



# Proceeding Paper The Valorization of a Crude Refinery's By-Product: A Case Study on the Heavy Residue Gasifier <sup>†</sup>

Miroslav Variny \*<sup>D</sup>, Slavomír Podolský and Tomáš Kurák

Institute of Chemical and Environmental Engineering, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 81237 Bratislava, Slovakia; xpodolsky@stuba.sk (S.P.); tomas.kurak@stuba.sk (T.K.)

\* Correspondence: miroslav.variny@stuba.sk

<sup>+</sup> Presented at the 30th International Conference on Modern Metallurgy—Iron and Steelmaking, Kosice, Slovakia, 27–29 September 2023.

Abstract: The conversion of locally available, low-value materials to useful products and media, thereby replacing high-quality and high-cost resources, belongs to one of the pillars of the circular economy of industrial conditions. A study on the potential implementation of a mixed oxygen- and steam-blown heavy vacuum residue gasifier in a refinery, processing 5 to 6 million t of crude oil per year, is performed, evaluating its mass and energy balance, and identifying and assessing the synergies of gasifier placement in a refinery, rather than its erection as a stand-alone plant. Industrial heat and power plants, as well as hydrogen production plants, represent the production units that are directly affected by gasifier implementation, while several other technical and economic issues result in: the operation of the steam network, in heavy residues' handling, and in the refinery's natural gas balance. Natural gas is currently the most important resource for hydrogen production in the refinery, and its partial replacement by hydrogen from a gasifier has different energetic and environmental impacts, based on the considered natural gas composition (current situation: natural gas with 10% vol. renewable hydrogen and natural gas with 20% vol. renewable hydrogen content). The power production and the overall refinery's power balance, the carbon dioxide emissions both within the refinery and external ones, and natural gas balance change are all evaluated. The preliminary results show that while gasifier commissioning is associated with an over EUR 1 billion investment, it can represent one of the few available solutions of how to reasonably dispose of heavy residues, utilizing it from both energy content and material potential point of views.

Keywords: vacuum residue; gasification; hydrogen; refinery; carbon dioxide

# 1. Introduction

The traditional linear economy is being replaced by a more efficient circular approach in many industrial branches. In line with this, industrial production processes need to increase their material and energy efficiency and decrease their footprint. One of the potential solutions to cope with this requirement is to convert the production facilities into polygeneration sites, utilizing multiple feedstocks to produce several products in one facility [1]. Complex industrial clusters and industrial parks can serve as one example [2]. Biorefineries, converting local, low-value materials (or feedstocks grown on purpose) into energy, fuels, chemicals, and other valuable products are another one [3]. Among the variety of materials facilitating this industrial transition, hydrogen stands out as both an energy carrier and a chemical reagent [4,5]. While the most widespread means of its production is the well-known steam methane reforming (SMR) process, with natural gas (NG) used as the most common feedstock [6], other large-scale production processes utilizing renewable energies or feedstocks have been researched intensely [7].

Oil refineries rely on SMR as a major hydrogen source for crude conversion processes into fuels and petrochemicals [8]. The heavy vacuum residue (VR) remaining after a



Citation: Variny, M.; Podolský, S.; Kurák, T. The Valorization of a Crude Refinery's By-Product: A Case Study on the Heavy Residue Gasifier. *Eng. Proc.* 2024, *64*, 10. https://doi.org/ 10.3390/engproc2024064010

Academic Editors: Branislav Buľko, Dana Baricová, Peter Demeter and Róbert Dzurňák

Published: 21 February 2024

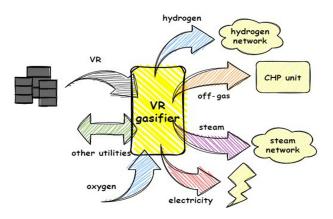


**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). series of crude conversion processes is a very viscous liquid, formed by hydrocarbon macromolecules resistant to further catalytic conversion [9]. Most refineries use it as a highly calorific fuel for their steam and power plants (CHP) or sell it as a fuel for large cargo ships. It still contains over 10% wt. hydrogen [9], which is much more than any kind of biomass possesses, even in a completely dry state [10]. As an alternative to using VR as fuel, it can be processed thermochemically via gasification into steam, electricity, hydrogen stream, and other products, meaning that such industrial VR gasifiers act as a polygeneration plant [11,12]. Due to the wide spectrum of its products and process synergies, placing the gasifier directly in a refinery is more advantageous than erecting it as a stand-alone plant. Its integration within a refinery has major impacts on its electricity, steam, and hydrogen balance, leading to a change in the refinery's NG purchase and greenhouse gas emissions [13].

Plans for an EU-wide energy transition include NG enrichment with hydrogen produced from renewables, as a means of industrial, residential, and public sector decarbonization [14]. Studies were conducted, identifying the optimal means of valorizing the hydrogen-enriched NG, using it either directly as a low-carbon fuel material in industry, or separating part of the hydrogen before [15,16]. In addition, the changed NG composition impacts the SMR process' efficiency and hydrogen yield [17]. Our previous study evaluated the VR gasifier integration in a refinery, in terms of carbon and energy balance. The present study focuses on several scenarios: combining the effect of VR gasifier integration and NG enrichment by hydrogen on the refinery's energy, NG, and CO<sub>2</sub> balance. A study encompassing all those aspects has, to our best knowledge, not been published yet.

## 2. Materials and Methods

A mid-size refinery is considered in this study, processing around 5 million tons of crude oil per year. The corresponding VR yield is 10%, representing 60 tons per hour. A combined steam–oxygen-blown VR gasifier is considered, with a capacity of up to 100% of VR production in the refinery, affecting the operation of other refinery's production plants and utilities networks, as schematically depicted in Figure 1.



**Figure 1.** Vacuum residue gasifier integration in a refinery. CHP unit = refinery's steam and power plant, VR = vacuum residue. Source: Adapted from [13].

Key refinery plants affected by VR gasifier integration include: 1. The CHP plant consuming part of the VR produced in the refinery, and producing steam and electricity; 2. SMR plants consuming NG, and producing hydrogen and steam. The interconnection of the gasifier with the plants, as well as a detailed scheme of the gasifier, are provided in [13]. Hydrogen produced in the VR gasifier replaces that produced in SMR, reducing both the corresponding NG consumption and steam production. Off-gas from the VR gasifier is a suitable fuel for the refinery's steam and power plant, replacing a portion of the VR consumed there. The steam network balance changes as well; this leads to a change in steam production in the CHP unit and, subsequently, to a change in both the fuel consumption and  $CO_2$  emissions. The electricity balance of the refinery includes the change

in electricity production in the CHP unit, net electricity produced in the VR gasifier, and the electricity consumed in the oxygen plant, supplying the gasifier with oxygen. Finally, changes in NG and electricity purchase, as well as in VR sales and  $CO_2$  emissions, are obtained. The calculation procedure is adapted from [13].

This study defines three operational states to be compared: A = the current refinery operation; B = The VR gasifier is integrated in the refinery, and the total amount of produced VR, hydrogen, and steam are the same as in A, VR is split between the gasifier, CHP unit and export, and the VR gasifier export steam, both in winter and in summer. Hydrogen production in SMR is minimized. VR sales are minimized; C = identical to B but the VR gasifier exports steam in winter only and produces extra electricity in summer instead. The real gasifier operation could vary between B and C, according to the refinery's energy management requirements.

Three options are evaluated: 0, 10, and 20% vol. content of hydrogen in NG. Accordingly, operational states A, B, and C are labeled as A0, B0, and C0, respectively, and six new operational states are created: A10 and A20, B10 and B20, and C10 and C20, reflecting the content of hydrogen in NG. The NG consumption in SMR changes because of hydrogen presence, and so does the steam export from SMR as well. This aspect was explored in [17], using the industrial SMR plant model published in [18]. Values presented in Table 1 were obtained, serving as an input for this study. The hydrogen present in NG is deemed to be produced from renewables, thus reducing the carbon footprint of NG.

**Table 1.** Key operation parameters of steam methane reformer (SMR) operation [17,18]. HHV = higher heating value, NG = natural gas.

Hydrogen Content in NG, % vol.	NG Consumption in SMR, kWh (HHV)/kg H <sub>2</sub>	Steam Export from SMR, kg/kg H <sub>2</sub>			
0	62.3	18.0			
10	61.5	17.2			
20	60.3	16.0			

Other calculation parameters and procedures, needed to set up the mass and energy balances and to calculate the electricity and CO<sub>2</sub> balances, were adopted from [13]. The method of total investment cost estimate for the VR gasifier and oxygen plant was taken from [19].

### 3. Results

Table 2 provides an insight into the key operation and balance parameters of the refinery without (A) and with an integrated VR gasifier (B, C), distinguished by hydrogen content in the purchased natural gas (0, 10, and 20% vol., respectively).

**Table 2.** Comparison of the key operation and balance parameters of the refinery in various operation modes depending on the VR gasifier operation and hydrogen content in natural gas. VR = vacuum residue.

Operational State	Utility/Medium	A0 <sup>1</sup>	B0 <sup>1</sup>	C0 <sup>1</sup>	A10	B10	C10	A20	B20	C20
Consumption (GWh/year)	NG	3043	1277	757	2998	1276	793	2933	1230	786
	VR	3402	5149	6259	3449	5153	6248	3476	5166	6206
Production (GWh/year)	Steam export total					1682				
	$H_2$ total					56				
	VR gasifier off-gas	0	2228	2820	0	2208	2799	0	2228	2820
	Electricity	363	277	335	365	279	337	369	272	321
Sale	VR (GWh/year)	2898	1151	41	2851	1147	52	2824	1134	94
	Refinery's CO <sub>2</sub> <sup>2</sup>	1633	1774	1975	1629	1772	1977	1613	1763	1963
Overall CO	$D_2$ balance <sup>2</sup>	2447	2098	1987	2429	2094	1992	2407	2082	1989

<sup>1</sup> Data from [13]; <sup>2</sup> ktons/year.

As the results from Table 2 demonstrate, the gasifier operation modes (B or C) have a much higher impact on the observed differences than the hydrogen content in NG does.  $CO_2$  emissions are calculated in two ways—as emissions of the refinery itself and as overall emissions—accounting for the external emissions from electricity and from sold VR.

The total investment costs (TIC) of the VR gasifier and oxygen plant commissioning reflected the complexity of the plant and were estimated at EUR 1.5 billion in 2023 equipment prices.

## 4. Discussion

The data shown in Table 2 indicate several noteworthy trends: 1. Gasifier implementation to the refinery leads to a significant NG purchase decrease and to a comparable increase in internal VR processing, thereby replacing a cleaner, but more expensive and valuable, energy and material source (NG) with refinery's own by-product; 2. The refinery's  $CO_2$  emissions increase as a result of a higher emission factor of VR compared to that of NG; 3. Vacuum residue sales fall near to zero in operational state C, regardless of the hydrogen content in NG; 4. The impact of hydrogen presence in NG on the calculation results is only minimal. It can be concluded that future hydrogen presence in the NG does not impact the refinery's utilities balance significantly, neither with nor without the VR gasifier being integrated in the refinery; 5. The overall  $CO_2$  balance shows a decrease with an increased VR utilization in the gasifier, on the contrary to the refinery's balance. This highlights the significance of the objective balance control volume setting; and 6. The electricity balance shifts only a little with the extra power production from the gasifier being consumed in the oxygen plant and by its decreased production in the CH unit.

The estimated TIC of EUR 1.5 billion represents a substantial hurdle to achieve feasible project economics. At present, while the VR is still saleable for a decent price and the prices of NG in Europe receded from the unprecedented 2022 values, such investment will unlikely be preferred. A rise in the carbon tax would further complicate the situation, as the refinery's emission increases due to the VR gasifier. On the contrary, the following scenarios would make the investment vital to further ensure the refinery's operation: 1. VR sales within the EU will be banned due to its high emission factor. As the VR is an inevitable refinery by-product, this would either convey massive costs associated with the disposing of it as waste, or the refinery's operation interruption; and 2. NG prices return to the 2022 level, while VR prices do not follow this increase (=2022 situation repeats).

#### 5. Conclusions

A study on the heavy vacuum residue gasifier from crude oil processing incorporation in a refinery was performed, and the refinery's key operation parameters without and with the gasifier were calculated and compared. In addition, the option of hydrogen content in NG was considered, and its impact on the refinery's energy and  $CO_2$  balance without and with VR gasifier was examined. As the most important finding, gasifier implementation increases the refinery's  $CO_2$  emissions. Second, there is only a limited influence of the refinery's energy and utilities balance by the presence of hydrogen in NG, even at the highest considered level of 20% vol. In addition to this, NG enrichment by hydrogen does not change the identified trends in the utilities and  $CO_2$  balance of the refinery, resulting from the VR gasifier implementation. The estimated total investment cost of the VR gasifier and oxygen plant commissioning is too high to be acceptable for the refinery at present. However, in future market scenarios when VR sales are banned due to environmental reasons, or NG price rises to the 2022 level, the associated investment might represent the only feasible and viable option for the refinery to continue its operation.

**Author Contributions:** Conceptualization, M.V. and S.P.; methodology, S.P.; software, T.K.; formal analysis, T.K.; investigation, S.P.; resources, M.V.; data curation, S.P.; writing—original draft preparation, M.V.; writing—review and editing, S.P. and T.K.; supervision, M.V.; funding acquisition, M.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was financially supported by the Slovak Research and Development Agency, Grant No. APVV-18-0134 and APVV-19-0170.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data obtained using calculations are presented in the contribution.

**Conflicts of Interest:** The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

#### References

- 1. Murugan, S.; Horák, B. Tri and polygeneration systems—A review. *Renew. Sustain. Energy Rev.* 2016, 60, 1032–1051. [CrossRef]
- Neves, A.; Godina, R.; Azevedo, S.G.; Matias, J.C.O. A Comprehensive Review of Industrial Symbiosis. J. Clean. Prod. 2020, 247, 119113. [CrossRef]
- 3. Stöcker, M. Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. *Angew. Chem. Int. Ed. Engl.* 2008, 47, 9200–9211. [CrossRef] [PubMed]
- 4. Rajabloo, T.; De Ceuninck, W.; Van Wortswinkel, L.; Rezakazemi, M.; Aminabhavi, T. Environmental management of industrial decarbonization with focus on chemical sectors: A review. *J. Environ. Manag.* **2022**, *302*, 114055. [CrossRef] [PubMed]
- 5. Abdin, Z.; Zafaranloo, A.; Rafiee, A.; Mérida, W.; Lipiński, W.; Khalilpour, K.R. Hydrogen as an energy vector. *Renew. Sustain. Energy Rev.* **2020**, *120*, *109620*. [CrossRef]
- 6. Wu, W.; Kuo, P.-C. Conceptual designs of hydrogen production, purification, compression and carbon dioxide capture. *Energy Convers. Manag.* **2015**, *103*, 73–81. [CrossRef]
- Navarro, R.M.; Peña, M.A.; Fierro, J.G.L. Hydrogen Production Reactions from Carbon Feedstocks: Fossil Fuels and Biomass. Chem. Rev. 2007, 107, 3952–3991. [CrossRef]
- 8. Sarabia, D.; de Prada, C.; Gómez, E.; Gutierrez, G.; Cristea, S.; Sola, J.M.; Gonzalez, R. Data reconciliation and optimal management of hydrogen networks in a petrol refinery. *Control Eng. Pract.* **2012**, *20*, 343–354. [CrossRef]
- 9. Choi, Y.C.; Lee, J.G.; Yoon, S.J.; Park, M.H. Experimental and Theoretical Study on the Characteristics of Vacuum Residue Gasification in an Entrained-flow Gasifier. *Korean J. Chem. Eng.* **2007**, *24*, 60–66. [CrossRef]
- Szwaja, S.; Poskart, A.; Zajemska, M.; Szwaja, M. Theoretical and Experimental Analysis on Co-Gasification of Sewage Sludge with Energetic Crops. *Energies* 2019, 12, 1750. [CrossRef]
- Reyhani, H.A.; Meratizaman, M.; Ebrahimi, A.; Pourali, O.; Amidpour, M. Thermodynamic and economic optimization of SOFC-GT and its cogeneration opportunities using generated syngas from heavy fuel oil gasification. *Energy* 2016, 107, 141–164. [CrossRef]
- Al-Rowaili, F.N.; Khalafalla, S.S.; Al-Yami, D.S.; Jamal, A.; Ahmed, U.; Zahid, U.; Al-Mutairi, E.M. Techno-economic Evaluation of Methanol Production via Gasification of Vacuum Residue and Conventional Reforming Routes. *Chem. Eng. Res. Des.* 2022, 177, 365–375. [CrossRef]
- Podolský, S.; Variny, M.; Kurák, T. Carbon-Energy Impact Analysis of Heavy Residues Gasification Plant Integration into Oil Refinery. *Resources* 2023, 12, 66. [CrossRef]
- 14. Cheli, L.; Guzzo, G.; Adolfo, D.; Carcasci, C. Steady-state analysis of a natural gas distribution network with hydrogen injection to absorb excess renewable electricity. *Int. J. Hydrogen Energy* **2021**, *46*, 25562–25577. [CrossRef]
- 15. Dehdari, L.; Burgers, I.; Xiao, P.; Li, K.G.; Singh, R.; Webley, P.A. Purification of hydrogen from natural gas/hydrogen pipeline mixtures. *Sep. Purif. Technol.* 2022, 282, 120094. [CrossRef]
- Nordio, M.; Wassie, S.A.; Van Sint Annaland, M.; Tanaka, D.A.P.; Sole, J.L.V.; Gallucci, F. Techno-economic evaluation on a hybrid technology for low hydrogen concentration separation and purification from natural gas grid. *Int. J. Hydrogen Energy* 2021, 46, 23417–23435. [CrossRef]
- 17. Hoppej, D. Lowering Carbon Footprint of Hydrogen Production. Diploma Thesis, Slovak University of Technology in Bratislava, Bratislava, Slovakia, 2022. Available online: https://opac.crzp.sk/?fn=detailBiblioFormChildG9THL&sid=4F55101800366CEF5 CF4C0DB109A&seo=CRZP-detail-kniha (accessed on 2 August 2023). (In Slovak)
- Hoppej, D.; Variny, M. Industrial-Scale Hydrogen Production Plant Modelling. *Adv. Therm. Process. Energy Transform.* 2021, 4, 9–15. [CrossRef]
- 19. Podolský, S. Conceptual Design of Heavy Oil Residues Gasifier. Bachelor Thesis, Slovak University of Technology in Bratislava, Bratislava, Slovakia, 2022. Available online: https://opac.crzp.sk/?fn=detailBiblioFormChildE9UEM&sid=A8C5898CD77493B3 E1FB3F491516&seo=CRZP-detail-kniha (accessed on 2 August 2023). (In Slovak)

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.