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# Experimental assessment of acid gas energy recovery potential in refinery operations

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## Abstract

Sour and acid gas streams generated during crude oil refining are commonly flared, representing both an environmental liability and an underutilized energy resource. This study experimentally evaluates the feasibility of utilizing the acid gas from the Esmeraldas Refinery in Ecuador, as an alternative energy source for on-site power generation, addressing the combined challenges of flaring reduction and energy efficiency improvement.

A comprehensive physicochemical characterization based on gas chromatography, together with mass and energy balance analyses, was conducted under real operating conditions over a 48-month period.

The evaluated acid gas stream exhibited a higher heating value of 3,477.73 kcal/kg and a stable average mass flow rate of approximately 52.5 ton/day. Assuming a conservative global conversion efficiency of 15%, the recoverable energy potential was estimated at 33,466.88 kWh/day, corresponding to an equivalent substitution of 261.46 bbl/day of Fuel Oil No. 6 or 10.17% of the refinery's current fuel and energy demand.

Uncertainty and sensitivity analyses confirmed the robustness of the proposed energetic model, with propagated deviations below 0.3%, identifying conversion efficiency ( $\eta$ ) as the dominant parameter influencing overall performance. Assuming the integration of a Claus-based sulfur recovery scheme enables the production of approximately 42.3 ton/day of elemental sulfur, supporting by-product valorization within a circular-economy framework. These results demonstrate that acid gas recovery constitutes a technically viable, environmentally compliant, and replicable strategy for refinery energy optimization, extending prior studies through long-term industrial validation under real operating conditions and an integrated energy-sulfur framework, which remains largely unexplored for developing-region refineries.

**Keywords** Sour gas valorization, Refinery self-sufficiency, Gas-to-power systems, Physicochemical characterization, Desulfurization technologies, Flaring mitigation, Circular economy in refineries, Energy transition in oil refining, Combustion efficiency analysis, Sustainable power generation

## Introduction

The utilization of sour refinery gas has gained increasing attention as a potential pathway to reduce flaring-related emissions while enhancing on-site energy availability in refinery operations [70]. During crude oil processing, refineries generate residual gas streams composed of light hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ) alongside non-combustible and corrosive components such as  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{S}$  [1]. In many refinery settings (particularly in developing economies), these gas streams are routinely disposed of through flaring, often without prior quantitative evaluation of their energetic value. This practice results in substantial energy losses and avoidable environmental impacts, despite the presence of recoverable chemical energy within the flared streams [65].

## Objectives and scope of the study

Within the context of refinery operations in developing countries, where residual gas streams are frequently disposed through flaring regardless of their composition or environmental consequences, this study aims to quantitatively assess the energetic value of a high- $\text{H}_2\text{S}$  sour refinery gas stream currently treated as waste and flared to the environment. Esmeraldas Refinery operates under a conventional refining configuration in which acid gas streams generated during process operations are managed according to the existing infrastructure and operational constraints. Under current baseline conditions, high-acid gas streams are routed to controlled flaring systems as part of routine operation, a practice commonly adopted in refineries where dedicated sulfur recovery facilities are not yet integrated into the process scheme. This operational configuration defines the boundary conditions under which the present study was conducted.

The scope of the study is centered on the energetic and technical feasibility of utilizing such gas streams for internal power generation, supported by an experimental and analytical framework applicable to refinery operating conditions.

Focusing on: (i) experimental physicochemical characterization of generated gas during crude oil processing, with particular emphasis on combustible hydrocarbons and sulfur-containing compounds; (ii) determination of the higher heating value (HHV) for the sour gas stream, and evaluation of its theoretical suitability as a substitute for conventional refinery fuels used in power generation systems; (iii) quantification of electrical power generation potential and conversion efficiency analysis under representative operating conditions, including a theoretical estimation of recoverable elemental sulfur derived from measured gas composition; and (iv) comparative assessment of sour gas utilization performance against traditional fuels currently employed in refinery power generation, identifying potential advantages as well as technical limitations.

By identifying the key physicochemical and energetic parameters governing the use of high- $\text{H}_2\text{S}$  sour refinery gas as fuel, this research provides a technical basis for assessing operational challenges and feasibility pathways under specific refinery conditions. This approach is particularly relevant for refineries operating in developing economies, where flaring remains prevalent, and contributes to strategies aimed at improving energy efficiency and supporting the transition toward cleaner and more sustainable power generation practices.

### Critical evaluation of existing methods

Recent studies have addressed the challenge of residual and sour gas utilization primarily through conceptual, regulatory, and simulation-based approaches, with varying degrees of technical depth. Khalili-Garakani et al. [50] proposed a hybrid approach combining gas reinjection into mature reservoirs with partial utilization in reciprocating internal combustion engines, highlighting the potential for improved resource efficiency. While the approach introduces an innovative integration of recovery pathways, it lacks experimental validation and detailed quantitative modeling, limiting its direct applicability to refinery-scale power generation scenarios [50].

Similarly, Beigiparast et al. [15] evaluated flaring reduction strategies in petrochemical facilities using simulated recovery scenarios, identifying operational and regulatory challenges and estimating a potential flaring reduction of up to 27%. Despite offering useful insights into system-level constraints, the study remains largely descriptive and does not provide a quantitative assessment of energy conversion performance or fuel substitution potential [15].

From an environmental perspective, Taha et al. [67] investigated sour gas flaring and its contribution to greenhouse gas emissions, proposing large-scale recovery and conversion into natural gas for urban residential use in Egypt. Although the study demonstrates the environmental benefits of sour gas recovery, its focus lies outside refinery-based power generation and does not address the energetic performance of sour gas as an internal fuel source [67].

In a related context, Mansoor & Tahir [56] examined strategies to reduce energy losses associated with LNG and refinery gas streams, presenting a preliminary framework for improved utilization. While environmentally advantageous, the proposed model remains qualitative and does not incorporate experimental characterization or detailed energy balance analysis [56].

Complementing these efforts, Nezhadfar and Khalili-Garakani [58] assessed the economic and environmental implications of sour and associated gas flaring in Iran, suggesting the use of combined engine configurations to mitigate emissions. However, their analysis is confined to a conceptual level, without experimental validation or quantitative evaluation of power generation performance [58].

Overall, existing literature provides valuable insights into flaring mitigation and residual gas management; however, it predominantly lacks experimentally grounded, quantitative assessments that integrate gas composition, heating value and residual determination, and energy conversion performance. This limitation is particularly evident for high- $H_2S$  refinery gas streams, which are frequently flared in developing economies due to infrastructure constraints and operational practices yet remain insufficiently evaluated in terms of their potential contribution to on-site power generation.

### Research gap analysis

Despite increasing global attention to flaring reduction and residual gas utilization, existing studies on sour and acid gas management in refineries have predominantly focused on environmental diagnostics, regulatory frameworks, reinjection strategies, or large-scale commercialization pathways. Most published works rely on conceptual analyses, simulation-based assessments, or qualitative evaluations, with limited incorporation of

experimental characterization coupled with quantitative energy performance analysis under realistic refinery conditions [2].

Moreover, current literature rarely addresses high-H<sub>2</sub>S refinery gas streams that are routinely flared in developing economies, where operational decisions are often driven by infrastructure limitations rather than detailed energetic assessment. As a result, the actual energy recovery potential of such gas streams remains insufficiently quantified, particularly in the context of internal power generation within refinery facilities.

The absence of experimentally grounded quantitative assessments constitutes a critical gap in the existing literature, constraining informed technical decision-making on the energetic feasibility of recovering value from residual sour gas streams that are routinely disposed of through flaring.

### **Contribution of this study**

This study addresses the identified research gap by presenting an applied and experimentally supported assessment of a high-H<sub>2</sub>S sour refinery gas stream currently subjected to routine flaring. The main contributions of this work are summarized as follows: i. Experimental physicochemical characterization of a refinery gas stream with high hydrogen sulphide content, providing reliable compositional data beyond assumed or simulated values, ii. Quantitative determination of the heating value and energy potential of the gas streams, enabling direct comparison with conventional fuels employed in refinery power generation systems, iii. Development of an integrated methodological framework that combines experimental characterization with energy balance analysis to estimate the potential for on-site electrical power generation under representative operating conditions, iv. Comparative performance assessment between sour refinery gas and traditional refinery fuels, identifying potential operational advantages as well as inherent technical constraints associated with high-H<sub>2</sub>S streams.

Collectively, these contributions demonstrate that flared gas can be quantitatively evaluated as a recoverable energy resource rather than an unavoidable waste stream, providing practical engineering insight grounded in experimental evidence.

Beyond its immediate technical contributions, this study offers broader international relevance, particularly for refinery operations in regions where gas flaring remains a prevalent practice. The proposed framework is adaptable to diverse regulatory and operational contexts and supports evidence-based decision-making aimed at improving energy efficiency, enhancing energy self-sufficiency, and reducing flaring-related emissions. In this context, the work aligns with circular economy principles and contributes to global sustainability objectives related to clean energy, industrial innovation, and climate action, consistent with the United Nations Sustainable Development Goals (SDGs 7, 9, and 13).

## **Methods**

### **Study site and system description**

This study was conducted at the Esmeraldas Refinery, located in Ecuador, a refining facility that processes crude oil and generates residual gas streams as by-products of its main conversion and separation units. Within the refinery gas handling system, two independent sour gas streams are routed to flaring through process units designated as U and U1 [24, 25]. These streams are characterized by elevated concentrations of acid

components, particularly hydrogen sulfide ( $H_2S$ ), and are currently disposed of through routine flaring due to operational and infrastructure constraints. Each stream is monitored by a mass flow measurement system, identified as U\_FY59.PV and U1\_FY60.PV, respectively, which provide continuous flow rate data under refinery operating conditions [69].

#### **Sour gas flow monitoring and data acquisition**

Sour gas flow rates associated with process units U and U1 were continuously monitored using two independent mass flow meters, identified as U\_FY59.PV and U1\_FY60.PV, respectively. These instruments are part of the refinery's permanent process monitoring system and record gas flow rates under normal operating conditions [23].

For the purposes of this study, monthly representative flow data were collected for each sour gas stream over a continuous operating period of 48 months. Each monthly data point corresponds to an individual sour gas stream, resulting in a total of 96 monthly flow measurements (48 per stream) used for subsequent analysis. Monthly averaging was applied to reduce the influence of short-term operational fluctuations and to ensure that the evaluated data reflected stable, representative refinery operating conditions [9].

The acquired flow data served as the primary input for mass balance development and energy potential estimation. Data covering periods of start-up, shutdown, or abnormal operation were excluded to maintain consistency with steady-state operating conditions relevant to long-term energy feasibility assessment [44].

#### **Gas sampling and physicochemical characterization**

Representative acid gas samples were collected from each process stream upstream of the respective mass flow meters (U\_FY59.PV and U1\_FY60.PV) under normal refinery operating conditions [17]. Sampling was conducted on a monthly basis to coincide with the acquisition of representative flow data, ensuring consistency between compositional and flow measurements [11].

The physicochemical composition of the acid gas was determined using gas chromatography (GC) in accordance with ASTM D1945-14 and ASTM D1946-90 standards [12, 13]. The analytical procedure enabled the identification and quantification of light hydrocarbon components (including  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$ ) as well as non-combustible and acid components such as  $CO_2$ ,  $N_2$ ,  $H_2S$ ,  $SO_x$  and  $NO_x$  [16].

Calibration of the gas chromatograph was performed using certified reference gas mixtures, and analytical quality control procedures were applied in compliance with ISO/IEC 17025 requirements. The resulting compositional data served as input for mass balance development, heating value determination, and energy potential assessment [54].

#### **Mass balance determination**

Steady-state mass balances were formulated for each process unit based on measured gas streams flow rates obtained from the mass flow meters U\_FY59.PV and U1\_FY60.PV. The system boundaries were defined from the point of gas streams generation at each unit outlet up to the inlet of the corresponding disposal system [26].

For each unit, the monthly mass flow rate of acid gas was calculated directly from the recorded flowmeter data, assuming negligible accumulation within the defined control

volume over the monthly averaging period. The overall acid gas generation rate for the refinery was then obtained as the sum of the individual contributions from units U and U1 [53].

Auxiliary process inputs, including neutralizing agents and corrosion inhibitors, were excluded from the mass balance due to their negligible mass flow rates relative to the acid gas streams [20]. The resulting mass balance provided the quantitative basis for subsequent energy content calculations and fuel substitution analyses [24, 25].

#### Determination of calorific value

The higher heating value (HHV) of gas stream based on its experimentally measured chemical composition [35]. Representative gas samples were analyzed by gas chromatography in accordance with ASTM D1945, enabling the quantification of combustible components (e.g., CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, H<sub>2</sub>) and non-combustible components (CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S) [12, 13].

The HHV of the gas mixture (HHV<sub>GM</sub>) was calculated as the weighted sum of the individual higher heating values of each combustible component (HHV<sub>i</sub>) using standard thermodynamic reference data, while non-combustible components were assigned zero heating value. [21].

Using the equation:

$$\text{HHV}_{GM} = \sum_{i=1}^n \text{HHV}_i \times Y_i \quad (1)$$

where Y<sub>i</sub> is the molar fraction of component i. [34]. Results were expressed on a mass basis (kJ/kg and kWh/kg) and represent the theoretical chemical energy content of the untreated gas streams [5], serving as the baseline for subsequent energy potential and fuel substitution analyses [78].

#### Energy potential and power generation estimation

The energy potential of the gas stream was estimated by converting its theoretical chemical energy content into an equivalent electrical output under a conservative and strictly conceptual framework. The assessment was based on the higher heating value (HHV) derived from the experimentally determined gas composition and the measured mass flow rates, allowing the calculation of the total thermal energy available per unit time [79].

Given the exceptionally high H<sub>2</sub>S content of the gas stream, direct combustion in conventional gas turbines or internal combustion engines is not technically feasible. Consequently, electrical power generation was conceptually associated with indirect energy recovery pathways typically integrated within sulfur recovery units (SRU) such as Claus unit where a fraction of the H<sub>2</sub>S is combusted in the thermal reactor at temperatures generally exceeding 1000 °C, generating a significant amount of recoverable heat through waste heat boilers (WHB) and converted into electricity via steam turbine generators (STG) [22]. In this study, the Claus unit and the associated heat recovery system are considered strictly at a conceptual level. In order to focus exclusively on the theoretical conversion of thermal energy released during H<sub>2</sub>S oxidation into electrical energy, using representative overall efficiency values reported for WHB–steam turbine systems

in industrial practice [14]. Considering typical combined efficiencies for heat recovery and steam-based power generation associated with Claus–WHB–STG systems (generally reported in the range of 10–20%), and accounting for cumulative thermodynamic, mechanical, and auxiliary losses inherent to this indirect conversion chain, an overall electrical efficiency of 15% was adopted. This value represents a conservative benchmark consistent with sulfur recovery–associated energy recovery systems and is intentionally lower than efficiencies characteristic of direct-fired power generation technologies [29].

The theoretical electrical energy recovery from the gas stream was estimated as:

$$E_{ERGS} = \dot{m}_{GS} \times HHV_{GS} \times n_e \quad (2)$$

where  $E_{ERGS}$  denotes the effective recoverable gas stream energy (Kwh/day),  $\dot{m}_{GS}$  the daily mass flow (kg/day), and  $HHV_{GS}$  the higher heating value (kcal/kg) and  $n_e$  is the electrical efficiency. The resulting energy was subsequently converted into kilowatt-hours (kWh) for comparison purposes, using the standard equivalence of 1 Kwh = 860.421 kcal.

The estimated electrical energy potential therefore represents a theoretical upper bound, intended to quantify the order of magnitude of recoverable energy from the flared high- $H_2S$  gas stream [10].

The conversion efficiency of the refinery's current fuel-based power generation system was benchmarked against the proposed gas streams utilization scenario, [77]. Comparative performance indices were calculated to assess net efficiency gains, operational feasibility, and potential reductions in greenhouse gas emissions [28].

#### Fuel substitution analysis

The fuel substitution assessment was performed on a purely energetic basis to compare the theoretical electrical energy recoverable from the high- $H_2S$  sour gas stream with the energy content of conventional fuels used in refinery power generation [68].

At the Esmeraldas Refinery, Fuel Oil No. 6 is commonly employed for utility and power generation purposes and was therefore selected as the reference fuel [6]. The comparison was based on higher heating value (HHV) equivalence, relating the theoretical electrical energy estimated from the gas stream to an equivalent fuel oil mass flow according to [32]:

$$V_{eq} = \frac{E_{ERGS}}{PI_{FO6}} \quad (3)$$

where  $V_{eq}$  represents the equivalent daily substitution expressed in barrels of Fuel Oil No. 6 (bbl/day),  $E_{ERGS}$  is the effective recoverable gas stream energy (Kwh/day) and  $PI_{FO6}$  denotes the plant production index of Fuel Oil No. 6 (Kwh/bbl) [38].

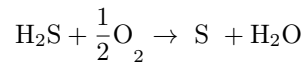
This approach serves to contextualize the energetic relevance of the flared sour gas stream relative to conventional refinery fuels and to support subsequent discussions on energy recovery potential [7].

#### Theoretical sulfur recovery estimation

The theoretical recovery of elemental sulfur from the high- $H_2S$  gas stream was estimated based on mass balance principles and the reaction stoichiometry of the Claus sulfur recovery process [8]. Given the exceptionally high hydrogen sulfide concentration of the

analyzed stream, sulfur production was evaluated assuming acid gas processing conditions [3].

The overall Claus process can be represented by the following net reaction, obtained from the combination of the thermal and catalytic stages [66]:



This global stoichiometry indicates that one mole of H<sub>2</sub>S yields one mole of elemental sulfur on a theoretical basis. Accordingly, sulfur recovery was calculated directly from the measured hydrogen sulfide content of the acid gas stream.

The mass flow rate of hydrogen sulfide was determined as [52]:

$$\dot{m}_{\text{H}_2\text{S}} = \dot{m}_{\text{GS}} \times Y_{\text{H}_2\text{S}} \quad (4)$$

where  $\dot{m}_{\text{GS}}$  represent the mass flow of gas stream and  $Y_{\text{H}_2\text{S}}$  is the experimentally measured molar fraction of hydrogen sulfide.

The corresponding molar flow rate of H<sub>2</sub>S was calculated by:

$$n_{\text{H}_2\text{S}} = \frac{\dot{m}_{\text{H}_2\text{S}}}{M_{\text{H}_2\text{S}}} \quad (5)$$

where  $M_{\text{H}_2\text{S}}$  is the molar mass of hydrogen sulfide.

Based on the global Claus stoichiometry, the molar production rate of elemental sulfur is given by:

$$n_{\text{S}} = n_{\text{H}_2\text{S}} \quad (6)$$

The theoretical sulfur mass flow rate was then obtained as:

$$\dot{m}_{\text{S}} = n_{\text{S}} \times M_{\text{S}} \quad (7)$$

where  $M_{\text{S}}$  is the molar mass of elemental sulfur.

To account for incomplete conversion under industrial operating conditions, an overall sulfur recovery efficiency  $n_{\text{SRU}}$  was introduced. Reported recovery efficiencies for conventional Claus-based sulfur recovery units typically range between 90 and 97%. In this study, a conservative efficiency value of 92% was adopted to represent realistic conversion levels while avoiding optimistic assumptions [39].

The effective sulfur recovery rate was therefore calculated as:

$$\dot{m}_{\text{TRS}} = \dot{m}_{\text{S}} \times n_{\text{SRU}} \quad (8)$$

where  $\dot{m}_{\text{TRS}}$  represents the theoretical recoverable sulfur production rate.

The resulting sulfur production rate, expressed in tons per day, provides a quantitative basis for evaluating the potential magnitude of elemental sulfur recovery associated with the flared high-H<sub>2</sub>S gas stream.

### Uncertainty propagation

The combined standard uncertainty of the derived quantities was evaluated according to the Guide to the Expression of Uncertainty in Measurement (ISO GUM) methodology [48]. For a general model  $Y=f(X_1, \dots, X_n)$ , the combined standard uncertainty  $u_Y$  was computed as [64]:

$$u_Y = \sqrt{\sum_{i=1}^n \left( \frac{\partial f}{\partial X_i} u_{X_i} \right)^2 + 2 \sum_{i=1}^{n-1} \sum_{j=1+1}^n \left( \frac{\partial f}{\partial X_i} \frac{\partial f}{\partial X_j} cov(X_i, X_j) \right)} \quad (9)$$

For the principal equations employed in this study, the uncertainty propagation expressions were derived and are presented in the Annex section for detailed verification [76].

The standard uncertainties  $u_{X_i}$ , were obtained from the specifications of the instrumentation used, including mass flowmeters [80], volumetric flowmeters, and bomb calorimetry systems, as well as from replicate analytical determinations [36]. Expanded uncertainties  $U$  are reported with coverage factor  $K=2$  corresponding to a confidence level of approximately 95% [31].

### Sensitivity analysis

To evaluate the relative influence of input variables on the model's performance regarding fuel substitution potential, a One-At-a-Time (OAT) sensitivity analysis was applied [20]. This method consists of perturbing each input parameter  $X_i$  individually within its defined range, while keeping all other parameters constant, to quantify the direct impact on the output variable [61].

For each parameter, perturbed values were computed as:

$$X_i^{\pm} = X_i \times (1 \pm \mu x_i) \quad (10)$$

where  $ux_i$  represents the relative uncertainty or operational variation assigned to each input [19]. The corresponding responses were then compared to the nominal value:

$$\Delta Y_i = \frac{Y_i^+ - Y_i^-}{2} \quad (11)$$

expressed in percentage points (pp), representing the absolute sensitivity of the output to each variable [75].

In addition, a normalized sensitivity coefficient was calculated as:

$$S_i = \frac{Y_i^+ - Y_i^-}{2Y} X 100\% \quad (12)$$

The analysis was performed using the metrological uncertainties experimentally determined for the gas stream and fuel oil parameters [71]. Furthermore,  $\pm 1\%$  operational perturbations were applied to assess the robustness of the comparative evaluation under realistic refinery conditions [51]. The variables were ranked according to their influence magnitude, and results were graphically represented through a tornado plot to visualise the dominant factors in substitution performance.

## Results

### Physicochemical characterization of gas streams

Table 1 summarizes the volumetric composition and key physicochemical properties of the gas stream sampled at Esmeraldas Refinery. The data were obtained under standard sampling procedures and analyzed by gas chromatography; results are reported as %V/V unless otherwise indicated.

**Table 1** Compositional analysis and properties of gas streams produced at esmeraldas refinery

Characteristic	Gas Stream (%V/V)
Nitrogen (N <sub>2</sub> )	8.88
Methane (CH <sub>4</sub> )	0.14
Carbon Dioxide (CO <sub>2</sub> )	0.12
Ethane (C <sub>2</sub> H <sub>6</sub> )	0.01
Ethylene (C <sub>2</sub> H <sub>4</sub> )	0.01
Acetylene (C <sub>2</sub> H <sub>2</sub> )	0.00
Hydrogen Sulfide (H <sub>2</sub> S)	88.55
Oxygen (O <sub>2</sub> )	1.85
Hydrogen (H <sub>2</sub> )	0.44
Molecular weight (g/gmol)	33.36
Higher heating value HHV (kcal/kg)	3477.73

**Table 2** Mass balance of Sour Gas Streams at Esmeraldas Refinery

Stream	Amount (ton/day)
U_FY59.PV	28.8
U_FY60.PV	26.4
Total (ton/day)	55.2

Due to the dominant hydrogen sulfide content H<sub>2</sub>S of 88.55%, the stream is classified as an acid gas and exhibits hazardous and corrosive characteristics that necessitate stringent conditioning and safety measures to energy recovery. The hydrocarbon fraction is low total light hydrocarbons < 1% v/v, which implies a low volumetric energy content despite a moderate gravimetric HHV 3,477.73 kcal/kg. Consequently, the assessment of energetic utilization potential must prioritize sulphur removal pathways, and total gas mass flow availability rather than hydrocarbon concentration alone.

#### Mass balance of acid gas streams flow

Table 2 summarizes the mass balance of acid gas flowrates recorded from the two main process lines U and U1 at the Esmeraldas Refinery. Flow data were obtained from calibrated process instrumentation under steady-state operating conditions and expressed as tons per day (ton/day).

The combined acid gas flowrate reached an average of 55.2 ton/day, indicating a substantial mass availability for potential valorization once appropriate treatment is applied. This baseline establishes the foundation for subsequent evaluations of energy recovery potential, equivalent fuel substitution, and theoretical sulphur recovery potential within refinery operations.

#### Evaluation of Fuel Oil No. 6 used as fuel for electricity generation

Table 3 presents the current consumption of Fuel Oil No. 6 utilized for electricity generation at the Esmeraldas Refinery, along with its corresponding energy production metrics. The production index (kWh/BBL) was calculated to evaluate conversion efficiency and to establish a reference baseline for subsequent comparative analyses.

The results indicate a daily average consumption of approximately 2,572 barrels of Fuel Oil No. 6, yielding a generation output of 329,323 kWh/day with an average energy productivity of 128 kWh per barrel. This performance indicator defines the reference energy benchmark against which the potential substitution capacity of the acid gas derived energy will be evaluated in subsequent analyses.

**Table 3** Energy generation performance of Fuel Oil No. 6 at Esmeraldas Refinery

Consideration	Average (day)	Average (month)
Fuel Oil No. 6 consumption (BBL)	2571.92	77,157.6
Energy generation (Kwh)	329,323.366	9'879,700.98
Production index (Kwh/BBL)	128	
Higher heating value HHV (kcal/kg)	10,240	
Density (kg/bbl)	154.22	
Production index (Kwh/kg)	0.829	

### Estimation of energy recovering from acid gas streams

Using the experimentally determined higher heating value (HHV) and measured mass flowrates, the theoretical chemical energy potential of the acid gas stream was quantified. The energy balance was established based on the relationship between calorific value (kcal/kg), and total flow rate, expressed as:

$$E_{TGS} = \dot{m}_{GS} \times HHV_{GS} \quad (13)$$

where  $E_{TGS}$  represents the total theoretical energy from gas stream (kcal/day),  $\dot{m}_{GS}$  the daily mass flow rate (kg/day), and  $HHV_{GS}$  the higher heating value (kcal/kg). The resulting energy was subsequently converted into kilowatt-hours (kWh) for comparison purposes, using the standard equivalence of 1 Kwh = 860.421 kcal.

$$E_{TGS} = 55.2 \frac{\text{ton}}{\text{day}} \times 3477.73 \frac{\text{kcal}}{\text{kg}} \times \frac{1000 \text{ kg}}{1 \text{ ton}}$$

$$E_{TGS} = 191970696 \frac{\text{kcal}}{\text{day}} \times \frac{1 \text{ Kwh}}{860.421 \text{ kcal}}$$

$$E_{TGS} = 223,112.52 \frac{\text{Kwh}}{\text{day}}$$

Based on the measured acid gas flow rate and its calorific value, the total theoretical chemical energy available was therefore estimated at approximately 223,112.52 kWh/day.

Given the extremely high H<sub>2</sub>S concentration of the stream, the potential for electrical energy recovery is conceptually associated with indirect heat recovery schemes typically integrated into sulfur recovery units, where the thermal energy released during H<sub>2</sub>S oxidation is partially recovered via waste heat boilers and converted into electricity using steam turbine generators.

Consistent with the methodological framework previously defined, a representative overall electrical conversion efficiency of 15% was adopted to account for cumulative thermodynamic and mechanical losses in the WHB–STG conversion chain. Under this conservative assumption, the corresponding theoretical electrical energy recovery potential is estimated as:

$$E_{ERGS} = E_{TGS} \times n_e \quad (2)$$

$$E_{ERGS} = 223,112.52 \frac{\text{Kwh}}{\text{day}} \times 0.15$$

$$E_{ERGS} = 33,466.88 \frac{Kwh}{day}$$

This value represents an upper-bound estimate of the recoverable electrical energy associated with the acid gas stream and is intended to quantify its energetic relevance within the refinery system, serving as a basis for subsequent comparative and substitution analyses.

#### Comparative analysis and estimation of fuel–oil substitution

The conversion of the acid gas energy potential into equivalent volumes of Fuel Oil No. 6 (BPD) was performed on a purely energetic basis. The assessment was conducted in two sequential stages: (i) estimation of the recoverable electrical energy associated with the acid gas stream, and (ii) conversion of this electrical energy into an equivalent Fuel Oil No. 6 consumption using the refinery's measured electrical production index.

Consistent with the methodological framework previously defined, the recoverable electrical energy was estimated considering an indirect energy recovery route via sulfur recovery and waste heat utilization. The plant electrical production index, derived from operational data in Table 3, quantifies the average electrical output per barrel of Fuel Oil No. 6 and is expressed as:

$$PI_{FO6} = \frac{E_{FO6}}{V_{FO6}} \quad (14)$$

where  $PI_{FO6}$  is the plant production index (Kwh/bbl),  $E_{FO6}$  denotes the energy generated (Kwh/day) and  $V_{FO6}$  represents the volume of Fuel Oil No. 6 consumed (bbl).

The equivalent daily substitution in barrels of Fuel Oil No. 6 ( $V_{eq}$ ) corresponding to the effective recoverable gas stream energy ( $E_{ERGS}$ ) was therefore calculated as:

$$V_{eq} = \frac{E_{ERGS}}{PI_{FO6}} \quad (15)$$

Substituting the measured and derived values:

$$V_{eq} = \frac{33,466.88 \frac{Kwh}{day}}{128 \frac{Kwh}{BBL}}$$

$$V_{eq} = 261.46 \frac{Bbl}{day}$$

Accordingly, the theoretical energy recoverable from the acid gas stream corresponds to an energetic equivalence of approximately 261.46 BPD of Fuel Oil No. 6, or 7,843.8 bbl/month. This result is intended to contextualize the magnitude of the acid gas energy potential relative to conventional refinery fuels under representative operating conditions.

#### Energy equivalence and fuel Oil No. 6, substitution efficiency

The energy equivalence between the recoverable electrical energy associated with the acid gas stream and the current Fuel Oil No. 6 consumption was quantified to estimate

the potential substitution ratio on a purely energetic basis. The substitution percentage was calculated as:

$$\%n_{sub} = \frac{V_{eq}}{V_{FO6}} \times 100 \quad (16)$$

where  $\%n_{sub}$  is the substitution ratio (%),  $V_{eq}$  represents the equivalent volume of Fuel Oil No. 6 that could be replaced by acid gas (bbl/day) and  $V_{FO6}$  the actual daily Fuel Oil No. 6 consumption (bbl/day).

Substituting the evaluated values:

$$\%n_{sub} = \frac{261.46 \frac{Bbl}{day}}{2571.92 \frac{Bbl}{day}} \times 100$$

$$\%n_{sub} = 10.17\%$$

This result indicates that, from an energetic equivalence perspective, the recoverable energy associated with the acid gas stream corresponds to 10.17% of the refinery's current Fuel Oil No. 6 consumption for power generation.

#### Estimation of recoverable sulfur from acid gas streams

Based on the measured acid gas flowrate of 55.2 ton/day and an experimentally determined hydrogen sulfide content of 88.55% v/v, the corresponding hydrogen sulfide mass flow was calculated as:

$$\dot{m}_{H_2S} = \dot{m}_{GS} \times Y_{H_2S} \quad (4)$$

$$\dot{m}_{H_2S} = 55.2 \frac{ton}{day} \times 0.8855 = 48.9 \frac{ton}{day}$$

Using a molar mass of 34.08 g/mol for  $H_2S$ , the molar flow rate of hydrogen sulfide is:

$$n_{H_2S} = \frac{\dot{m}_{H_2S}}{M_{H_2S}} \quad (5)$$

$$n_{H_2S} = \frac{48.9 \frac{ton}{day} \times \frac{1000 Kg}{ton}}{34.08 \frac{g}{mol} \times \frac{1 Kg}{1000 g}} = 1434859.155 \frac{mol}{day} = 1434.86 \frac{kmol}{day}$$

According to the global Claus stoichiometry ( $1 \text{ mol } H_2S \rightarrow 1 \text{ mol } S$ ), the molar production rate of elemental sulfur is identical:

$$n_S = n_{H_2S} \quad (6)$$

$$n_S = 1434.86 \frac{kmol}{day}$$

Using a molar mass of 32.06 g/mol for elemental sulfur, the theoretical sulfur production rate is:

$$\dot{m}_S = n_S \times M_S \quad \text{Eq. (7)}$$

$$\dot{m}_S = 1434.86 \frac{\text{kmol}}{\text{day}} \times 32.06 \frac{\text{g}}{\text{mol}} \times \frac{1000 \text{ mol}}{\text{kmol}} \times \frac{1 \text{ Kg}}{1000 \text{ g}} \times \frac{1 \text{ ton}}{1000 \text{ Kg}} = 46 \frac{\text{ton}}{\text{day}}$$

To account for incomplete conversion under practical operating conditions, an overall sulfur recovery efficiency of 92% was applied. The resulting effective recoverable sulfur production is therefore:

$$\dot{m}_{TRS} = \dot{m}_S \times n_{SRU} \quad (8)$$

$$\dot{m}_{TRS} = 46 \frac{\text{ton}}{\text{day}} \times 0.92 = 42.3 \frac{\text{ton}}{\text{day}}$$

From a results perspective, this finding demonstrates that sulfur recovery constitutes a quantitatively significant valorization pathway, capable of complementing energy recovery strategies and contributing to improved resource efficiency within refinery operations.

#### Uncertainty analysis

The uncertainty associated with experimental measurements and derived energy estimations was quantified to assess data robustness and methodological reliability. The mass flowmeters installed on acid gas streams U\_FY59.PV and U1\_FY60.PV exhibited an operational uncertainty of  $u_m = 0.08\%$ , uncertainty associated with HHV, calculated from gas composition obtained by gas chromatography was estimated as  $u_{HHV} = 0.1\%$  accounting for chromatographic repeatability and component property data. The conversion efficiency uncertainty was estimated as  $u_n = 0.18\%$ , the production index uncertainty of Fuel Oil No.6 is  $u_{PIFO6} = 0.1\%$ , the uncertainty of volumetric flowmeters to determine Fuel Oil No.6 consumption is  $u_{VFO6} = 0.1\%$ , and recoverable sulfur uncertainty based on instrumentation accuracy and literature-reported variability for conventional Claus-based sulfur recovery units  $u_{mTRS} = 0.08\%$ . This procedure ensures the reliability of the comparative evaluation between acid gas streams and Fuel Oil No. 6 under conditions of operational variability.

Table 4 summarises the nominal values and combined uncertainties of the principal derived metrics in this study. The detailed calculation procedures for each parameter are provided in the Annex section for verification. Standard uncertainties were propagated according to the ISO/GUM framework, as described in the Methods section. Expanded

**Table 4** Uncertainty analysis of acid gas in energy generation

Parameter	Nominal value	Standard uncertainty (u) (absolute)	Standard uncertainty (u) (relative %)	Expanded uncertainty (U) (k=2) (absolute)	Expanded uncertainty (U) (k=2) (relative %)
Theoretical energy from gas stream, $E_{TGS}$ (Kwh/day)	223,112.52	±258.58	±0.128%	±517.16	±0.256%
Recoverable electrical energy, $E_{ERGS}$ (Kwh/day)	33,466.88	±73.96	±0.221%	±147.92	±0.442%
Barrels-equivalent, $V_{eq}$ (Bbl/day)	261.46	±0.63	±0.243%	±1.26	±0.486%
Substitution equivalence, $\%ns_{ub}$ (%)	10.17	±0.025	±0.263%	±0.05	±0.526%
Recoverable sulfur $m_{TRS}$ (ton/day)	42.3	±0.0478	±0.113%	±0.0956	±0.226%

uncertainties  $U$  are reported with a coverage factor  $k=2$ , corresponding to an approximate confidence level of 95%.

The combined uncertainty of the derived parameters, including theoretical energy potential, equivalent fuel substitution, and recoverable sulfur production; does not affect the order of magnitude of the reported results. These findings confirm the robustness of the proposed energy recovery and sulfur valorization strategy under typical refinery operating conditions.

### Sensitivity analysis

Following the uncertainty assessment, a local sensitivity analysis was performed focusing on two key performance parameters: the residual energy conversion efficiency associated to Claus process ( $\eta$ ) and the Sulfur Recovery Unit efficiency governing the elemental sulfur production process. These variables were selected as the representative output because they directly control the transformation of acid gas into recoverable energy material products and because they integrates the combined influence of the main input parameters: mass flow rate, higher heating value ( $\text{HHV}_{\text{GS}}$ ), and process energy recovery, and exhibits the most notable variation under different operating conditions.

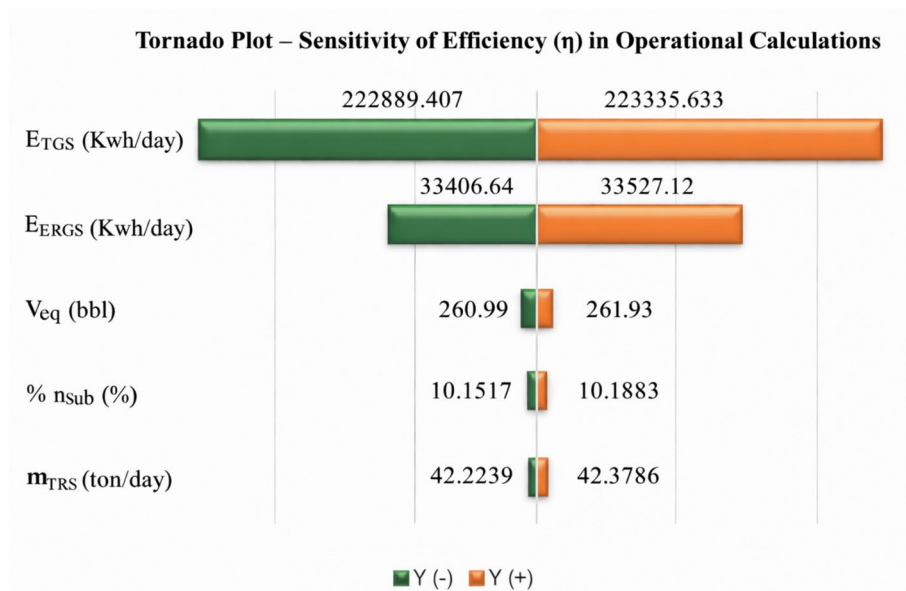
The one-at-a-time (OAT) approach was applied to quantify the effect of incremental variations within the metrological uncertainty range of each input variable on the calculates outputs. This analysis evaluates the sensitivity of theorical energy generation, theoretical recoverable energy, fuel substitution equivalence, and recoverable sulfur production, thereby enabling a consistent interpretation of the operational behavior of the system and its substitution potential relative to Fuel Oil No. 6. The corresponding numerical results are summarized in Table 5, while the full computational dataset is provided in the Annex to ensure reproducibility.

The sensitivity analysis clearly demonstrates that the conversion efficiency ( $\eta$ ) is the dominant variable influencing all energy-related outputs. Minor deviations in efficiency generate the most significant variations in recoverable energy, equivalent barrels, and substitution ratio, confirming its operational criticality. Conversely, variations in the higher heating value ( $\text{HHV}_{\text{GS}}$ ) exert a moderate yet consistent effect, indicating that process performance is more sensitive to conversion efficiency than to fuel quality within the evaluated uncertainty range.

Regarding sulfur recovery, the sensitivity of recoverable sulfur production  $m_{\text{TRS}}$  is governed predominantly by the sulfur recovery unit efficiency  $\eta_{\text{SRU}}$ , although the associated uncertainty range is relative narrow, its influence is systematic and directly proportional, highlighting the importance of stable SRU operation for reliable sulfur valorization.

**Table 5** Sensitivity evaluation of operational variables affecting conversion efficiency and energy indicators

Parameter (input)	Parameter (output)	Y (-)	Nominal Output	Y (+)	Sensitivity ( $S_i$ )	Impact (%)
$\text{HHV}_{\text{GS}}$	$E_{\text{TGS}}$ (Kwh/day)	222,889.41	223,112.52	223,335.63	1	0.1
$\eta$	$E_{\text{ERGS}}$ (Kwh/day)	33,406.64	33,466.88	33,527.12	1	0.18
$\eta$	$V_{\text{eq}}$ (BLS)	260.99	261.46	261.93	1	0.18
$\eta$	$\%n_{\text{sub}}$ (%)	10.1517	10.17	10.1883	1	0.18
$\eta_{\text{SRU}}$	$m_{\text{TRS}}$ (ton/day)	42.2239	42.3	42.3761	1	0.18



**Fig. 1** Tornado Plot – sensitivity of efficiency ( $\eta$ ) in operational calculations

To reinforce this interpretation, the corresponding variable influence is depicted through a Tornado Plot in Fig. 1.

The Tornado Plot derived from the sensitivity analysis confirms that the conversion efficiency ( $\eta$ ) exerts the predominant influence on both operational and energetic parameters of the system. Variations in process efficiency clearly govern the substitution potential, outweighing the impact of other operational variables. These findings highlight the critical importance of maintaining stable conversion efficiency to ensure optimal energy recovery and to maximize the overall energetic advantage of acid gas utilization, while confirming the secondary but consistent influence of  $\eta_{SRU}$  on sulfur recovery metrics and  $HHV_{GS}$  on energy indicators respectively.

Simultaneously, the limited sensitivity to  $HHV_{GS}$  variability and the predictable influence of SRU efficiency underline the robustness and operational reliability of the proposed valorization framework. Overall, these results demonstrate the technical feasibility and replicability of the proposed approach, supporting its applicability to similar refinery contexts at both national and international scales.

## Discussion

### Interpretation of physicochemical and energetic characteristics

The acid gas stream analyzed at Esmeraldas Refinery exhibited a predominant hydrogen sulfide content (88.55% v/v). Despite its high sulphur concentration, the stream demonstrated a gravimetric higher heating value  $HHV_{SG} = 3,477.73$  kcal/kg, indicating a non-negligible intrinsic energetic potential. Combined with a molecular weight of 33.36 g/mol, this confirms that the gas possesses sufficient calorific strength to sustain combustion once adequately conditioned through sulphur removal or controlled blending with refinery fuel gases. The presence of sulphur compounds contributes to the overall heating value compared with typical acid-gas emissions, suggesting that the stream can be effectively integrated into internal power-generation systems after standard purification. Its consistent composition and stable energetic profile provide a solid basis for

valorization, reinforcing its suitability as a partial substitute for conventional refinery fuels under regulated treatment and combustion conditions.

#### **Influence of flow distribution and mass balance on overall system performance**

The mass balance evaluation determined that approximately  $\dot{m}_{GS} = 55.2$  ton/day of acid gas are continuously flared, representing a substantial loss of recoverable energy. Throughout a four-year monitoring period, the average gas stream flow rate ( $\dot{m}_{GS}$ ) remained stable within a narrow operational range, confirming the temporal consistency of the dataset and supporting the reliability of the derived energy indicators.

Variations in  $\dot{m}_{GS}$  were found to directly influence the recoverable energy and combustion stability, evidencing that steady and well-regulated acid gas constantly delivered. When combined with the proposed conversion efficiency of  $\eta = 15\%$ , which accounts for cumulative thermodynamic and mechanical losses along the waste heat boiler–steam turbine generator (WHB–STG) conversion chain, the results demonstrate that both flow uniformity and process efficiency act as dominant variables governing the achievable energy recovery.

The propagation of measurement uncertainties across the mass and energy balances remained below the defined tolerance thresholds, validating the robustness of the instrumentation and data acquisition system.

Consequently, maintaining precise control over  $\dot{m}_{GS}$  and  $\eta$  is critical for ensuring consistent energy output, enhancing substitution reliability, and consolidating the technical feasibility of acid gas integration into refinery power systems.

#### **Energy substitution potential within refinery operations**

The comparative analysis between acid gas and Fuel Oil No. 6 demonstrated that the recovered gas stream possesses sufficient calorific capacity to replace a fraction of the conventional fuel currently used for power generation. The estimated substitution potential reached an equivalent energy of  $E_{ERGS} = 33,466.88$  kWh/day, corresponding to approximately  $V_{eq} = 261.46$  bbl/day of Fuel Oil No. 6, which represents about  $\%n_{sub} = 10.17\%$  possible substitution of the total energy demand.

These findings confirm that, under stable operating conditions, acid gas can effectively support a non-negligible share of the refinery's internal power requirements. Although the higher heating value ( $HHV_{GS}$ ) of acid gas is slightly lower than that of Fuel Oil No. 6, this difference is compensated by the available  $\dot{m}_{GS} = 52.5$  ton/day of acid gas streams currently subjected to flaring.

The adopted energy conversion efficiency  $\eta = 15\%$  associated with energy recovery within the SRU and subsequent utilization, represents a conservative yet operationally realistic baseline. This consideration accounts for cumulative thermal losses, auxiliary consumption and process constraints, while still demonstrating a tangible potential for reducing fuel consumption, enhancing energy self-sufficiency, and minimizing  $CO_2$  and  $SO_x$  emissions to the environment.

It is important to clarify that the acid gas stream evaluated in this study is not intended for direct use as a sulfur-free fuel, in compliance with refinery fuel specifications and environmental regulations. The energy recovery potential quantified in this work refers to an external utilization route associated with indirect heat recovery schemes typically integrated within SRU configurations, where the thermal energy released during  $H_2S$

oxidation is partially recovered via waste heat boilers and subsequently converted into electricity using steam turbine generators. This approach enables recovery of the intrinsic energy content of the stream without altering the primary environmental function of the SRU. Accordingly, the energetic benefit discussed arises from the recovered energy potential associated with external heat recovery, rather than from the sulfur recovery unit itself as a standalone process.

This energetic equivalence, achieved under real operational conditions, validates the technical feasibility of redirecting the currently flared acid gas streams toward electricity generation following proper treatment and controlled integration into refinery energy systems.

### **Implications of conversion efficiency and energy production**

The analysis of conversion efficiency  $\eta$  and the associated energy production indicators confirm a strong correlation with the energetic and operational stability of the system. The evaluated global efficiency of  $\eta = 15\%$ , representing the lower operational limit of associated with energy recovery from acid gas within the Claus-based treatment and utilization chain, demonstrates that even under conservative conditions, acid gas utilization provides a stable contribution to internal power generation.

Variations in  $\eta$  directly influence the effective recoverable energy  $E_{\text{ERGS}}$  and equivalent fuel substitution metrics, indicating that overall system performance is primarily governed by conversion efficiency rather than by short-term fluctuations in fuel quality or mass flow rate. This behavior highlights the critical role of process efficiency optimization in maximizing energy recovery from gas streams.

The operational stability observed throughout the 48-month monitoring period further supports the system's capability to sustain consistent energy output over time. Collectively, these findings reinforce the technical feasibility of incorporating acid gas to the refinery energy requirements when supported by stable conditions and controlled efficiency management.

### **Uncertainty and sensitivity impact on model robustness**

The integration of uncertainty and sensitivity analyses confirms the reliability and internal consistency of the proposed energy assessment model. The quantified metrological uncertainties associated with the principal input parameters as: mass flow  $u_m = 0.08\%$ , high heating value  $u_{\text{HHV}} = 0.1\%$ , and process efficiency  $u_\eta = 0.18\%$  remained within narrow limits, demonstrating consistent measurement accuracy and instrumentation stability under refinery operating conditions.

The sensitivity evaluation, based on the one-at-a-time (OAT) approach, revealed that conversion efficiency ( $\eta$ ) exerts the greatest influence on energy-related outputs. In contrast, variations in higher heating value ( $\text{HHV}_{\text{GS}}$ ) and acid gas mass flow rate  $\dot{m}_{\text{GS}}$  exhibit secondary systematic effects, reflecting their comparatively lower leverage on the energetic performance of the system. For sulfur recovery, uncertainty in recoverable sulfur production is primarily governed by process efficiency consistent with instrumentation accuracy and literature-reported variability for conventional Claus-based sulfur recovery units  $u_{\text{mGS}} = 0.08\%$ .

The consistency observed between conversion process efficiency  $u_\eta = 0.18\%$ , substitution efficiency  $u_{\% \text{sub}} = 0.263\%$ , recoverable sulfur  $u_{\text{MTRS}} = 0.113\%$  and energy recovery

uncertainties  $u_{\text{EERSG}} = 0.221\%$  corroborates the internal coherence of the model and confirms the correct propagation of uncertainties across the mass and energy balances. The tornado plot further validated  $\eta$  as the dominant operational driver, indicating that even minor deviations in efficiency can induce measurable variations in energy recovery and fuel substitution potential. Collectively, these results demonstrate the methodological robustness, reproducibility and practical applicability of the proposed framework for evaluating the energetic feasibility of acid gas utilization under refinery operating conditions.

#### **Acid gas treatment strategies within an integrated energy-sulfur framework**

To address the elevated concentrations of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in the acid gas stream, several treatment strategies were within the proposed methodological framework [27]. The selection criteria considered impurity concentrations, gas composition, corrosivity, operating conditions [37], and compliance with international environmental regulations [49]. The methodology incorporated  $\text{H}_2\text{S}$  removal by a Claus process configuration adapted to refinery scale [57]. Tail-gas treatment units (TGTU) were also included as an additional step to ensure minimum residual emissions, [60].

Given the exceptionally high sulfur content of the acid gas streams evaluated, the implementation of an efficient desulfurization process is essential prior to any energy recovery to ensure a safe and stable operation. In industrial practice, acid gas handling and processing are governed by established safety standards and material selection guidelines, such as NACE MR0175/ISO 15156, which define suitable alloys, operational limits and mitigation strategies for sour and acid service. While a detailed corrosion or materials engineering assessment fall outside the scope of this work the integration of sulfur recovery and gas treatment inherently reduces corrosive species and mitigates safety risks before downstream energy recovery.

Among available technologies, the Claus process represents the most technically and industrially established route for converting hydrogen sulfide ( $\text{H}_2\text{S}$ ) into elemental sulfur [39]. This process allows the recovery of up to 90–97% of total sulfur through controlled thermal oxidation and catalytic conversion, minimizing the emission of  $\text{SO}_2$  while generating a commercially valuable by-product [18]. Integrating a Claus unit upstream of the proposed utilization system would ensure compliance with environmental standards and preserve combustion stability by reducing corrosive and toxic components [30]. Importantly, while acid gas treatment alters chemical composition of the stream, the system-level energetic assessment demonstrates that sufficient recoverable energy remains available for supplementary power generation, enabling simultaneous sulfur recovery and energy valorization. This integrated energy-sulfur framework supports emission reduction objectives contributing directly to the United Nations Sustainable Development Goals.

#### **Valorization of by-products**

Following the treatment stage, methodological consideration was given to valorization routes for recovered by-products [62]. The analysis evaluated the potential integration of recovered sulfur into agricultural (fertilizers) and industrial sectors (chemical manufacturing, vulcanization) [33]. These pathways were integrated into the methodology to

align the study with circular economy principles and to provide a framework for quantifying sustainability benefits in accordance with SDG 7, SDG 9, and SDG 13, [4].

The theoretical elemental sulfur recovered from acid gas treatment  $m_{\text{TRS}} = 42.3$  ton/day represents a valuable resource within the refinery's circular-economy strategy [73]. Recent studies have shown that sulfur derived from refining processes can be effectively converted into agronomic formulations that enhance soil sulfate availability and nutrient uptake in sulfur-deficient soils. Field trials demonstrate that controlled application of micronized sulfur improves crop yield and soil restoration, providing an environmentally responsible reuse route for what would otherwise be an industrial waste [74].

Beyond agricultural use, incorporating recovered sulfur into industrial and chemical products, such as slow-release fertilizers, vulcanizing agents, and catalytic materials; has proven to deliver measurable environmental and economic benefits [55]. These valorization pathways help close material cycles within the refinery, reducing waste management needs and creating additional economic value [72]. Integrating sulfur recovery into productive systems strengthens operational sustainability and supports the global objectives of clean industrial innovation and climate-resilient production. Future research should focus on the techno-economic analysis, cost sensitivity and payback considerations including optimization and scalability of these sulfur recovery schemes to facilitate their implementation across similar refining contexts.

#### **Technical validation and replicability**

The validation of the proposed energetic model was achieved through the consistent agreement between calculated and observed operational parameters during the monitoring period. The low propagation of metrological uncertainties and the stable behavior of key variables:  $u_{\text{mGS}}$  mass flow rate,  $u_{\text{HHVGS}}$  higher heating value,  $u_{\eta}$  conversion efficiency and  $u_{\text{MTRS}}$  for recoverable elemental sulfur, confirm the technical soundness and reproducibility of the methodology. These outcomes demonstrate that the model can be reliably applied under real refinery operating conditions, maintaining accuracy even under fluctuating process loads.

Furthermore, the analytical framework and procedures developed are fully adaptable to other refinery systems or industrial facilities handling hydrocarbon-derived streams. The model's modular structure allows recalibration with site-specific process data, enabling scalable replication across different operational contexts and supporting its use as a standardized tool for decision-making in industrial energy optimization and resource valorization.

Overall, the validated performance indicators and the reproducibility of the analytical structure demonstrate that the proposed framework constitutes a technically robust and scalable solution for integrating acid gas treatment, energy recovery, and by-product valorization. This positions the model as a practical reference for refineries seeking to reduce flaring, enhance energy efficiency, and improve environmental performance under realistic industrial conditions.

#### **Conclusions**

This study experimentally demonstrated the technical feasibility of utilizing acid gas from the Esmeraldas Refinery as an alternative fuel for internal power generation under real operating conditions. Despite the high hydrogen sulfide content of the evaluated

stream, its stable composition, sustained mass flow rate over a 48-month monitoring period, and significant calorific potential confirm that acid gas can be effectively integrated into refinery energy systems once appropriate treatment is implemented.

The proposed energy assessment framework quantified a substitution potential for conventional Fuel Oil No. 6, enabling partial displacement of fossil fuel consumption through acid gas utilization. This finding confirms the energetic viability of redirecting flared acid gas toward controlled combustion systems, thereby improving energy self-sufficiency, reducing fuel consumption, and mitigating atmospheric emissions of CO<sub>2</sub> and SO<sub>x</sub>.

Uncertainty propagation and sensitivity analyses confirmed the robustness and reproducibility of the developed model, with low metrological deviations and conversion efficiency identified as the dominant parameter governing energy recovery performance. This validation supports the applicability of the framework under variable load conditions and its transferability to refineries with similar flaring profiles.

The integration of sulfur recovery through a Claus-based configuration further strengthens the proposed strategy by ensuring environmental compliance while enabling the production of elemental sulfur as a valuable product. The valorization of recovered sulfur within agricultural and industrial applications reinforces circular-economy principles, transforming a hazardous stream into both an energy resource and a marketable material input.

Overall, the integrated energy-sulfur framework presented in this work constitutes a technically sound, scalable and industrially replicable solution for the controlled utilization of acid gas streams. By coupling energy recovery, emission reduction, and sulphur recovery as an unified process scheme, the proposed approach provides a practical pathway for refineries seeking to enhance operational efficiency and sustainability while reducing dependence on conventional fuels and routine flaring practices.

#### Abbreviations

ASTM	American Society for Testing and Materials
ISO	International Organization for Standardization
GUM	Guide to the Expression of Uncertainty in Measurement
IEC	International Electrotechnical Commission
SDG 7	Affordable and Clean Energy
SDG 9	Industry, Innovation and Infrastructure
SDG 13	Climate Action
CH <sub>4</sub>	Methane
C <sub>2</sub> H <sub>6</sub>	Ethane
C <sub>3</sub> H <sub>8</sub>	Propane
C <sub>4</sub> H <sub>10</sub>	Butane
CO <sub>2</sub>	Carbon Dioxide
N <sub>2</sub>	Nitrogen
H <sub>2</sub> S	Hydrogen Sulphide
LNG	Liquefied Natural Gas
GC	Gas Chromatography
HHV	Higher Heating Value
Kwh	Kilowatt-hour
u <sub>xi</sub>	Standard Uncertainties
K	Coverage Factor
U	Expanded Uncertainties
OAT	One At a Time
TGTU	Tail Gas Treatment Units
BBL	Barrel
E <sub>TGS</sub>	Total Theoretical Energy From Gas Stream (Kwh/day)
E <sub>ERGS</sub>	Effective Recoverable Gas Stream Energy (Kwh/day)
PI <sub>FO6</sub>	Production Index-Fuel Oil No. 6 (Kwh/bbl)
V <sub>FO6</sub>	Volume of Fuel Oil No. 6 consumed (Bbl)
V <sub>eq</sub>	Equivalent substitution Volume of Fuel Oil No. 6 (Bbl)

$\%n_{\text{sub}}$	Substitution Percentage (%)
GS	Gas Stream
$\eta$	Conversion Efficiency
$\dot{m}_{\text{GS}}$	Mass Flow of Gas Stream (kg/day)
SRU	Sulfur Recovery Unit
WHB	Waste Heat Boiler
STG	Steam Turbine Generator
$m_{\text{H}_2\text{S}}$	Mass flow rate of hydrogen sulfide
$Y_{\text{H}_2\text{S}}$	Experimentally measured molar fraction of hydrogen sulfide
$n_{\text{H}_2\text{S}}$	Molar flow of hydrogen sulfide
Ms	Molar mass of elemental sulfur
$n_{\text{SRU}}$	Sulfur recovery efficiency
$m_{\text{TRS}}$	Theoretical recoverable sulfur production rate
NACE	National Association of Corrosion Engineers

## Supplementary Information

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Supplementary Material 1.

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### Authors' contributions

IAMC is responsible for the conception, design, and execution of the study, including the development of the methodological framework, field data collection, analysis of risk and performance indicators, and interpretation of the results. The author also drafted and critically revised all sections of the manuscript, ensured compliance with international technical standards, and prepared the final version for submission. All research activities, including the elaboration of appendices and tables, were independently carried out by the author. The author has read and approved the final manuscript.

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### Data availability

All data supporting the findings of this study are presented within the article and its appendices. Additional datasets or detailed information are available from the corresponding author upon reasonable request.

### Declarations

#### Competing interests

The author declares that he has not competing interests.

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