Revitalizing Plastic Waste with Pyrolysis: a UniSim Design© Simulation Case study for Renewable Energy Production from Car Fluff

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Abstract

This study addresses the imperative of substituting fossil fuels with energy from wastes, focusing on car fluff pyrolysis. The environmental viability of fuels produced through this method is assessed, aligning with the European Union's Renewable Energy Directive II (RED II) emissions assessment methodology. Using UniSim Design©, the entire inventory for an industrial-scale process is modeled, examining emissions contributions from each facility. By repurposing automotive waste, waste reduction and renewable energy generation are simultaneously achieved, in line with RED II objectives. UniSim Design© optimizes the heat integration system, minimizing energy wastage and reducing reliance on external sources, thereby lowering associated greenhouse gas emissions. Therefore, this research not only meets sustainability goals and regulatory compliance but also ensures the long-term viability of the plant in a changing regulatory environment.

**Keywords**: Plastic Pyrolysis, Simulation, Renewable Energy, process system, Renewable Fuel.

* 1. Introduction

The plastic industry faces challenges due to soaring demand, production growth, and insufficient recycling, necessitating innovative solutions (Qureshi et al., 2020). Recent studies have revealed that only 7% of generated plastic wastes are recycled, about 8% incinerated, and the rest landfilled (Nyika and Dinka, 2022), resulting in greenhouse gas (GHG) emissions, soil and water contamination, and economic loss (Fahim et al., 2021; Maitlo et al., 2022). The most effective solution is recycling, which involves primary, secondary, tertiary, and quaternary processes. Tertiary recycling involves plastic wastes thermal degradation, leading to chains breakage. Pyrolysis, a non-oxidizing thermochemical process, is promising for chemical recycling and power generation. Unlike incineration, it converts materials into versatile gas, solid, or liquid products, crucial for producing power and biofuels, contributing to CO2 emissions reduction (Honus et al., 2016). However, derived liquid fuels require upgrading for transport use, involving chemical modifications for thermal stability, volatility, and viscosity compliance with current legislation standards (Jahirul et al., 2022; Palos et al., 2021). Post-treatments units significantly impact the economic analysis, with small plant (~15000 million l/year) breakeven potentially taking 25 years (Faisal et al., 2023). Gaseous stream products from pyrolysis of plastic types, i.e. polyethylenes (PEs) and polypropylene (PP), include H2, CH4, ethane, ethene, propene, propane, butane and butene; PET pyrolysis emits more CO2 and CO, while PVC pyrolysis produces mainly hydrochloric acid (HCl) (Williams and Williams, 1999). Gas from PE or PP pyrolysis has high heating value (HHV) of 42 - 50 MJ/kg, making it a potential heat source for industrial pyrolysis plants. Ethene and propene, separated from other components, can also serve as valuable feedstocks chemicals production. Additionally, pyrolytic gas can be used in internal combustion engines (ICEs) for electricity generation and directly employed in boilers without requiring fuel gas treatment (Maqsood et al., 2021). Simultaneously, evaluating the current legislative landscape is essential for producing sustainable fuels. To determine if recycled carbon-based fuels (RCFs) qualify as renewable energy sources, their GHG emissions during production and use must be compared to those of fossil fuels. This assessment is vital for understanding the RCFs potential in reducing environmental pollution. On February 10th 2023, the Recast Renewable Energy Directive empowered the European Commission (EC) to the Directive (EU) 2018/2001 (RED II), aiming to set a minimum threshold for GHG emissions savings from RCFs and establishing an assessment methodology (Annex I of the delegated act). Proposed criteria deem RCFs renewable if their total emissions are reduced by at least 70% compared to those associated with using a fossil fuel, set at a default value of 94 gCO2eq/MJ (paragraph 19, Annex V, part C, of Directive 2018/2001). In this framework, the objectives of this work are threefold: 1) conduct experimental activities to determine yields for pyrolysis process simulation; 2) develop a rigorous UniSim Design© simulation of the pyrolysis process for enhanced thermal efficiency and avoiding external energy supply; 3) use CO2 equivalent flow rates from the simulation model for emission calculation in different scenarios, adhering to Annex I guidelines in the delegated act.

* 1. Materials and Methods
		1. Process Description

The car fluff material, representing the light fraction of automobile shredder residues, is the plastic material processed in the first part of this study, undergoing pyrolysis in a lab-scale double-stage thermal reactor, including a pyrolysis reactor and a homogeneous cracking reactor. The pyrolysis process occurs in an inert atmosphere, at atmospheric pressure and fixed temperature (500 °C). Thermal cracking of pyrolytic vapors is carried out at 800 °C. After operative temperature is reached, 5 g of car fluff material is fed midway into the pyrolysis unit where the reaction lasts 30 minutes. Liquid and gaseous phases are collected post-separation: condensable vapors separate through cooling, with a liquid CO2 and ethanol mixture, while the gaseous phase is collected in the 5 L Tedlar Bag and analyzed using a gas chromatograph (Agilent 990) equipment.

* + 1. Process Modeling Methodology

Experimental results, specifying gaseous and liquid yields, serve as the basis for modeling simulation, to predict plant performance and enable process optimization for efficient industrial-scale operations. A flowsheet of the car fluff pyrolysis process is built using the simulation software UniSim Design© to evaluate the operative conditions, and estimate material, energy balances and utility requirements. The Peng–Robinson thermodynamic property fluid package is chosen for accurate modeling of hydrocarbon and light gases components in refinery applications (Fivga and Dimitriou, 2018). Through differential scanning calorimetry (DSC) analysis, PP is identified as the primary hydrocarbon in car fluff and modeled using group contribution methods (UNIFAC). All pyrolysis products, including compounds (H2, CO and CO2) and the hydrocarbons (CH4, C2H4, C2H6, C3H6 and C4H8) in the gaseous phase, are selected/defined to model the process, providing essential thermodynamic data for energy balances computation. Hydrocarbon compounds, namely octene for the gasoline fraction and octacosane, for the diesel fraction, represent the primary components in the liquid phase. Yield shift reactors (*R1* and *R2* in Figure 1) simulate both pyrolysis units utilizing product yield data from experimental results. These reactors calculate thermal energy requirements for maintaining constant temperatures profiles at 500 and 800 °C in the pyrolysis (*R1*) and homogenous cracking reactor (*R2*), respectively. The heat reaction value (set at 2000 kJ/kg) in the model configuration section of yield shift reactor block, is determined by summing the enthalpy of the PP pyrolysis reaction (541 kJ/kg, Jin et al., 2018), sensible and latent heats to raise the fed material temperature up to 500°C (80 kW). The vapor-liquid stream resulting from pyrolysis and cracking reactions (stream *3*), leave the top of the simple solid separator (*S1*), while char residue (stream *4*) is collected at its bottom. Simulating coke end-of-life uses a conversion reactor (*R-coke*), providing enthalpy and post-incineration CO2 amount (assumed stoichiometric). Stream *3* is cooled down to 0 °C (in *E-1*) and then separated in *V-1*, allowing near-complete separation of octane and octacosane from the compounds identified by micro-GC in the gaseous stream during the experimental analysis. The internal combustion engine (ICE) is simulated using a combination of unit operations. First, in a conversion reactor (*R-ICE*), complete combustion of pyrolytic gases is achieved by adding air (stream *AIR7*). Subsequently, a first cooling step (*E-ICE*), adjust the outlet gas temperature to reach a thermal power of 562.5 kW (*En-ICE*), representing the energy production phase. The chosen heat power value, when multiplied by the electrical efficiency of the ICE (0.4) and divided by its thermal efficiency (0.45), results in the specified target electrical power of 500 kWe. The next cooling operation (*E-ICErec*) focuses only on thermal power recovery (*En-ICErec*). Process simulation uses a car fluff mass flow rate of 200 kg/hr, obtained iteratively to achieve the target electrical power, at atmospheric pressure. Two scenarios for supplying energy required for the pyrolysis endothermic reactions in *R1* are considered: in the first one (scenario A) fossil fuel (FF) combustion is performed in *R3*, as shown in Figure 1; in the second one (scenario B) thermal integration of process streams is applied. Specifically, half of the pyrolytic oils (stream *13* containing 0.22 wt% of octene and 0.78 wt% of octacosane) from *V-1* (stream *8*) undergo combustion in *R3* and the energy stream (*E-CG*) derived from flue gases cooling is used for heat integration in *R1*. Combustion in both scenarios involves an excess of air equal to 12% with the temperature of air entering *R3* set at 300 °C. Moreover, in scenario B, the thermal duty recovered by the second cooling (*En-ICErec*) of the ICE flue gases is used to pre-heat stream *Air13*. The heat integration does not involve the *R2* section since it is assumed an autothermal behavior of this reactor due to a partial combustion of the pyrolytic vapors (stream *5)*.

* 1. Emission Calculation Methodology

The correlation to assess GHG emissions from production and use of RCFs for transport, in Eq. (1), and the correlation to evaluate the GHG emission savings, in Eq. (2) are reported in 1(A) and 2(A) of Annex I of the Delegated Act 20/05/22.

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| --- | --- |
|  | (1) |
|  | (2) |

The term , representing fossil fuel emissions, is set at 94 gCO2eq/MJfuel (paragraph 19 of Annex V, part C of Directive (EU) 2018/2001). If emissions savings exceed 70%, the produced gas distributed as electrical power qualifies as renewable. The term accounts for inputs supply emissions, including power use, feedstock transportation to the site, and conventional treatments. Emissions from processing (), encompass pyrolytic oils transport, the CO2 from solid residue disposal, and gaseous fuel combustion in ICE unit. Emissions from final fuel use () are assumed zero, considering direct use in the pyrolysis process through the ICE, included in the process boundaries, that allow to exploit thermal and electrical recovery. Transport and distribution () and carbon capture and geological storage savings () are set at zero, as the fuel is directly injected into the ICE, and no carbon capture is involved. Contributions of and terms affecting co-products yields undergo to the emission allocation criterion (paragraph 15 of Annex I, part A of Delegated Act 20/05/22) and, according to the Annex I, they should be multiplied for the allocation factor (fA). In this study, fA is evaluated based on physical causality as the ratio of gaseous fuel mass and total co-products mass (i.e., oil and gas).

* 1. Results and Discussion

The flowsheet resulting from the scenarios described in Section 2.2 and obtained using Unisim Design© is reported in Figure 1.



Figure 1 Flowsheet of the two scenarios considered in which the striped fill represents the common section shared by both. The grey fill indicates the boundaries of Scenario A; green fill indicates the boundaries of Scenario B.

Based on the simulation outcomes, the pyrolysis plant produced 126 kg/h of gaseous fuel (stream *7*) having a low heating value equal to 5104 MJ/h. In Scenario A, the resulting mass flows are = 19 kg/h and = 48.39 kg/h for pyrolytic oils and char, respectively, while in Scenario B, = 11.64 kg/h and = 48.39 kg/h. Pyrolysis is an endothermic reaction requiring a constant source of energy and the available thermal energies from burning FF or pyrolytic oils are calculated in the model to be 98.69 kW and 99.44 kW, respectively. As discussed in Section 2.2, the total thermal energy for the pyrolysis reactor (*R1*) is approximately 99 kW; therefore, an additional duty is not required. In Scenario B, thermal power, is recovered from the flue gases produced in the ICE, generating up to 572.8 kWth, that are partially used (i.e., 10 kWth) to pre-heat air stream up to 300 °C. In Scenario A, the same value of thermal power, needed to pre-heat the air to be mixed with FF (*AirFuel*), is ensured by providing heat from an external source. Moreover, mass balances results carried out by the simulation software are used as inventory to assess the GHG emissions according to the guidelines reported in Annex I of the Delegated Act 20/05/22. To evaluate the term, reported in Eq. (1), the mass flows of CO2 derived from FF/pyrolytic oils combustion (*R3*), coke incineration (*R-coke*) and pyrolytic gases burning in *R-ICE* resulted equal to 24.3 kg/h, 177.3 kg/h and 274.8 kg/h, respectively. On the contrary, the term is calculated using literature data and making some assumptions. To evaluate the term, the emissions intensity of generated grid electricity in Italy are considered. They are set equal to 103 gCO2eq/MJfuel (Table A of Annex I) and multiplied for the electrical process inputs (reactor screwing, 10 kWe, and cooling system, 0.47 kWe). The manufacturing term of is considered zero since the processed material is classified as waste (Table 3 of Annex I). To evaluate the term describing the emissions associated with the plastic transport to the production site, it is assumed that 150 5-LH per year are used to transport 13 tons of waste, covering 100 km, and characterized by an emission factor of 56.60 gCO2eq/t·km (International Council of Clean Transportation (ICCT). Moreover, the also considers the difference in energy between what would be produced by waste-to-energy treatment and what is produced by the simulated pyrolysis plant. The energy amount recovered by waste-to-energy is equal to 5.9·106 MJe/y, that is obtained considering that only 66% of the processed material generally undergoes to this treatment and setting the electrical process efficiency equal to 0.21; whereas the pyrolysis plant analyzed in this scenario provides 1.3·107 MJe/y, that corresponds to the chosen target value. The value determined is 49.7 gCO2eq/MJfuel, evaluated considering the amount of GHG emissions that would be produced by conventional treatments and that are avoided by replacing them with pyrolysis. Specifically, the waste-to-energy, incineration, and landfill processes produce emissions equal to 898, 2894, and 60 gCO2eq/tfuel respectively, that are then multiplied by the corresponding plastic weight percentages subjected to these treatment methods (i.e., 66.5%, 12.6%, and 20.9%, respectively). The values of each term contributing to determine the final value of in Eq. (1) are reported in Figure 2 and they are evaluated by multiplying them for a period corresponding to full-time 300 working days per year (*ft* = 300\*24 h/y) and dividing each emission value for the gaseous fuel low heating value previously reported (5104 MJ/h).



Figure 2. *ei*/*ep* and allocation factor (fA) terms calculation for the two scenarios.

Even though, almost each term has the same value for the two considered scenarios, the calculation of the overall GHG emissions provides different results (as reported in Fig. 2). This variation is due to the calculation of fA. Indeed, for Scenario A, fA is evaluated as the ratio between = 126 kg/h (Fig. 1) and the sum of = 126 kg/h and = 19 kg/h (Fig. 1), leading to 0.87 value. Regarding Scenario B, the resulting allocation factor increased with respect to that corresponding to Scenario A (i.e., 0.91) since the burning of bio-oil produced (= 6.5 kg/h) lowered the total amount of the obtained co-products. Therefore, the variation of and between the two analyzed scenarios is mainly affected by the different allocation methods. Indeed, the allocation factor is increased and in the second case not only the emissions from the burner are allocated, but also those derived from ICE, since its fumes are also used as source of heat integration. Then, the emission savings are calculated using Eq. (2) and resulted equal to 65% and 73% for Scenario A and B, respectively. According to the threshold value reported in the REDII (i.e., 70%), it is possible to claim that only the gaseous fuel produced considering the second scenario can be considered renewable.

* 1. Conclusions

The scrap from automobile shredder residues was effectively processed in a pyrolysis plant to yield co-products of higher economic value compared to the original waste. The methodology outlined in Annex I of the Delegated Act 20/05/22 was applied to assess GHG emissions for each analyzed scenario. Each emission factors, as specified in Annex I, were determined based on simulation outcomes, accounting for CO2 from combustion reactions, energy supply, and heat integration. This analysis revealed that, despite being produced from recycled carbon, fuels may not always qualify as renewable under the overarching directive framework. Engineering choices, such as minimizing energy demand through thermal integration and by-product valorization, strongly influence emission factor values, making simulation models a useful tool to predict such trends. Future perspective, include exploring additional scenarios to enhance gaseous fuel production and corresponding emission savings.

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