Measurement of Energetic Properties of Residual Sludge and Catalysts from the Textile, Tannery, and Galvanic Industries Using Differential Scanning Calorimetry

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Abstract:
This study investigates the energetic properties of catalysts derived from residual sludge generated by the textile, galvanic, and tannery industries. The research involved an initial heat treatment to activate the catalytic properties, followed by thermal analysis using differential scanning calorimetry (DSC). This technique enabled the examination of the materials' thermal behavior over a temperature range of 142 to 550°C, under controlled heating rates and pressure conditions. The resulting data were used to construct specific heat models through polynomial regression, employing the least squares method. These models allowed for the estimation of variations in enthalpy and entropy for both the sludge and catalysts via integration. The specific heat models, primarily represented by third-degree polynomials, accurately depicted the thermal behavior of the samples, accounting for variations in their physicochemical properties. The catalysts from the textile industry showed the strongest statistical fit, while the catalysts from the galvanic industry exhibited notable consistency with bibliographic data across various temperature points. The specific heat (Cp) was determined as a function of temperature and used to estimate the enthalpy and entropy changes in the sludge and catalysts. The highest enthalpy values were observed for the sludge and catalysts from the tannery industry, with Cp values of 5.60 J/g-K at 603 K and 2.45 J/g-K at 445.6 K. The third-degree polynomial models were found to be the most effective, as they (1) accounted for variations in the physicochemical properties affecting Cp as a function of temperature, (2) provided superior statistical fit, and (3) aligned with existing literature data for the textile and galvanic industries.

Keywords: catalyst; sewage sludge; differential scanning calorimetry; specific heat; enthalpy; entropy

1. Introduction

In 2022, Ecuador enacted a law to encourage the circular economy [1], focusing on the promotion of waste material trade, especially in the manufacturing sector. A significant component of this effort involves the recycling and reuse of industrial residues, such as sewage sludge from the textile, galvanic, and tannery industries, as well as from petroleum storage tank bottoms and mining tailings. Previous research by this group has demonstrated that these industrial residues can be transformed into catalysts, primarily composed of iron, which show catalytic activity in processes such as petroleum cracking and methane decomposition. Notably, the highest specific surface area for catalysis was achieved with waste sludge from the textile industry, which reached 31.73 m^2/g [2], followed by 20.05 m^2/g for the tannery industry [3], and 17.68 m^2/g [3] for the galvanic industry. These findings emphasize the potential of utilizing industrial residues for producing high-value-added products, contributing to the advancement of the circular economy.

Thermal analysis techniques, such as thermal differential studies and differential scanning calorimetry (DSC), are essential for the synthesis and characterization of catalysts. DSC, in particular, is widely used to assess the thermal behavior of materials, including metals and alloys, by measuring the heat flow. This technique helps determine the potential for reusing catalysts while minimizing the loss of catalytic activity [4]. Furthermore, DSC has been successfully applied in the development of kinetic models for reactions involving metallic catalysts, such as the combustion of petroleum with metallic chlorides [5] and the catalytic combustion of methane over cobalt catalysts [6]. Additionally, DSC is instrumental in evaluating the hazard characteristics of metallic nano powders, including the explosion potential of materials derived from iron and zinc [7].

Understanding the thermal properties of catalysts—specifically their specific heat, enthalpy, and entropy—is critical for defining the operational conditions in real-world reactors. The heat capacity of a catalyst can have a profound impact on a reactor's temperature and heat flux, thereby influencing the overall energy balance. This, in turn, affects safety and operational efficiency, as temperature control is vital to avoid mechanical issues, chemical hazards, and physical risks like burns due to thermal stress. For example, improper temperature regulation may lead to reactor overpressurization, corrosion, or unintended reactions, all of which can compromise both safety and productivity.

Despite the growing interest in utilizing industrial waste for catalyst synthesis, comprehensive information on the performance of sludge and metals used as catalysts remains limited. High surface temperatures are known to promote catalytic reactions, and the heat transfer phenomenon—along with temperature profiles under both wet and dry conditions—can significantly influence catalytic activity. Therefore, the study of the energetic properties of catalytic materials and residual sludge from industries such as textiles, tannery, and galvanic processing is crucial. These studies, which involve heat addition or extraction, provide valuable insights into the potential for alternative catalyst production from industrial residues.

This research aims to investigate the energetic properties of catalysts synthesized from industrial sludge. Differential scanning calorimetry (DSC) is employed to explore the thermal variations in these catalysts, capturing heat flux data over a temperature range of 142 to 550°C. Polynomial regression using the least squares method is used to create specific heat models that satisfy statistical criteria, allowing for the estimation of enthalpy and entropy variations within specific temperature intervals. These findings are expected to contribute to the understanding of how industrial sludge can be transformed into useful catalytic materials, with applications in methane decomposition, homogeneous reactions (such as lactic acid production), and sustainable wastewater treatment methods for eliminating hazardous pollutants like bisphenol in hydrogen production [13]. This research opens up new possibilities for the scaling up of catalyst production derived from industrial waste, offering environmentally sustainable alternatives for a range of chemical and industrial processes.

2. The Methodological Framework

2.1. Experimental Design

Residual sludges from galvanic [3], textile [2], and tannery [14] processes were collected from factories located in Quito and Ambato, Ecuador. These sludges were dried following ASTM-D2216 standards in a drying oven (Nabertherm-TR60, Bahnhofstr, Lilienthal, Germany) for four hours to prepare them as catalysts. The dried sludges were then sieved between 150 and 180 µm using Tyler's Sieve series. The sludges and catalysts are shown in Figure 1.

This study investigates the effect of different temperatures on the mechanical strength and textural properties of these materials. Several techniques were employed to characterize the structure of the materials, including elemental analysis, Fourier-transform infrared spectroscopy (FTIR), nitrogen adsorption, X-ray diffraction, and programmed temperature reduction. Additionally, catalytic properties were evaluated through industrial application reactions, such as those involving glycerol [2], crude oil [15], and methane thermal decomposition [16].

The experimental setup includes the following sludge and catalyst types:

- **L1**: Textile sludge 1, **C1**: Textile catalyst 1
- **L2**: Textile sludge 2, **C2**: Textile catalyst 2
- **L3**: Tannery sludge, **C3**: Tannery catalyst
- **L4**: Galvanic sludge 1, **C4**: Galvanic catalyst 1
- **L5**: Galvanic sludge 2, **C5**: Galvanic catalyst 2
- **L6**: Galvanic sludge 3, **C6**: Galvanic catalyst 3

The properties of the samples used are summarized in Table 1, categorized by the type of industry: textile [2], tannery [14], and galvanic [3]. The surface characteristics of the materials were analyzed using nitrogen adsorption–desorption with a surface area analyzer (Horiba-SA 9600, Minami-ku, Kyoto, Japan). This analyzer measures the gas adsorption and desorption profiles, and the surface area is determined using the single-point BET method.

For analysis, 0.15 g of each sample was placed in a U-tube and degassed at 300 °C for two hours to purify the surface. The nitrogen adsorption–desorption procedure was performed using liquid nitrogen (Enox S.A., Quito, Pichincha, Ecuador).

The residual sludges were calcined between 400 and 900 °C for four hours in a muffle furnace (Thermo Scientific—Thermolyne, Waltham, MA, USA). This thermal treatment removed organic residues and oxidized the metallic phases

in the sludges, turning them into catalytic materials. Following this process, the residual sludges were considered for use as catalysts.
Table 1 presents the specifications of the sludge properties used in this study.

Table 1. Properties of sludge and catalysts.

Industry		Properties					
		% Humidity	T. Calcination (°C)	Oxides	Metal (Phase Act.)	Specific Surface (m^2/g)	Pore Volume (cm^3/g)
Textile	L1	76.50	-	-	Fe	-	-
	C1	-	600	Fe_2O_3, Al_2O_3, SiO_2, Cr_2O_3, ZnO, Ni_2O_3, Co_3O_4.		30.36	0.0375
	L2	66.01	-	-	Cr, Zn	-	-
	C2	-	600	Fe_2O_3, Al_2O_3, SiO_2, Cr_2O_3, ZnO, Ni_2O_3 y Co_3O_4		31.73	0.0518
Tannery	L3	12.65	-	-	-	-	-
	C3	-	400	Cr_2O_3		25.829	0.0250
Galvanic	L4	58.00	-	-	Fe, Zn	-	-
	C4	-	400	FeO, Fe_2O_3, Fe_3O_4 y ZnO.		96.15	0.12
	L5	53.83	-	-		-	-
	C5	-	500	FeO, Fe_2O_3, Fe_3O_4, ZnO.		63.36	0.09
	L6	74.47	-	-	Fe	-	-
	C6	-	550	FeO, Fe_3O_4.		17.68	0.02

2.2. Laboratory Method

The energetic characterization of the sludge and catalysts was conducted using a NETZSCH 3500 Sirius calorimeter, located at the Thermodynamic Lab of the Facultad de Ingenieria Quimica, Universidad Central del Ecuador. The experimental procedure followed the ASTM E1269-1 standard [17].

For the analysis, alumina crucibles with a 150 µL capacity were used, containing approximately 10 mg of the sample. The experiment was carried out under a nitrogen atmosphere at a flow rate of 30 mL/min. A temperature ramp of 15 °C/min was applied during both isothermal and dynamic processes (as illustrated in Figure 2).

Initially, the temperature was increased to 100 °C to remove any organic phase and ambient moisture from the catalyst. This pre-treatment step ensured that the calorimetry measurements focused on the thermal properties of the catalyst and sludge, excluding phase changes such as evaporation. Additionally, temperatures were kept below 600 °C to prevent any fusion effects that might alter the material's behavior during the experiment.

The calorimetric analysis generated heat flow data (Φ) for both the sludge and the catalysts. These data were subsequently used to estimate the energetic properties of the materials, including specific heat, enthalpy, and entropy. Mathematical models were applied to process these results, facilitating the determination of key thermodynamic properties that are essential for evaluating the performance and potential applications of the synthesized catalysts.

2.3. Analysis of Data

The specific heat equation is a crucial tool for determining the temperature-dependent variations of specific heat and for characterizing important energy properties such as enthalpy and entropy. The specific heat equation helps in describing the relationship between temperature and the thermal behavior of a material, allowing for a deeper understanding of its thermodynamic properties. The manner in which a material's specific heat changes is highly influenced by the temperature range under consideration. Therefore, conducting a preliminary analysis of the Differential Scanning Calorimetry (DSC) thermogram is vital for identifying the appropriate temperature intervals to apply polynomial regression models.

The DSC thermograms exhibited a trend consistent with previous studies, and the high degree of compatibility between the third-degree polynomial model for heat capacity and the experimental data [18] led us to choose the following model for specific heat (Cp):

$$Cp = a1 + a2T + a3T2 + a4T3Cp \ = \ a_1 + \ a_{2T} + \ a_{3T}^2 + \ a_{4T}^{3Cp} = a1 + a2T + a3T2 + a4T3$$

where TTT represents the temperature and a1,a2,a3,a4 are the polynomial coefficients to be determined.
To fit this model to the experimental data, the least squares method was employed. This technique is effective in determining the partial slopes and intercepts of the polynomial function. Variance analysis was used within our regression models to assess the statistical significance of the results. The efficacy of the model was also evaluated using the adjusted coefficient of determination (R^2), which indicates how well the model explains the variability of the data.
Furthermore, assumptions related to the normality of the residuals and the homogeneity of variance were thoroughly tested to ensure the reliability of the results. To quantify the uncertainty in the model, confidence bands were established at a 95% confidence level, ensuring that the estimated specific heat values are within a reliable range. This comprehensive data analysis provides a solid foundation for the thermodynamic evaluation of the catalysts and sludge derived from the industrial wastes studied.

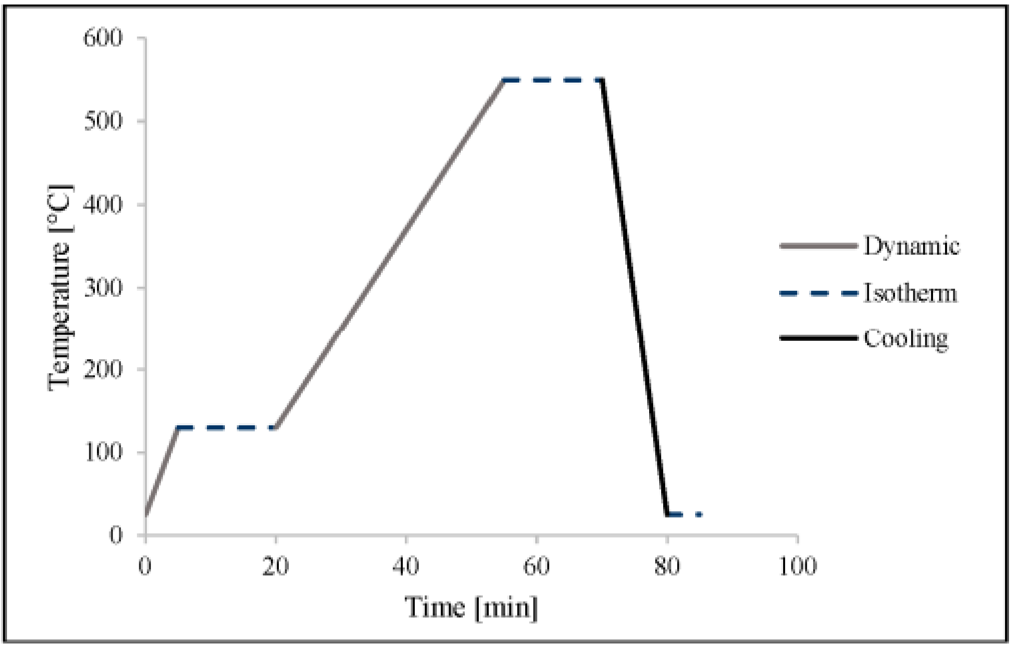

Figure 2. Methodology for the calorimetric analysis of sludge and catalysts.

3. Results and Discussion

3.1. Differential Calorimetry Analysis

The Differential Scanning Calorimetry (DSC) thermograms for each sample were obtained under two heating conditions: isothermal heating to 130 °C and dynamic heating between approximately 142 and 550 °C. The thermograms revealed endothermic peaks in the positive direction, indicative of heat absorption by the samples during thermal transitions (Figure 3). These thermograms were instrumental in analyzing the thermal behavior of the sludge and catalysts derived from the textile, tannery, and galvanic industries.
Table 2 presents the energy peaks observed for each material across different industries. Notably, the textile industry sludge (L1) and catalyst (C1) showed significant endothermic peaks above 200 °C. Specifically, the peak between 200 and 275 °C aligns with a phase transition in SiO_2 from α-SiO_2 to β-SiO_2 [19]. Catalyst C1 exhibited fewer peaks and a lower heat flow than sludge L1, suggesting greater thermal stability.
Comparing the textile industry sludges (L1 and L2) with the catalysts (C1 and C2), it became apparent that sludges require higher heat fluxes than catalysts. This increased energy demand is linked to enhanced thermal stability in the catalysts, which display a more controlled and stable thermal profile.
In the case of the tannery industry (L3 and C3), the thermograms revealed a decrease in the intensity of energy peaks, with catalyst C3 showing better visibility of these peaks, reflecting higher thermal stability compared to L3.

For the galvanic industry, the analysis of thermograms from the three samples (L4, L5, L6 for sludge and C4, C5, C6 for catalysts) showed that catalysts generally exhibit higher thermal stability than their corresponding sludges. The

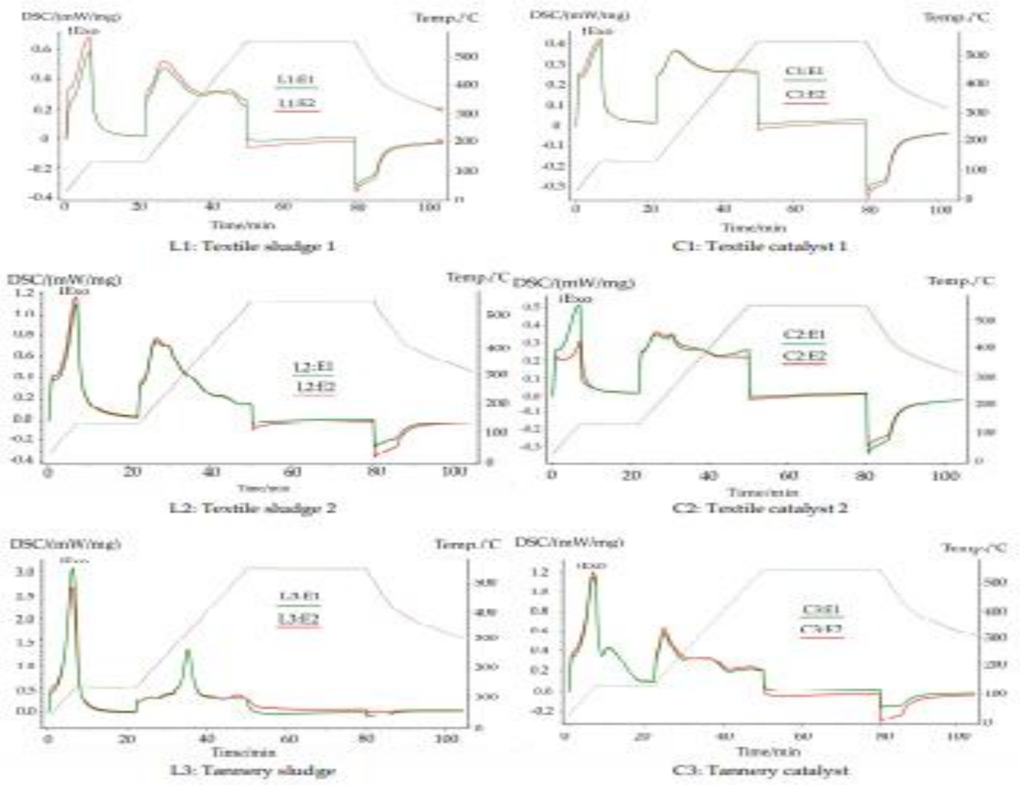

Figure 3. Cont.

thermograms for L4, for example, indicated higher heat fluxes than those for C4, which exhibited greater stability, with distinct peaks corresponding to transitions in w-ZnO and ε-Fe_2O_3 at specific temperatures [20][21].
The analysis of the galvanic industry samples (L5 and C5) further confirmed this trend, with catalysts showing lower heat fluxes compared to sludges. Specifically, the heat flux from 400 °C in C5 was attributed to the transition from γ-Fe_2O_3 to α-Fe_2O_3 [22]. These findings underscore the enhanced thermal stability of catalysts, which are more robust and require less energy input for phase transitions compared to the sludges from which they are derived.

3.2. Specific Heat

Given the extensive data collected during the DSC analysis, the thermogram was segmented by peaks corresponding to structural changes, as reported in the literature. Spline interpolation was applied to these peaks, and third-degree polynomials were used to model the specific heat behavior of each material. This polynomial approach ensured improved correlation and more accurate modeling of the heat capacity data.
The third-degree equations (Equation 1) were chosen based on their compatibility with the experimental specific heat data [23], and their statistical validity was assessed through analysis of variance (ANOVA) and t-tests. Polynomial models of higher degrees were avoided to prevent sensitivity to rounding errors in the coefficients.
The polynomial regressions for each material were calculated using the STATGRAPHICS program. In some models, the p-value for certain constants exceeded 0.05, indicating statistical insignificance. In these cases, a lower-order polynomial was selected to improve the model's accuracy and statistical significance. Table 3 presents the final polynomial models, including their statistical significance as determined by ANOVA and t-tests, ensuring the reliability of the derived specific heat values across the temperature ranges considered.

4. Conclusions

The specific heat models typically expected for solids exhibit linear behavior due to the thermal stability and homogeneity of materials. However, the calculated specific heat capacity (Cp) models for the three industries in this study generally demonstrated a better fit with third-degree equations. This deviation can be attributed to the heterogeneity of the materials and the structural changes within their components.
Among the catalysts tested, Catalyst C3 (from the tannery industry) exhibited high variability between replicates, resulting in low R^2 values (0.4989 and 0.0149) for the prediction models. This suggests a weak correlation between the predictor variables and the response, which may be due to an inverse relationship between Cp and porosity.

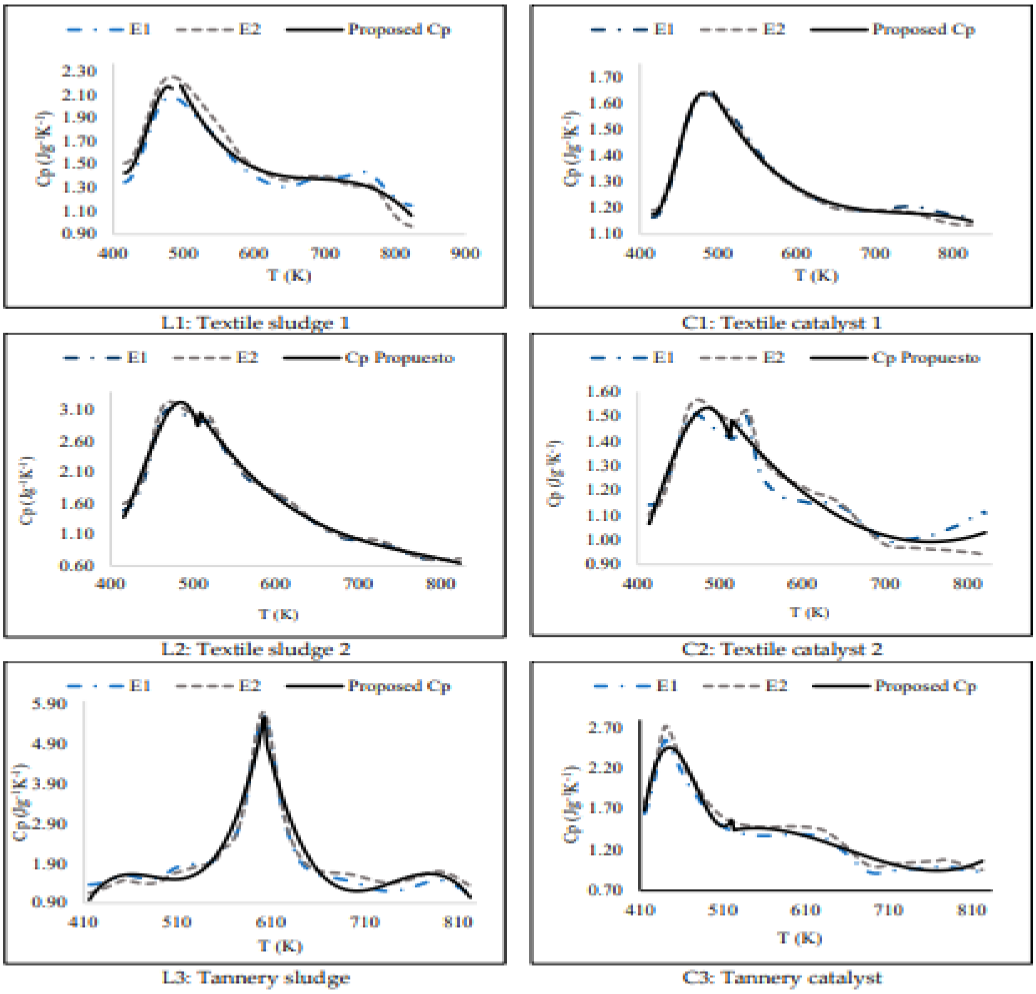

Figure 4. *Cont.*

The material was exposed to temperatures above the optimal calcination temperature (400 °C), which likely led to a reduction in the number of active sites on the catalyst.
The catalysts synthesized from the textile industry (C1 and C2) showed the best model adjustments for specific heat capacity, with a coefficient of determination no less than 0.9031. These materials also exhibited relatively high enthalpy values (up to 530.761 J/g), making them suitable for high-thermal-load industrial processes. Their high model fit and thermal properties suggest they are well-suited for simulating the operating profiles and temperature conditions

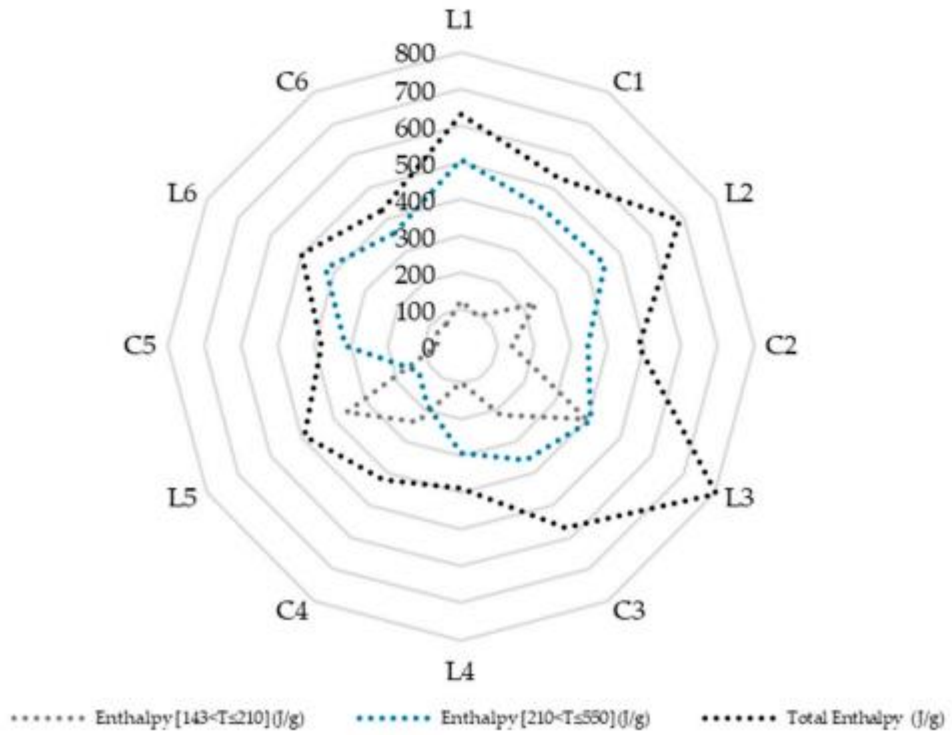

Figure 5. Enthalpy of catalysts and sludge from the textile, tannery, and galvanic industry.

of reactors.

In contrast, the catalysts from the galvanic industry showed less consistent thermal stability. Catalyst C4 did not demonstrate stability due to significant variations in behavior with increasing temperature, which renders it unsuitable for robust chemical process modeling. However, C5 and C6 showed characteristics more consistent with iron oxide components, particularly at temperatures above 300 °C.

The development of catalysts from alternative materials is a critical step in advancing sustainability and reducing waste. This approach contrasts with traditional catalysts that often rely on non-renewable resources.

In summary, while each type of catalyst has its strengths and weaknesses, the textile industry catalysts (C1 and C2) are the most promising for future industrial applications, offering both thermal stability and high enthalpy values.

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