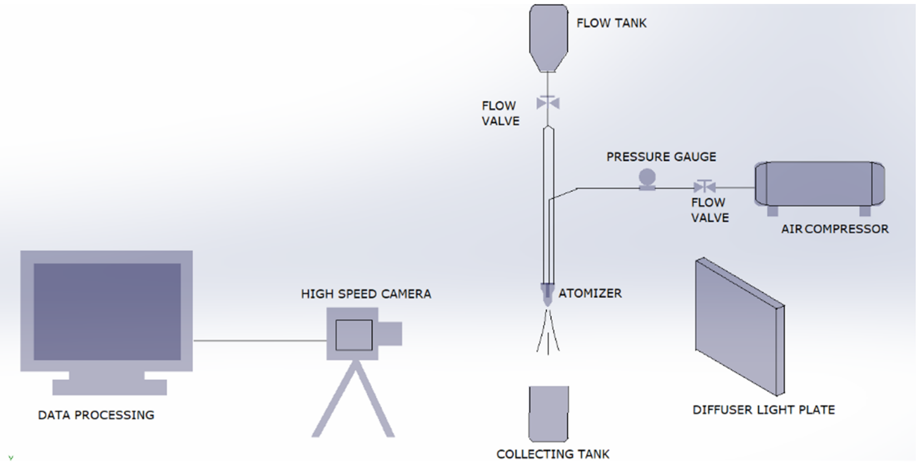
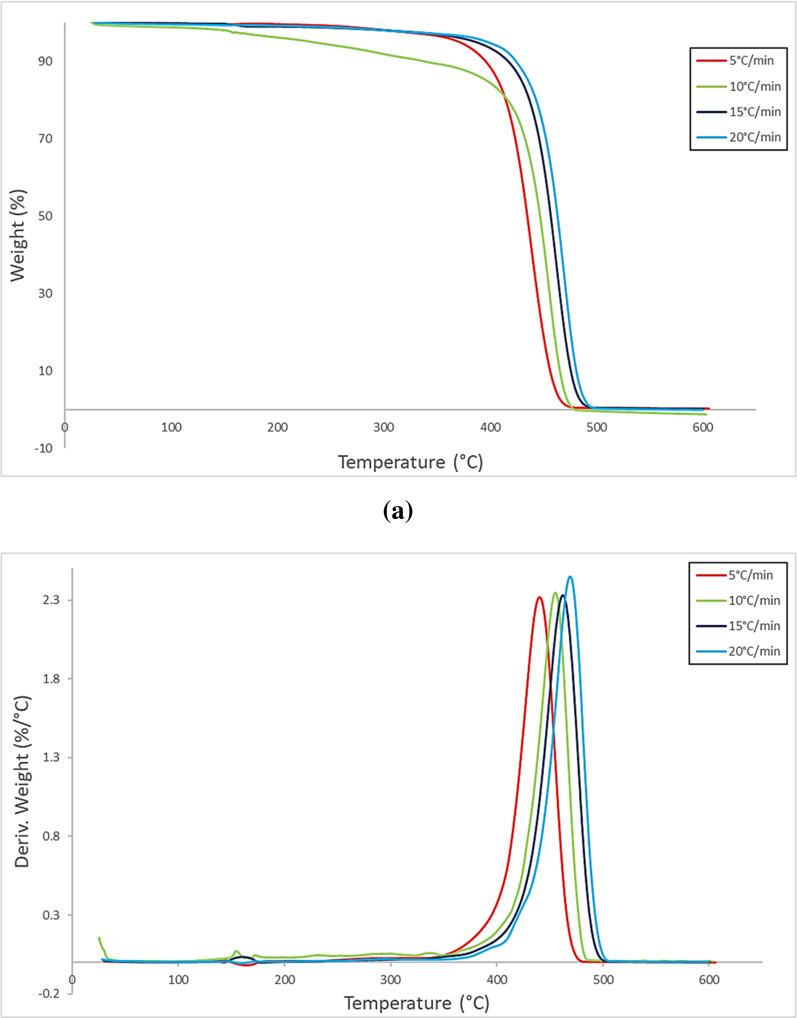


Figure 2. Illustration of the experimental setup of flow visualization system.

3. Results and Discussion

3.1. Thermal analysis

Thermogravimetric analysis was conducted on waste polypropylene (PP). In Figure 3(a), the weight-loss curves of polypropylene at different heating rates ranging from 5 to 20°C/min are displayed. As the heating rate increases from 5°C/min to 20°C/min, the T_{max} values also increase from 440.70°C to 469.20°C. This is due to the fact that at lower heating rates, equilibrium is reached quickly at any given temperature point. However, at faster heating rates, equilibrium is achieved more slowly causing the curve to shift towards higher temperature regions [36, 37]. The degradation of polypropylene occurs in a single step without any release of water content at the initial stages of the degradation process. Furthermore, in Figure 3(b), the DTG curves exhibit a single pronounced peak, indicating that the degradation of polypropylene occurs through the breakage of the polymer chain in a single-step process.



(a)

(b)

Figure 3. (a) TG and (b) DTG curves for the pyrolysis of PP with heating rate of 5 ºC/min, 10 ºC/min, 15 ºC/min & 20 ºC/min.

3.2. Kinetic analysis

The kinetic parameter analysis involved the use of iso-conversional models, namely KAS, Starink, and OFW, to determine the apparent activation energy (E_a). From the KAS model (4), the activation energies were determined by plotting $\ln\left(\frac{\beta}{T^2}\right)$ against $\frac{1}{T}$ at different conversions, as shown in Figure 4(a). The slopes of these plots were used to calculate the activation energy. Likewise, the Starink and OFW models were also plotted based on (5) and (6), and the corresponding apparent activation energies were obtained from their respective slopes, as shown in Figure 4(b) and Figure 4(c). These activation energy values have been summarized in Table 4. The relationship between activation energy (E_a) and the degree of conversion (α) is clearly demonstrated in Table 3. As the conversion increases from 0.1 to 0.9, the activation energy also exhibits a corresponding increase for the KAS, Starink, and OFW methods. This suggests that the degradation of polypropylene is a multi-stage process involving consecutive or competitive reactions, with random chain scission occurring at high temperatures [38]. The average activation energies obtained from the KAS, Starink, and OFW methods were found to be 178.17 kJ/mol, 178.65 kJ/mol, and 190.06 kJ/mol, respectively. Correspondingly, the average R^2 values for these methods were 0.852, 0.834, and 0.884, respectively, as shown in Figure 4 and Figure 5. The obtained activation energies (E_a) of PP were found to fall within similar ranges as reported in other studies by [3].

Table 3. Kinetic parameters obtained using various isoconversional model-free techniques to analyze the kinetics of PP.

Conversion ratio (α)	**KAS**		**Starink**		**OFW**	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
0.1	12.0586256	0.0517	12.4926164	0.0553	22.900082	0.1635
0.2	147.299138	0.8235	147.764722	0.8245	158.95537	0.8447
0.3	180.12281	0.8235	180.596708	0.8245	191.937	0.9723
0.4	190.091296	0.9907	190.565194	0.8245	202.01357	0.9918
0.5	197.382674	0.9962	197.864886	0.9962	209.38809	0.9966
0.6	203.219102	0.9971	203.701314	0.9971	215.29103	0.9974
0.7	211.865662	0.9965	212.356188	0.9965	224.01242	0.9969
0.8	223.363924	0.994	223.85445	0.994	235.5855	0.9946
0.9	238.129588	0.9903	238.628428	0.9904	250.45925	0.9913
Average	178.170313	0.8515	178.647167	0.8337	190.06026	0.8832

3.3. Thermodynamic analysis

Thermodynamic analysis such as changes in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) of PPE kit (PP), was performed using the apparent activation energy obtained from each KAS, Starink, and OFW iso-conversional method, as shown in (7), (8), and (9). In Figure 6, the plot of changes in enthalpy (ΔH) against conversion ratio (α) reveals interesting trends in the energy exchange during the chemical reaction process of PPE kit polypropylene. The average ΔH value obtained through model-free methods for PPE kits polypropylene is recorded as 132.67 kJ/mol. It is observed that ΔH shows a significant increase for conversion ratio values 0.2, while beyond $\alpha > 0.3$, it exhibits a more gradual rise. The pronounced increase in positive ΔH values suggests an endothermic nature of the pyrolysis process.

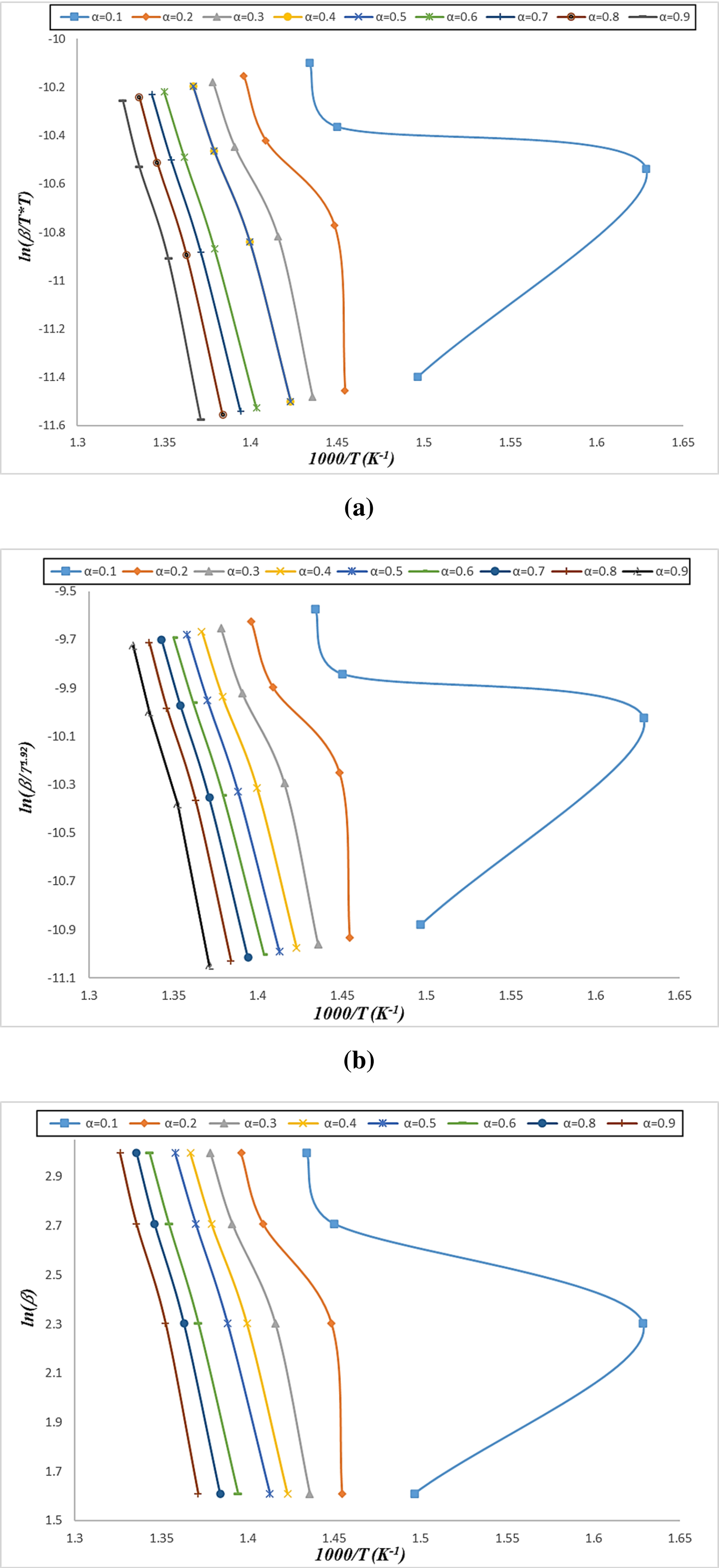


Figure 4. Kinetic parameter analysis of PP through iso-conversional models: (a) – KAS model, (b) - Starink model and (c) - OFW model.

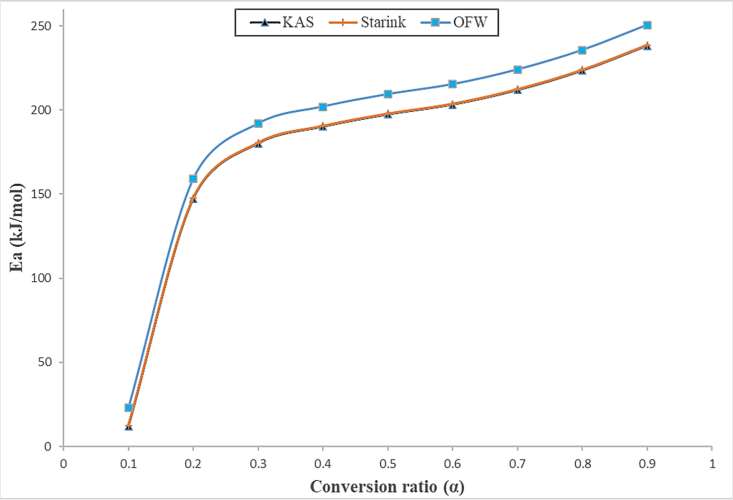


Figure 5. Activation energy Variation with respect to conversion ratio for KAS, OFW and Starink models.

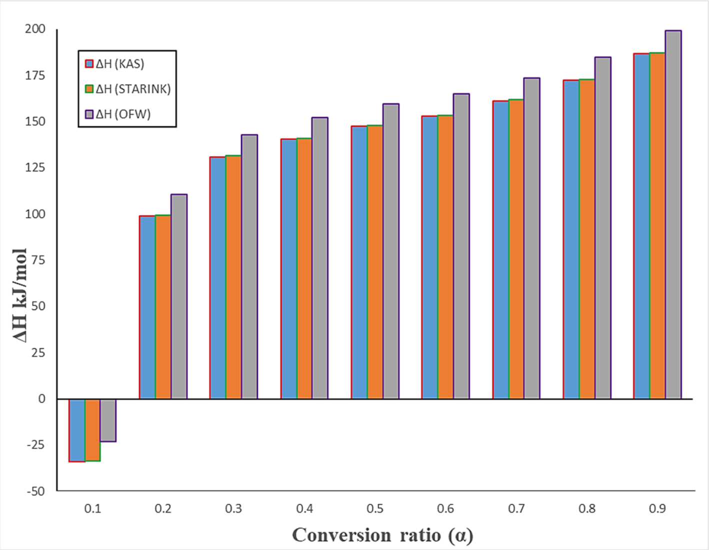


Figure 6. ΔH difference with respective to conversion for KAS, Starink and OFW.

In Figure 7 illustrating the change in entropy (ΔS) against conversion ratio (α) during the pyrolysis of PPE kit polypropylene. The results show that ΔS initially shows negative values in the range of 0.1 to 0.4 conversion ratio, indicating a decrease in disorderliness as the conversion ratio increases. However, as the conversion ratio goes beyond 0.4, ΔS crosses the zero-point suggesting a transition towards increased disorderliness. The average ΔS value obtained for PPE kits polypropylene is calculated to be -0.018 J/mol.K. The negative entropy value indicates that the degree of disorder of the products is significantly lower than that of the biomass [39, 40].

The change in Gibbs free energy reflects the total energy increase of the system during the approach of the reagents and the formation of the activated complex. In Figure 8, the obtained ΔG values for the pyrolysis reaction range from 147 to 139 kJ/mol for various conversion ratios from 0.1 to 0.9. A higher ΔG value indicates that the reaction is thermodynamically unfavorable and non-spontaneous. For the OFW model-free method, the initial ΔG value is found to be 144 kJ/mol, while the KAS and Starink models exhibit an initial ΔG value of 147 kJ/mol.

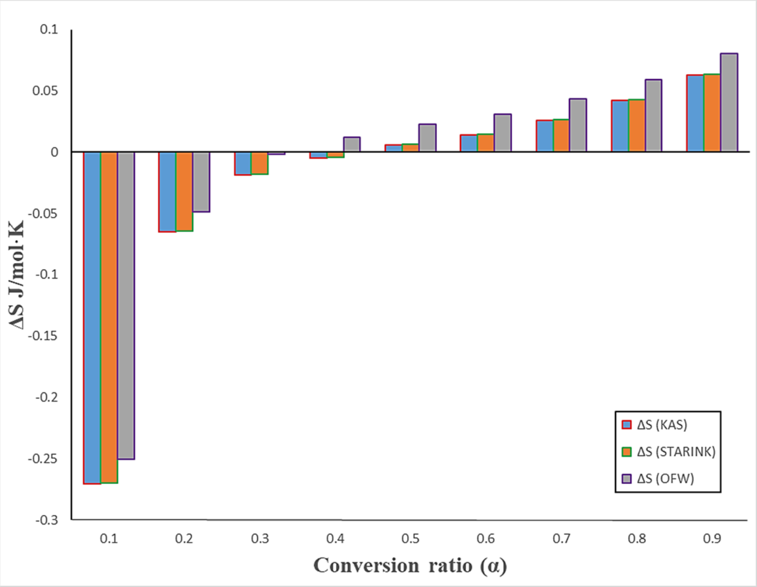


Figure 7. ΔS difference with respective to conversion for KAS, Starink and OFW.

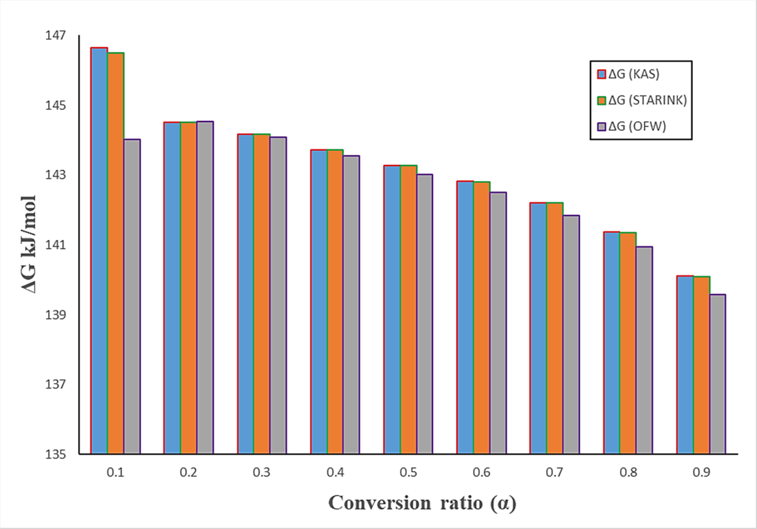


Figure 8. ΔG difference with respective to conversion for KAS, Starink and OFW.

The average values of ΔH, ΔS, and ΔG for different models are summarized in Table 4. For the KAS model, the average ΔH, ΔS, and ΔG values were found to be 128.5386 kJ/mol, -0.02313 J/mol.K, and 143.2056 kJ/mol, respectively. Similarly, the Starink model exhibited average values of 129.0154 kJ/mol, -0.02243 J/mol.K, and 143.1779 kJ/mol for ΔH, ΔS, and ΔG, respectively. The OFW model showed average values of 140.4285 kJ/mol, -0.00581 J/mol.K, and 142.6735 kJ/mol for ΔH, ΔS, and ΔG, respectively. The tabulated values provide valuable insights into the thermodynamic behavior in-depth analysis of the pyrolysis process of polypropylene of PPE kit, specifically in terms of enthalpy, entropy, and Gibbs free energy.

Table 4. Thermodynamic parameters of PPE kit using three different model-free iso-conversional methods

Conversion (α)	**KAS**			**Starink**			**OFW**		
	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)
0.1	-34.0656	-0.27079	146.6459	-33.6316	-0.2699	146.487	-23.2241	-0.2506	144.0191
0.2	98.84677	-0.06508	144.5034	99.31235	-0.06442	144.5035	110.503	-0.04848	144.5223
0.3	130.922	-0.01856	144.1753	131.3959	-0.01789	144.1715	142.7362	-0.00184	144.0931
0.4	140.4295	-0.00453	143.7282	140.9034	-0.00386	143.7208	152.3518	0.01235	143.5523
0.5	147.3667	0.005717	143.2762	147.8489	0.006398	143.2657	159.3721	0.022659	143.0254
0.6	152.8935	0.013906	142.8162	153.3757	0.014586	142.8031	164.9654	0.030927	142.4978
0.7	161.2442	0.026051	142.2128	161.7347	0.026743	142.1971	173.3099	0.04316	141.8331
0.8	172.426	0.042195	141.3793	172.9165	0.042885	141.3611	184.6476	0.059385	140.9356
0.9	186.7839	0.062894	140.1113	187.2827	0.063595	140.0913	199.1135	0.080209	139.5832
Average	128.5386	-0.02313	143.2056	129.0154	-0.02243	143.1779	140.4285	-0.00581	142.6735

3.4. FTIR Spectroscopy analysis of pyrolysis-oil of PP

The FTIR analysis of the pyrolyzed PP oil at the optimum condition was conducted to identify different functional groups present within the waveband of 500–3500 cm^{-1} as shown in Figure 9 The peaks observed at around 2954 cm^{-1} and 2916 cm^{-1} correspond to the symmetric and asymmetric stretching of CH_3, indicating the presence of alkane functional groups. Peaks at 1454 cm^{-1} and 1375 cm^{-1} indicate the symmetrical bending of CH_3. The peaks at 886 cm^{-1} represent the out-of-plane bending modes of C–H. These FTIR results are consistent with findings from other studies, such as those reported by Panda et al. [41], who also observed peaks corresponding to C-H stretching and bending in alkene and alkane functional groups. Similar results were found in the study conducted by Nisar et al. [37].

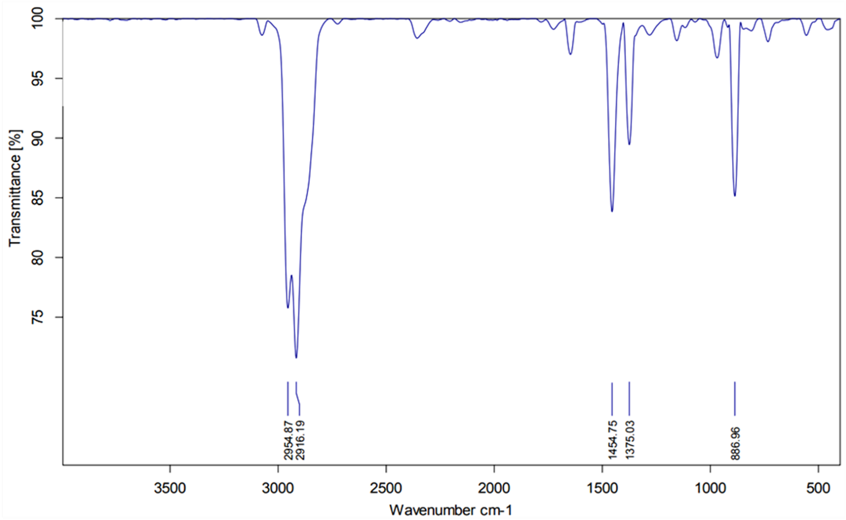


Figure 9. FTIR analysis of pyrolyzed oil from PPE kits.

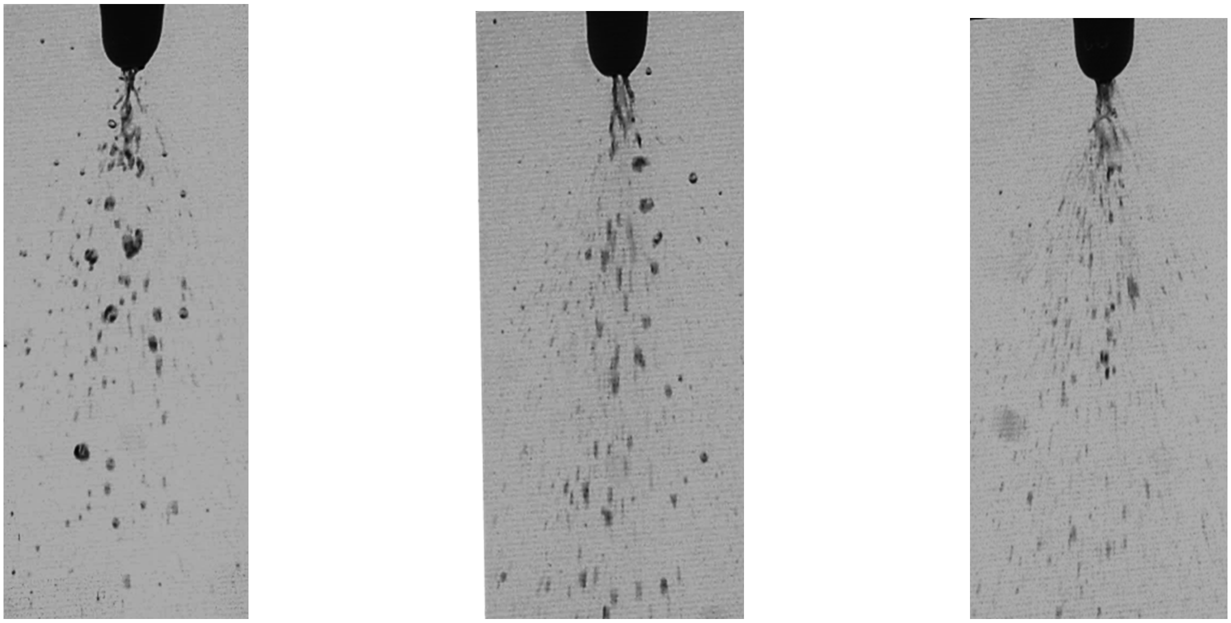
3.5. Visualizing Flow and Analyzing Spray Characteristics of Bio-diesel Blend

Figure 10 illustrates the visual representation of the liquid fuel jet breakup achieved using the effervescent atomizer at two distinct fuel liquid velocities (V_a) 0.110 and 0.129 m/s, and for a range of air velocities (V_a) from 5.65 m/s and 5.85 m/s, also jet without air velocity in Figure 10.

The observed sequence of events demonstrates a decrease in the breakup length and an increase in the spray angle as the air velocity increases. Additionally, there is a noticeable reduction in the size of air bubbles. These changes can be attributed to the intensified aerodynamic shear forces, which play a significant role in reducing the breakup length of the liquid jet [23]. The interaction between the fuel and air streams leads to enhanced atomization, resulting in a wider spray angle and smaller air bubbles. The captured video footage of the spray showcases the simultaneous occurrence of dilatational modes of breakup, as illustrated in Figure 11. These dilatational modes, also known as symmetric waves, were observed during the initial breakup phase of the liquid fuel jet.

3.5.1. Qualitative Analysis of Bio-diesel Liquid Jet Breakup

The primary stability characteristics related to the initial breakup of the biodiesel blend of PP, including the breakup length and spray angle, were determined based on the analysis of the recorded images. The breakup length and spray angle were determined by analyzing the recorded images using IMAGEJ software. At a fuel velocity of 0.110 m/s and an air velocity of 5.65 m/s, the measured breakup length was 9.14 mm, and the spray angle was 66.9°. However, when the fuel velocity remained the same at 0.110 m/s and the air velocity increased to 5.85 m/s, the breakup length decreased to 6.16 mm, and the spray angle increased to 80°. Similarly, at a fuel velocity of 0.129 m/s and an air velocity of 5.65 m/s, the breakup length was found to be 5.9 mm, and the spray angle measured 81.5°.



(a) **(b)** **(c)**

Figure 10. Image sequence of jet breakup of bio-diesel blend with (a) $V_f = 0.110$ & $V_a = 5.65$ m/s, (b) $V_f = 0.110$ & $V_a = 5.85$ m/s, and (c) $V_f = 0.129$ & $V_a = 5.67$ m/s.

Additionally, in a specific case, the breakup length of the liquid jet without air velocity was investigated and depicted in Figure 11, showing a measured breakup length of 63 mm. It was observed that this particular jet exhibited primary breakup with dilatational modes, while the other jets did not demonstrate similar characteristics. The results indicate that as the air velocity increases, the breakup length of the liquid fuel jet decreases while the spray angle increases. This suggests that higher air velocities lead to shorter breakup lengths and wider spray angles, resulting in the formation of smaller liquid fuel ligaments.

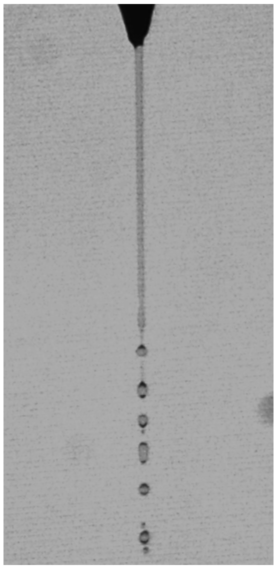


Figure 11. Image sequence of jet breakup.

4. Conclusions

In this research, polypropylene plastic waste from PPE kits underwent pyrolysis at 450 to 500 ° C, and its activation energy, kinetics, and thermodynamics were studied using KAS, Starink, and FWO models based on TGA analysis. Activation energy values ranged from 178.17 to 190.02 kJ/mol, and average thermodynamic parameters were determined as ΔH: 132.66 kJ/mol, ΔS: -0.017 J/mol.K, and ΔG: 143.01 kJ/mol. Pyrolysis yielded 31.1% oil, characterized using FTIR spectroscopy, showing various alkyl hydrocarbons. This oil was blended with diesel, sharing similar fuel properties. A 3D-printed effervescent atomizer was used to analyze the spray characteristics of the biodiesel blend, studying breakup length and spray angle. Breakup length ranged from 9.2 to 5.9 mm, and spray angle varied from 66.9 to 81.50 degrees, showing an inverse relationship between them. The present study is limited to only 10% of pyrolytic oil blend due to the availability of minimum oil quantity. This study contributes to converting polypropylene waste into renewable energy, offering solutions to plastic waste problems. This research also explored advanced atomization methods, such as effervescent atomizers, to enhance combustion efficiency by producing finer droplet sizes and better fuel-air mixing. Analyzing spray properties and combustion efficiency of blends with these atomizers could maximize the better evaporation rate of mixing. This would help to enhance the combustion efficiency under various input parameters.

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