

# Experimental Analysis of the Oxidative Liquefaction of the Municipal Solid Wastes

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The pursuit of sustainable waste management solutions has led to the emergence of the oxidative liquefaction of municipal solid waste (MSW) as a promising approach for waste valorization. The primary objective of this study involves the investigation of a novel oxidative approach to decompose the integrated organic matrix of MSW into liquid-phase products of potential utility. The selected MSW samples have a carbon content of  $50.30 \pm 0.50$  %, as revealed through ultimate and proximate analysis. Oxidative liquefaction of MSW samples is carried out using a structured design of experiments. Temperature (200-300 °C), oxidant concentration (30-60 %), waste-to-liquid ratio (3-7 %) were taken as experimental parameters. Liquid products were analyzed through gas chromatography with flame ionization detection (GC-FID), and oxygenated organic compounds (OOCs) were found to be in the range of 13-51 g/kg. Total solid reduction (TSR) was assumed as an indicator of the efficiency of the process. It was equal from 49 to 93 %. The current research article introduces the concept of oxidative liquefaction for treating MSW as a waste-to-fuel concept.

## 1. Introduction

The increasing utilization of energy and goods, coupled with rapid population growth and elevated living standards, has led to a significant upsurge in the production of Municipal Solid Waste (MSW), giving rise to critical environmental concerns if not managed or recycled efficiently (Sukor et al., 2023). MSW encompasses a diverse array of solid wastes routinely disposed of in both urban and rural areas (Phu et al., 2023). On average, each individual is estimated to generate 0.74 kg of waste per day (World Bank, 2024). Current approximations indicate an annual global production of 2 Bt of MSW, with approximately 33 % remaining uncollected by municipal services (World Bank, 2024). According to World Bank forecasts, the generation of MSW could potentially reach 3.4 Bt by 2050 (World Bank, 2024). Roughly 70 % of the collected MSW is directed to landfills, 19 % undergoes recycling, and 11 % is utilized for energy recovery (Sobek and Werle, 2021). The 2024 data from the US Census Bureau suggests a global population of 8.02 B people, with roughly half lacking access to basic waste management services (US Census Bureau, 2024). This number is projected to escalate to 9.7 B by 2050, emphasizing the pressing need for enhanced waste management strategies (Aleluia and Ferrão, 2016).

To address the issue of increasing polymeric waste in municipal solid waste (MSW) streams, a variety of recycling methods have been utilized in the past, including mechanical recycling, anaerobic digestion, material recovery facilities (MRFs), waste-to-energy recovery techniques (such as pyrolysis, gasification, incineration, and gasification), hydrothermal carbonization, and chemical recycling (Werle and Dudziak, 2013). Mechanical recycling effectively sorts and recycles MSW commodities like plastics, metals, paper, and glass based on segregation quality and contamination levels (Rogoff, 2013). Composting and anaerobic digestion prove effective in converting the organic components of MSW into compost or biogas (Hartmann and Ahring, 2006). Material Recovery Facilities play a crucial role in sorting MSW into recyclable categories.

However, the recycling methods mentioned above face various limitations in handling the heterogeneous composition of MSW (Lin et al., 2022). Their effectiveness also varies with changing waste compositions. This situation calls for a unified and innovative approach capable of treating diverse and complex waste streams without prerequisites, while effectively achieving the ultimate goals of a comprehensive and sustainable waste management framework (Nanda and Berruti, 2021). To address this gap, the current research article introduces the concept of oxidative liquefaction for treating MSW. This approach aims to reduce waste and produce oxygenated chemical compounds (OCCs) to support the concept of waste-to-resource recovery.

## 2. Oxidative liquefaction process

The process of oxidative liquefaction involves reacting organic matter with oxygen or an oxygen donor at high pressures and elevated temperatures to convert it into useful liquid products. The process entails decomposing complex organic compounds into more manageable and useful chemical entities. The effectiveness of the method in treating the composite waste from wind turbine blades has already been proven by Mumtaz et al. (2023), where the focus was recovering the glass fibers. Moreover, the same group demonstrated the usefulness of this method for processing plastic waste to produce oxygenated liquid chemical compounds, including volatile fatty acids (VFAs) (Mumtaz et al., 2024). On the other hand, Zhang, with their co-workers, determined the applicability of this method for processing rubber waste (Zhang et al., 2021). The successful application of oxidative liquefaction to intricate materials has motivated scientists to investigate its efficacy in dealing with two of the most common and widespread waste streams of municipal solid waste (MSW). Figure 1 presents a general idea of the oxidative liquefaction process. The diagram presented in Figure 1 is conceptual and illustrates the essence of the oxidative liquefaction process. The values of temperature and pressure were assumed based on preliminary studies for other waste groups (Mumtaz et al., 2023). It was confirmed that these parameters yield the solid reduction yield and the highest content of liquid products. Therefore, the same range of temperature and pressure was adopted for the studies on MSW (Municipal Solid Waste).

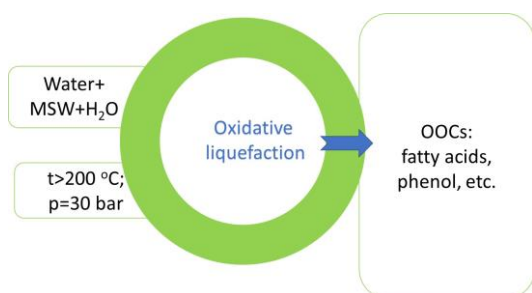


Figure 1: The oxidative liquefaction process idea

## 3. Materials and methods

### 3.1 MSW samples

The municipal solid waste (MSW) analyzed in this study comprised a diverse and complex mixture of waste components typically found in urban and suburban areas of Poland. The selected type of MSW consisted of a wide range of materials, including metals, glass, polymers, organic matter, and other components. Prior to the experimental investigation, the MSW underwent a meticulous sorting process to ensure its representativeness. This step was crucial to ensure that the findings of the study could be applied to real-world waste streams, allowing for the assessment of waste-to-resource conversion systems and their potential economic and environmental benefits. The test samples were obtained from proficiency testing providers who prepared them in accordance with ISO standards applicable to this type of material. The LECO TruSpec CHN and SC 632 analyzers were utilized to conduct the final analysis, aimed at determining the levels of elemental carbon, oxygen, hydrogen, nitrogen, and sulfur. The sample's total moisture, volatile matter, and ash levels were measured using a weighing method in accordance with the proper standards (CEN/TS 15414-2:2010, 2010), (EN 15403:2011, 2011), and (EN 15402:2011, 2011). The experimental protocol strictly adhered to established standards and protocols, involving high-temperature combustion coupled with infrared detection. The results of ultimate and proximate analysis are presented in Table 1.

Table 1: Ultimate and proximate analysis results of MSW samples

Parameter	Symbol	MSW, wt %
Moisture content in the analytical state	$M_{ad}$	$2.5 \pm 0.2$
Ash content in the analytical state	$A_{ad}$	$15.1 \pm 0.8$
Volatile matter	VM	$84.9 \pm 0.3$
Content of total carbon in the analytical state	$C_{ad}$	$50.3 \pm 2.3$
Content of total hydrogen in the dry state	$H_a$	$7.2 \pm 0.2$
Content of nitrogen in the analytical state	$N_{ad}$	$1.1 \pm 0.1$
Content of oxygen in the analytical state from differences	$O_{diff.}$	23.3
Content of total sulphur in the analytical state	$S_{ad}$	<0.5
Content of total chlorine in the analytical state	$Cl_{ad}$	$0.03 \pm 0.01$

### 3.2 Experimental setup

The experimental setup utilized the Parr reactor series 4650, a 500 ml batch reactor manufactured by Parr Instruments (Parr Instr., ILL, USA). This reactor was outfitted with a high-temperature spiral for heating and a Parr 4838 reactor controller capable of reaching temperatures up to 800 °C. The controller offers accuracy up to 1 °C for both displayed and desired temperatures, ensuring precise temperature control throughout the experiments. Temperature during the process was monitored using K-type thermocouples and recorded by a data acquisition device from National Instruments (NI).

The upper part of the Parr reactor, referred to as the head, features a pressure gauge on top capable of measuring pressure, with a maximum range of 344 bar. Two straight walls are present: one connects the reactor to a pressure source for filling with inert gas, such as nitrogen, while the other valve is used to remove unwanted gases or collect useful ones after the process is complete. The head also includes a hole allowing access to the thermowell, where a thermocouple is placed to measure the internal reactor temperature.

The lower part is a cylindrical chamber for holding the reactants. Both parts are connected using drop-bolted W screws. Temperature control during the process is managed by the Parr controller, utilizing PID groups, each with a specific temperature value. Ports on the back of the controller are provided for connecting the power supply and pressure and temperature measuring sensors. J-type thermocouples are employed for temperature measurement. Another port, labeled as the Comm connector, is designated for communication purposes. On the front side of the controller, a switch determines whether the heater is off, operating at maximum capacity, or half capacity, while another switch turns the controller on or off. A high limit indicator light, glowing red, signals when either the temperature or pressure has reached the high limit and the high limit reset switch has been activated. Additionally, a small display shows the set value for the temperature inside the reactor and the current temperature value, both of which can be adjusted using the keys on the display.

Figure 2 presents the scheme of the installation for oxidative liquefaction process of MSW.

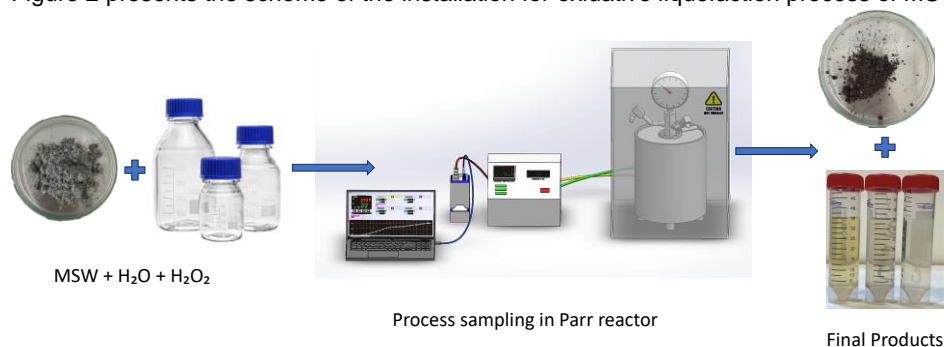


Figure 2: Oxidative liquefaction process of MSW

### 3.3 Experimental matrix

The experimental matrix is presented in Table 2. The tests were conducted to examine the effects of three variables, namely the temperature of the oxidative liquefaction process, the amount of oxidant used, and the waste-to-liquid solution ratio.

Table 2: The experimental matrix,  $p=30$  bar; process time 45 min

Sample type		Temperature, °C	40% H <sub>2</sub> O <sub>2</sub> addition, wt. %	Waste-Liquid ratio, wt. %
MSW	Lowest (-1)	200	30	3
	Average (0)	250	45	5
	Highest (1)	300	60	7

The experimental matrix was designed in accordance with the principles of the central composite face-centered design (CCF) method. The experimental matrix includes 3 variables ( $k=3$ ): temperature ( $k_1$ ), 40 % H<sub>2</sub>O<sub>2</sub> addition ( $k_2$ ), and waste-liquid ratio ( $k_3$ ). By applying the CCF method principle, the number of experiments is determined to be  $k + 2k + 2k = 17$ . Each variable was subjected to testing at three levels (-1, 0, 1), resulting in a robust experimental matrix. These experiment matrix design entailed the deliberate selection of a subset of factors from a larger set, resulting in a reduction in the total number of experimental runs to the 17 needed for the investigation. This technique was deemed relevant due to the delicate physical characteristics of MSWs, ensuring that the chosen experimental conditions were not overly stringent for these specific sample types. These design approaches not only offer a thorough understanding of the primary impacts and interactions of the variables being examined, but they also exhibit a practical regard for the distinct attributes of the materials being studied. Detailed information on the variables assigned to each experiment is shown in Table 3.

Table 3: Detailed information on the variables assigned to each experiment

k	Number of experiments																	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
k1	-1	x	x	x	x					x								
	0											x	x	x	x	x	x	x
	1					x	x	x	x		x							
k2	1	x	x			x	x					x						
	0									x	x			x	x	x	x	x
	1			x	x			x	x				x					
k3	-1	x		x		x		x						x				
	0									x	x	x	x			x	x	x
	1		x		x		x		x						x			

### 3.4 Total solid degradation TSD

To evaluate the degree of degradation of organic matrices during the process, we performed the calculation of total solid degradation (TSD), which can be represented using Eq(1). In this context, the variable  $m_f$  represents the mass of the solid product after drying, while  $m_i$  denotes the initial mass of the tested waste material.

$$TSD = \frac{m_i - m_f}{m_i} \cdot 100\% \quad (1)$$

To apply this formula, it is essential to first filter the entire mixture after the reaction is complete. This filtration process involves using filter paper to separate the liquid and solid components effectively. The solid sample is then subjected to drying in a laboratory dryer for 8 h at a temperature of 105 °C. Subsequent to the drying process, the sample is re-weighed. Following filtration, the liquid products are placed in a hermetically sealed container and sent for further analysis.

### 3.5 Oxygenated organic compounds (OOC) concentration

The liquid products obtained through oxidative liquefaction undergo analysis using Gas Chromatography with Flame Ionization Detection (GC-FID). In this study, DB-FAT WAX UI capillary columns were employed in a Clarus 500 gas chromatograph equipped with a flame ionization detector. Helium served as the carrier gas. The temperature program for the oven began at 40 °C initially, held for 4 min. Then, the temperature gradually increased at a rate of 5 °C per min until reaching 240 °C. This final temperature was maintained for 15 min. Calibration curves were constructed to facilitate the quantitative measurement of specific oxygenated organic compounds (OOCs).

## 4. Results

### 4.1 Total solid degradation TSD results

The combined data from 17 experiments carried out for MSW revealed that the total solid reduction TSR range under the studied conditions varied from 49 to 93 %. Analysing results presented in Figure 3 it can be concluded that MSW exhibited a rise in TSR when temperatures and oxidant concentrations rose. This indicates that increased heat levels and a greater presence of reactive oxygen promote the decomposition of organic substances, resulting in a more pronounced decrease in solid matter. An ideal waste-to-liquid ratio of around 3 seems to be the most effective in maximizing TSR as shown in experiment 7. This ratio probably signifies an optimal equilibrium between adequate availability of reactants and favorable heat and mass transmission conditions. Energy use patterns indicate slight rises as temperature increases but stay fairly consistent regardless of variations in oxidant concentrations and waste-to-liquid ratios. This suggests that elevated temperatures promote increased TSR but need a larger energy input, although the rise is not excessively significant.

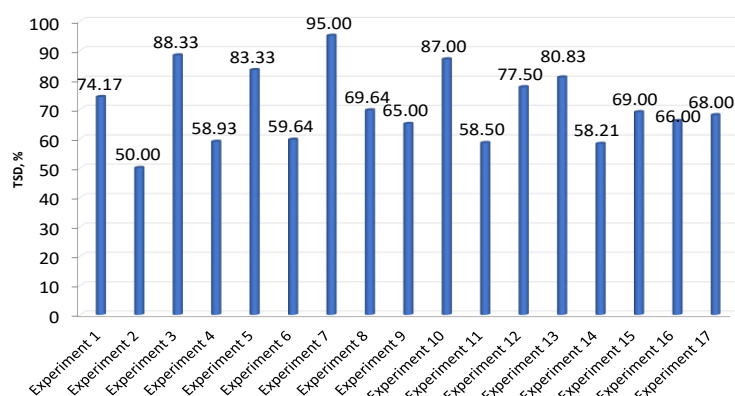


Figure 3: TSD for MSW

### 4.2 Oxygenated organic compounds (OOC) concentration results

The combined data from 17 experiments carried out for MSW revealed that the oxygenated organic compounds (OOC) concentration results varied from 49 to 93 %. The optimal conditions for achieving the highest yields of OCCs probably included elevated temperatures, increased oxidant concentrations, and a carefully balanced waste-to-liquid ratio. These circumstances improve the decomposition of waste materials and promote the creation of oxygenated chemicals.

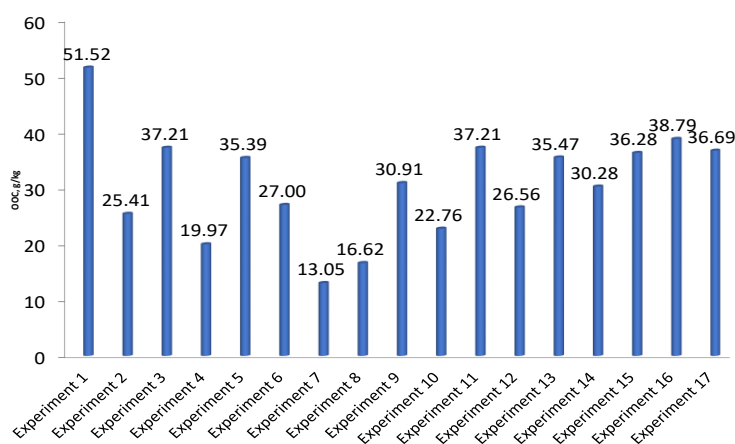


Figure 4: OOC for MSW

## 5. Conclusions

The thorough investigation of the oxidative liquefaction of MSW, supplemented by ultimate and proximate analysis, discloses unique features favorable to waste valorization. The TSR results highlight MSW's improved

capacity for reduction, and the OOC yields confirm MSW's favorable carbon profile for producing oxygenated compounds. Ideal reaction conditions, which prioritize lower temperatures, lower oxidant concentrations, and smaller waste-to-liquid ratios, point to a more complex strategy for optimizing sustainability and efficiency in waste treatment operations, with various waste kinds requiring different approaches. Among the tested parameters waste-to-liquid ratio and oxidant concentrations are found to be the most important parameter affecting the extent of MSW degradation and production of OCCs included Volatile Fatty Acides (VFAs). It was identified the optimal reaction conditions as a temperature of 200 °C, an oxidant concentration of 45 %, and a waste-to-liquid ratio of 3 %.

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### References

- Aleluia J., Ferrão P., 2016, Characterization of Urban Waste Management Practices in Developing Asian Countries: A New Analytical Framework Based On Waste Characteristics And Urban Dimension, *Waste Management*, 58, 415–429.
- CEN/TS 15414-2:2010, Solid Recovered Fuels - Determination of Moisture Content Using the Oven Dry <<https://standards.iteh.ai/catalog/standards/cen/1f025ad5-653e-4847-8293-2c181d215582/cen-ts-15414-2-2010>> accessed 12.04.2024.
- EN 15403:2011 - Solid Recovered Fuels - Determination of Ash Content <<https://standards.iteh.ai/catalog/standards/cen/0c9908dd-e915-4470-b9b9-b7c2011b71fa/en-15403-2011>, accessed> 12.04.2024
- EN 15402:2011 - Solid Recovered Fuels - Determination of the Content of Volatile Matter <<https://standards.iteh.ai/catalog/standards/cen/32c296e3-e4fa-443b-a9ae-fafcae85ef14/en-15402-2011>> accessed 12.04.2024
- Hartmann H., Ahring B.K., 2006, Strategies for The Anaerobic Digestion of The Organic Fraction Of Municipal Solid Waste: An Overview, *Water Science and Technology*, 53, 7–22.
- Kunsen L., Youcai Z., Jia-Hong K., Hao D., Feifei C., Zilong Z., Meilan Z., Chunlong Z., Xiaofeng G., Tao Z., Tao W., 2022, Toward smarter management and recovery of municipal solid waste: A critical review on deep learning approaches, *Journal of Cleaner Production*, 346, 130943.
- Mumtaz H., Sobek S., Sajdak M., Muzyka R., Werle S., 2023, An Experimental Investigation and Process Optimization Of The Oxidative Liquefaction Process As The Recycling Method Of The End-Of-Life Wind Turbine Blades, *Renewable Energy*, 211, 269–278.
- Mumtaz, H., Werle, S., Muzyka, R., Sobek, S., Sajdak, M., 2024, Oxidative Liquefaction, an Approach for Complex Plastic Waste Stream Conversion into Valuable Oxygenated Chemicals, *Energies*, 17, 1086.
- Nanda S., Berruti F., 2021, A technical review of bioenergy and resource recovery from municipal solid waste, *Journal of Hazardous Materials*, 403, 123970.
- Phu S.T.P., Asari M., Nguyen D.B., Dinh C.L., 2023, Developing A Thermal-Composting System for Recycling Household Biodegradable Solid Waste, *Chemical Engineering Transactions*, 106, 607-612.
- Rogoff M.J., 2013, *Solid Waste Recycling and Processing: Planning of Solid Waste Recycling Facilities and Programs*, Elsevier LTD, Oxford, UK.
- Sobek S., Werle S., 2021, Solar pyrolysis of waste biomass: A comparative study of products distribution, in situ heating behavior, and application of model-free kinetic predictions, *Fuel*, 292, 120365.
- Sukor M.Z., Daud A.R.M., Jamaludin S.I.S., Muhamad A.H.A., Samah N.A.A., Sanusi A.N.A., Annuar N.H.R., 2023, Biomass Wastes Hydrothermal Carbonization: A Mini-Review on Hydrochar Properties and Combustion Performance, *Chemical Engineering Transactions*, 106, 451-456.
- US Census Bureau, 2024, Census Bureau Projects U.S. and World Populations on New Year's Day <<https://www.commerce.gov/news/blog/2024/01/census-bureau-projects-us-and-world-populations-new-years-day>> Accessed 21 May 2024.
- Werle S., Dudziak M., 2013, Evaluation of toxicity of sewage sludge and gasification waste-products, *Przemysl Chemiczny*, 92, 1350 – 1353.
- World Bank, 2024, What a Waste Global Database <[https:// datacatalog.worldbank.org/search/dataset/0039597/What-a-Waste-Global-Database](https://datacatalog.worldbank.org/search/dataset/0039597/What-a-Waste-Global-Database)> Accessed 21 May 2024.
- Zhang, Z., Zhang, Y., Li, J., Adeel Ahmad H., Shifeng W., 2022, Accelerated liquefaction of vulcanized natural rubber by thermo-oxidative degradation, *Polymer Bulletin*, 79, 1767–1786.