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Butane Dehydrogenation: Thermodynamic Modeling and Performance Analysis of Selected Process Simulators

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Abstract. The critical role of process simulation in modern chemical engineering cannot be overstated, with its capacity to facilitate process scale-up, assess alternative designs, and comprehend plant efficiency. This research delves into the performance of three software programs, Cape-Open to Cape-Open (CC), DWSim, and Aspen HYSYS (AH), in modeling butane dehydrogenation. The focus is on their ability to accurately model thermodynamic properties and chemical reaction dynamics. Butane dehydrogenation was evaluated with specific thermodynamic parameters using a Gibbs reactor model with Gibbs minimization. The Soave Redlich-Kwong thermodynamic model was employed to investigate the impact of temperature of 700 °C and pressures of 0.1 MPa and 1.0 MPa on the yield and selectivity of butadiene and butene. The CC and AH simulation results closely agreed with the available experimental data. The consistency of freeware simulators with a commercial simulator was also assessed, with AH serving as the reference standard. It was revealed that CC demonstrates higher consistency with it than DWSim under both low- and high-pressure conditions. This study confirms that CC is a reliable process simulator suitable for use in resource-constrained settings where expensive commercial licenses are prohibitive.

Keywords: process innovation, process simulation, thermodynamic modeling, Gibbs minimization.

1 Introduction

Dehydrogenation is a crucial process in the chemical and petrochemical industries, serving as a primary source of high-value, reactive feedstocks such as ethylene, propylene [1–5], butene and butadiene [6–11], and other valuable olefins [12]. In addition to producing highly reactive chemicals, it generates hydrogen, which can be used as an alternative energy source. This study focuses on butane dehydrogenation to investigate how well free chemical process simulators predict outcomes compared to trusted commercial ones.

When handling chemical engineering issues like research problems (presented in the later part of the earlier paragraph), chemical process design and optimization and computational approaches for process simulation are essential for our study. It is important to note that the different simulation packages can be classified as open-source or commercial software; the paid packages include ASPEN HYSYS, ASPEN Plus, PROSIM, UniSim, ChemCAD, and many others.

2 Literature Review

Numerous studies have explored the dehydrogenation of butane to produce olefins like butadiene and butene using catalysts such as platinum, nickel [11], chromium oxide [12, 13], and other metals and metal oxides [6, 7]. However, these studies often report undesired side reactions leading to cracked products such as methane, ethylene, propylene, and coke, including rapid deactivation of the catalyst surface. Wu et al. [11] noted that using a pure nickel catalyst tends to favor hydrogen production over olefin production due to its promotion of deep dehydrogenation, which further dehydrogenates the olefins instead of desorbing them from the catalyst surface.

To address these challenges, researchers have explored alloying strategies to redesign catalysts for current cracking processes [10, 14].

Zhu et al. [10] demonstrated that introducing phosphorus can retard cracking activity while promoting dehydrogenation activity. Most efforts to solve the side reaction problem have not isolated the thermodynamic effect as a measure to appreciate or screen the activity of some catalysts. It is believed that a system operating solely under thermodynamic isolation requires more energy (i.e., higher temperature) than one operating with both thermodynamics and a catalyst, which should require less energy (i.e., lower temperature). Such investigations can also determine if side reactions occur without a catalyst and if thermodynamic or catalytic effects promote the side reaction activities.

Therefore, a good catalytic system should operate at lower temperatures and promote more production of the desired dehydrogenation products compared to systems studied in isolation from the catalyst. This study uses the Gibbs reactor model in various process simulation packages to explore these insights.

Free access to software like DWSim, COCO (Cape-Open Cape-Open), Open-Modelica, HYDROFLO, and others is available [15–18]. Process simulation software develops and optimizes plants and processes, simulates operations, and estimates costs for various processes under desired conditions. It also provides a learning tool to help students better understand chemical engineering principles and research efforts [19].

Since they can produce accurate process predictions, commercial software has been increasingly popular and is used to mimic offshore petroleum production processes [15]. This, among many other factors, has given them a niche in the simulation software market.

There has not been much research on using free, open-source simulators and their potential to accurately anticipate chemical process behavior compared to commercial simulators [20].

Moreover, the oil and gas separation process was assessed by Andreasen [21] using the DWSim simulator, and the results compare very favorably with information obtained using Aspen HYSYS, with only a 1 % difference.

Similar to how Naren and Subramanian [22] explained the role of Raoult's law and Peng-Robinson thermodynamic packages in the separation of benzene and chloroform mixtures using DWSim and Aspen Plus, whose findings are in agreement with one another.

Hassan and Maji [23] compared DWSIM with Aspen HYSYS in the power plant simulation under steady-state conditions by re-modeling the existing Aspen HYSYS simulated process using design performance. The design performance agreed with the Aspen HYSYS report in the literature.

The authors [23] showed that it gave lower and acceptable results close to practical data. Oyegoke et al. [2] employed the Aspen HYSYS simulator to investigate the effect of pressure and temperature on the dynamics of propane dehydrogenation into propylene. The study reveals the implication of propane purity on product distribution.

Other later reports include Dauda et al. [4], who reported the deployment of a freeware simulator for the parametric study of the pentane aromatization process.

However, the consistency of the thermodynamic properties and predictions concerning experimental reports or Aspen HYSYS is yet to be reported, especially in butane dehydrogenation.

In this study, the capabilities of the following three software tools were investigated: Cape-Open to Cape-Open, COCO [24], DWSim [16], and the for-profit software Aspen HYSYS [25] in the survey. The study compares the two freeware process simulators' abilities to accurately model and forecast thermodynamic parameters in contrast to commercial ones and experimental values.

The impact of temperature and pressures on the kinetics of dehydrogenating butane into olefins are also further investigated in the study while taking the selected commercial process simulator as a standard reference simulator for benchmarking other freeware prediction efficiencies. Analyzing freeware consistencies with commercial ones would go a long way in proving their reliability for any industrial and dedicated research applications.

3 Research Methodology

This study deployed two process simulation software classes: freeware and commercial. The Aspen HYSYS (AH) [25] was selected as a commercial process simulator model. In contrast, DWSim (DW) and COCO (CC) were chosen as the freeware simulators [16]. The three process simulators (AH, COCO, and DWSim) reported earlier were used to model a process for butane dehydrogenation into different ranges of products (product distribution) in this study. These products include the unconverted n-Butane and a new set of products like Butene, 1, 3-Butandiene, 1, 2-Butadiene, Isobutene, Trans-2-butene, Cis-2-butene, Methane, Dimethyl acetylene, Ethylene, Ethyl acetylene, Propylene, and Hydrogen. The list comprised the thirteen components used in this study, including the feed, reaction intermediate products, and the desired product (butadiene).

Feed was modeled to be pure butane at a flow rate of 100 mol/s, pressure of 0.1 MPa, and temperature of 25 °C. The simulation modeled the process using a compressor and a heater to explore the different reactor pressures 0.1 MPa and 1.0 MPa at a fixed temperature of 700 °C.

A Soave Redlich Kwong (SRK) thermodynamic model was employed in our simulation in agreement with [26], and the reaction process was modeled using the Gibb minimization approach using a Gibbs reactor, which runs isothermally. These conditions were employed across all three selected process simulators in this study, whose capability and reliability were investigated in this report.

In the analysis, we model a feed containing pure butane at a standard pressure of 1 atm and reference temperature of 25 °C across the simulators. The resulting thermodynamic properties predicted for the models were

comparably evaluated with experimental data obtained from the literature and the molecular simulation predictions (using PM3 and B3LYP) to understand the prediction accuracy of both the freeware and commercial ones.

Other analyses include comparing the predicted product distributions obtained at different pressures of 1 and 1.0 MPa at a constant temperature of 700 °C. In this analysis, the commercial simulator output was taken as a standard reference in the absence of experimental literature since the commercial one already has a high public confidence and industrial acceptability compared to the rising freeware.

The butane structure was modeled using the Spartan v20 software, and then a geometrical optimization and frequency vibration calculation were carried out using two methods. The two methods include using B3LYP density functional theory (DFT) with a 6-31G basis set and a semi-empirical calculation using the PM3 method in our study. To validate the level of accuracy of the methods, infrared spectra were computed using B3LYP and PM3. Each overlapped with the experimental ones to ascertain their agreement with experimental values. The various contributions, such as vibration, translation, electronic, and rotation, were used to compute the butane's entropy, enthalpy, and specific heat capacity. The resulting values were compared with the experiment reported by NIST.

4 Results

4.1 Analysis of the process simulators' properties

Findings from the analysis of the process simulators' property predictions are presented below. The benchmarking of the product distributions obtained for the simulation of the butane dehydrogenation across different process simulators is presented in the later section of this report.

The predicted thermodynamic properties of n-butane dehydrogenation among the different simulators were compared with experimental data obtained from the NIST database [27], as shown in Table 1.

Table 1 – Comparative analysis of thermodynamic properties at 25 °C (298 K) and 0.1 MPa

Parameter		Software			Simulation prediction		Experiment / Source
		DW	CC	AH	PM3	B3LYP	
Specific heat capacity, J/(mol·K)	*Sp*	102.2	102.2	98.91	90.33	93.22	98.49 / [27]
Specific enthalpy, kJ/mol	*H*	–0.190	–0.180	–	–	–	–
	H_F*	–	–126.0	–126.4	237.7	–415682	–125.6 / [24]
Standard entropy, J/(mol·K)	*S*	–0.390	–0.400	–	–	–	–
	S_F**	–	309.5	127.5	294.8	302.7	310.0 / [28]
Density, kg/m^3	*Rho*	2.440	2.440	2.440	–	–	2.440 / [28]
Thermal conductivity, W/(m·K)	*k*	0.016	0.016	0.016	–	–	0.017 / [28]
Molar internal energy, J/mol	Δ*U*	–2596	–2598	–	–	–	34069 / [27]

* enthalpy of formation, kJ/mol; ** absolute entropy, J/(mol·K).

These thermodynamic properties include specific heat capacity *Cp*, specific enthalpy Δ*Ho*, standard entropy Δ*So*, Gibbs free energy Δ*Go*, density *Rho*, thermal conductivity *k*, and molar internal energy *U* at a reference temperature of 25 °C and pressure of 0.1 MPa.

The results of the comparative analysis for the n-butane predicted thermodynamic properties are presented in Table 1. Evaluation of the data collated for the use of Molecular Simulation (PM3 and B3LYP), DWSim, COCO, and Aspen HYSYS simulator, when compared to experimental data [27, 28], shows that all the simulators employed were able to predict the specific heat *Cp*, density *Rho*, and thermal conductivity *k* accurately in agreement with the results in the available experimental data.

However, better accuracy was obtained for using B3LYP than the PM3, which was in line with the IR spectra match level evaluated concerning the experiment (Figure 1).

This suggests that the simulators can effectively predict specific heat capacity, density, and thermal conductivity correctly – except for the enthalpy *H* and entropy *S* predictions.

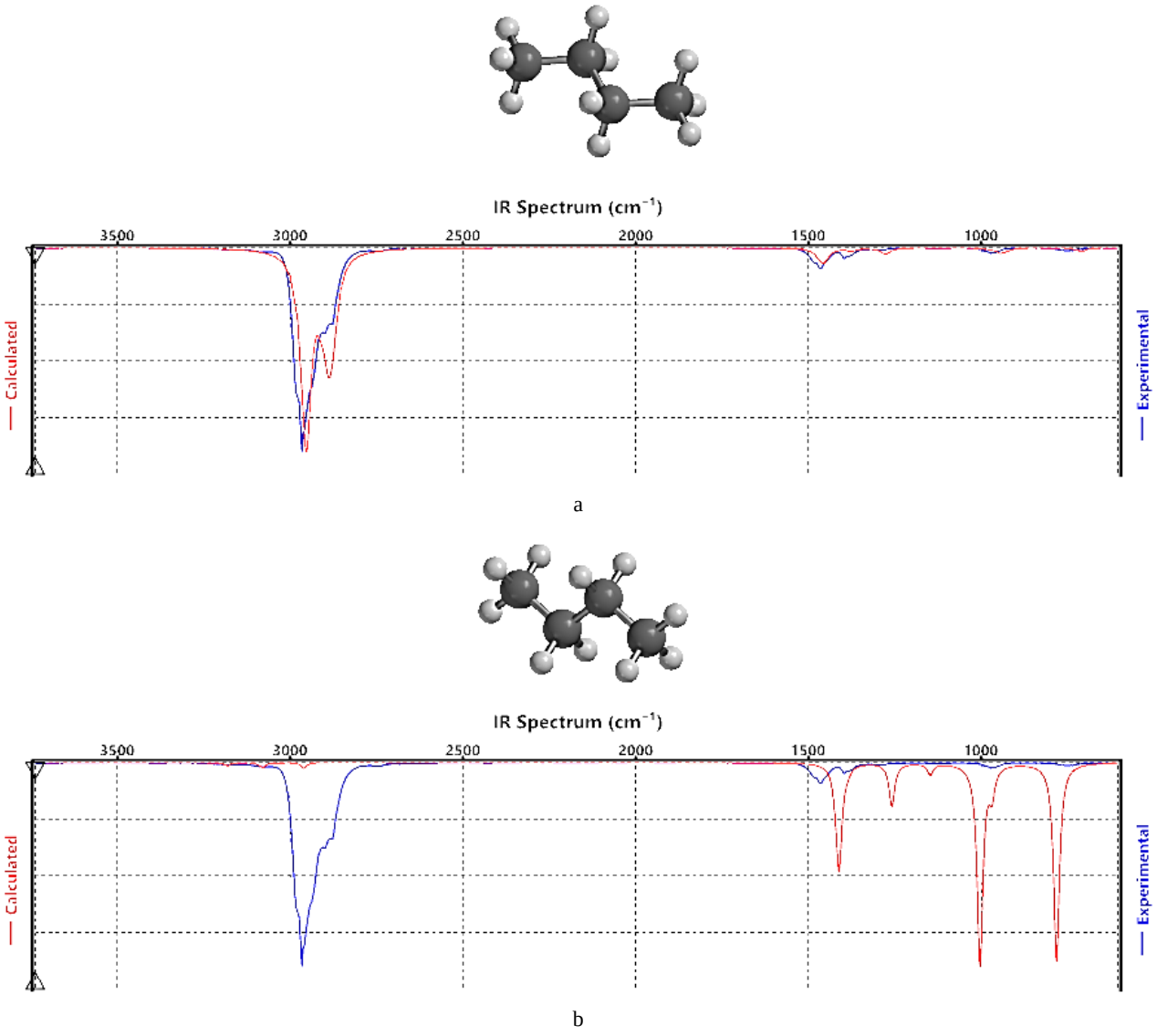

Figure 1 – Comparative analysis of the spectra agreement for the computed with the experimentally generated ones using B3LYP (a) and PM3 (b) methods

The analysis shows that COCO [24] has the capability of computing two types of entropy and enthalpy, which include the enthalpy with formation enthalpy H_F and ones without (H); similarly, the entropy with absolute entropy S_F and ones without (S).

The cases of the DWSim and Aspen HYSYS are different. The DWSim only predicted H and S, while Aspen HYSYS only predicted the H_F and S_F.

The cross-analysis of the enthalpy H or H_F shows that only the enthalpies computed with the inclusion of formation enthalpy H_F or absolute entropy S_F agree with the experimental data, while ones (H or S), PM3, and B3LYP computed values do not agree with the experiments [27, 28]. This disagreement obtained for using PM3 and B3LYP could be associated with the gas-phase approximation used by Spartan thermodynamic properties calculations, suggesting better approximation when computing the thermodynamics of liquids or solid phases in the code.

Regarding the calculated entropy S_F, the COCO open-source simulator and the molecular simulation (using PM3 and B3LYP) performed better compared to Aspen HYSYS concerning the reference experimental entropy with a discrepancy of –0.16 % and –58.87 % from the experimental value, respectively.

Compared to other simulators, a similar level of agreement with experimental results in the literature [27, 28] was also obtained for thermal conductivity k when COCO is used. This trend of results obtained using freeware simulators like COCO indicates that such a class can be trusted and reliable.

Due to a relatively high potential to predict thermodynamic properties effectively and reliably for different species of interest (practically agree with reality obtained in laboratory experiments or real-life situations), the same conditions and processes were subjected, similar to the capability demonstrated by some existing simulators [17, 25].

4.2 Benchmarking of the Butane dehydrogenation product distribution

In this analysis, we further explore the possible intermediates or side products that could compete with the formation of the desired product in the dehydrogenation of butane. The process is modeled to account for the thermodynamic effects of this process, which is investigated majorly. The study accounts for products obtainable via other possible reactions like cracking, alkylation, and other hydrogen production processes. The process flow diagram modeled from the process investigated is presented in Figure 2.

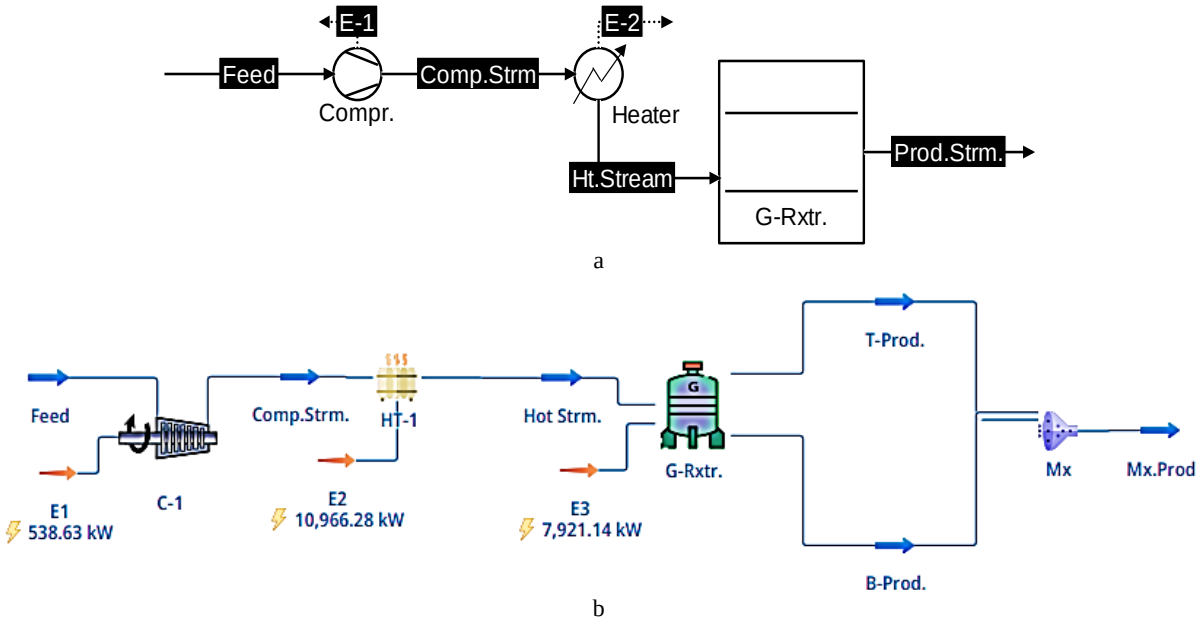

Figure 2 – The process flow diagram modeled for the simulation of n-butane dehydrogenation (a) into different ranges of product in COCO (upper PFD), DWSim (middle PFD), and AH (lower PFD) (b)

The corresponding product distribution obtained for dehydrogenating butane at 700 °C and 0.1 MPa across the three simulators is presented in Figure 3.

Findings made in Figure 3 and summarized in Table 2 have shown a high competition with the desired products (1, 3-Butadiene, and Butene) and a relatively low selectivity. Some of the identified competing products that do not form part of the desired product include molecules like methane, ethylene, and hydrogen.

The high percent of these light molecules from the simulation prediction results suggests that the thermodynamic condition of the process must have favored the cracking and some other hydrogen generation processes preferentially over the path for producing the desired products from the butane, in agreement with other sources [29, 30].

Moreover, the prediction outcomes across the simulator at 0.1 MPa show a percentage yield of Butene 0.05 %, 0.17 %, and 1.04 %, as well as 1,3-Butadiene 8.0 %, 17.3 %, and 16.5 % for DW, CC, and AH, respectively (Figure 3).

The analysis indicated that there was a significantly low yield of Butene relative to the production of Butadiene, which was found to have shown good agreement with the Tanimu et al. [9] report that reiterated that a low Butene and high Butadiene yield was obtained in the present of a Ni catalyst.

Despite the lower yield of the overall desired products, a higher yield of 17.3 % was obtained with the CC open-source simulator than the 16.5 % yield with Aspen HYSYS. The low yield of the desired products can be attributed to the fact that the reacting condition for the reaction favors some of the undesired products (Methane, Ethylene, and Hydrogen) more than the desired products (Butene and 1, 3-Butadiene).

A high yield of these light hydrocarbons was also reported by Kurokawa et al. [30], who further found that alloying with Pt with Ag aids in reducing the activities leading to the formation of undesired hydrocarbons, which would better favor the production of Butene and Butadiene.

Further evaluation of the consistency of the freeware with the commercial one, taking Aspen HYSYS [26] as the reference standard point, we found that across each of the products, prediction evaluated at 0.1 atm (Figure 4).

COCO [20, 24] consistently aligns better with the Aspen HYSYS than the DWSim [16], which essentially showed higher deviations. This suggests that COCO simulator prediction would better match the predictions obtainable from commercial simulators and improve for enhancing the agreement of DWSim prediction with Aspen HYSYS.

A high-pressure butane dehydrogenation product distribution at 1.0 MPa and 700 °C is shown in Figure 4.

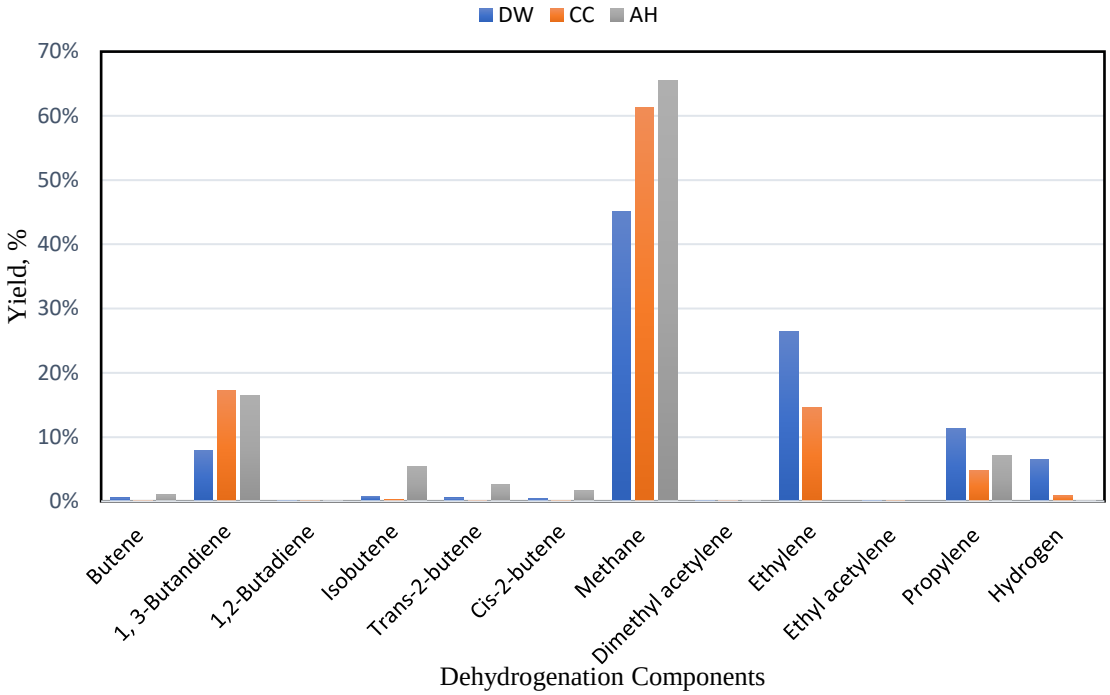

Figure 3 – A low-pressure butane dehydrogenation product distribution at 0.1 MPa and 700 °C

Table 2 – C_4 dehydrogenation product distribution was obtained at 700 °C and different pressure

Compounds	0.1 MPa			1.0 MPa		
	DW	CC	AH	DW	CC	AH
n-Butane	0.000215	0.00001	0.0010	0.00015	0.00015	0.0019
Butene	0.005552	0.00169	0.0104	0.006775	0.00671	0.0160
1, 3-Butandiene	0.079678	0.17254	0.1649	0.168727	0.16773	0.1438
1, 2-Butadiene	0.000467	0.00102	0.0001	0.000995	0.00099	0.0002
Isobutene	0.008232	0.00251	0.0545	0.010032	0.00996	0.0556
Trans-2-butene	0.005336	0.00165	0.0258	0.006494	0.00656	0.0298
Cis-2-Butene	0.004425	0.00135	0.0166	0.005407	0.00536	0.0202
Methane	0.451103	0.61286	0.6552	0.62849	0.62765	0.6399
Dimethyl Acetylene	0.000898	0.00199	0.0004	0.001936	0.00194	0.0008
Ethylene	0.264604	0.14621	–	0.092182	0.09205	–
Ethyl Acetylene	0.000258	0.00056	0.0000	0.000554	0.00054	0.0001
Propylene	0.113750	0.04843	0.0711	0.074485	0.07661	0.0913
Hydrogen	0.065481	0.00919	0.0001	0.003773	0.00375	0.0002

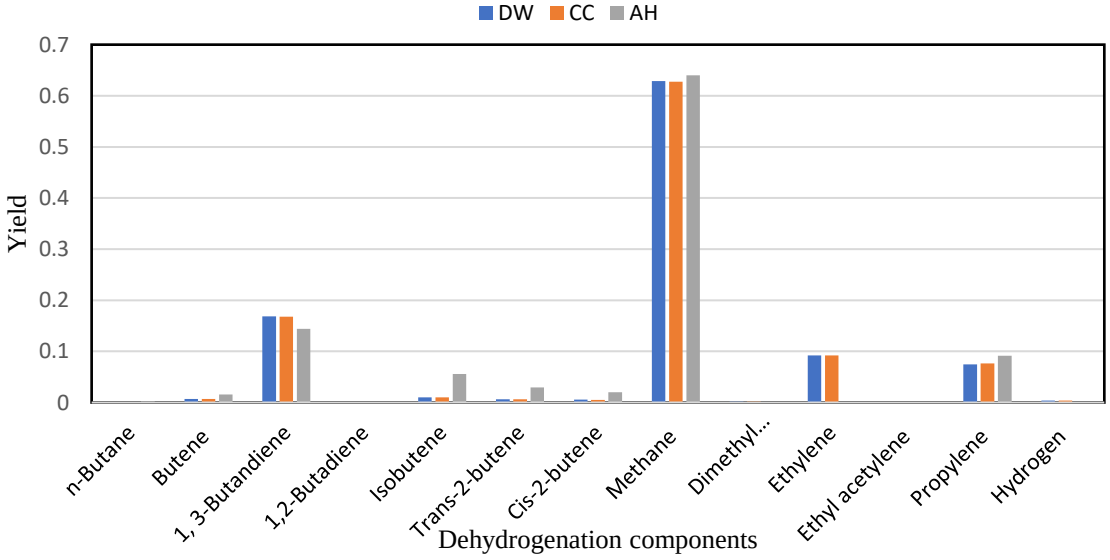

Figure 4 – A high-pressure butane dehydrogenation product distribution at 1.0 MPa and 700 °C

Further analysis of the dehydrogenation processes was evaluated at 1.0 MPa, where the butene yield was obtained as 0.68 %, 0.67 %, and 1.6 %, as well as 1, 3-Butadiene yield as 16.9 %, 16.8 %, and 14.4 % for DWSim [16], COCO [24], and Aspen HYSYS [25] simulators, respectively (Figure 4).

Similar to those obtained for operating at a low pressure of 0.1 MPa, a high yield of competing cracking and hydrogen generation process-based products (methane) was primarily obtained. However, a relatively lower ethylene yield was obtained at higher pressure while recording a less significant difference in the yield of the Butene and 1, 3-Butadiene.

5 Discussion

The analysis of the result presented in Figure 4 shows a high yield of methane as a cracked product compared to other cracked products, such as ethylene and hydrogen, at a lower temperature range of 525 to 575 °C.

Ajayi et al. [13] produced more dehydrogenation products in the present CrO_xVO_x/MCM-41 catalyst than cracking products in our study.

This suggests that introducing the catalyst reduces the reaction temperature and favors producing desired dehydrogenation products (with an activation energy of 96 kJ/mol) over the production of cracking products (with an activation energy of 130 kJ/mol).

However, this study did not employ a catalyst, giving a methane yield of 63 % for CC, DW, and 64 % for AH software at 700 °C and 1.0 MPa.

In contrast, in the experiment [13] conducted in the presence of CrO_xVO_x/MCM-41 catalyst, the yield was reported to be 1.72 at 525 °C at a contact time of 24 g of cat. min per 1 g of butane, which was higher when compared to other cracked products of ethane and propane, which is comparable.

Zhu et al. [7] similarly agreed with our findings despite using a 4 Ni-Sn/SiO_2 catalyst in their study. A higher yield of cracked products like methane and propylene was reported in the n-butane dehydrogenation study. This would be because the Ni-based catalysts often favor deeper dehydrogenation, which could eventually lead to the cracking of butane into propylene and other smaller molecules, which was in agreement with reports [24, 25] that confirm the catalyst is better for hydrogen production than olefins production.

However, the report of Zhu et al. [10] later suggests the introduction of phosphorus to the Ni to improve its selectivity for olefin production.

Using Aspen HYSYS as a reference standard (with high public and industrial acceptance), we deduced that COCO shows a higher consistency with the Aspen HYSYS better than the DWSim both at low- and higher-pressure conditions, unlike the DWSim, shows poorer consistency at low pressure (Figure 3), but a higher consistency at higher pressure (Figure 4) with the Aspen HYSYS.

Further revalidating the superiority of the COCO to DWSim (in terms of effectively predicting the product distribution in a given reaction using a Gibb minimization approach with the aid of a Gibbs reactor) agrees with the methane oxidation report [24] that also proves the reliability of COCO simulator.

Findings made from our studies have shown that the open-source simulator employed in this study displayed a potential comparable to the software in the dehydrogenation process of n-butane (C_4) in terms of product distribution and thermodynamic properties of concerned species.

Additionally, although commercial simulators are often unaffordable and expensive for people in low-income countries, they are more friendly and easier to use. Also, they do not allow for permanent access to a source code,

Moreover, a user of the freeware chemical process simulators, in most cases, has access to their source code, and the developers can be open to your contribution to growing the performance of the software.

Our studies suggest that free chemical process simulators such as COCO can be trusted and reliably deployed for teaching, learning, and research activities at training schools for chemical science and engineering, especially in communities where research and education are poorly funded. Freeware can further be said to be a more suitable alternative to the use of commercial process simulators, and in case of bug identification during their usage, it can always be communicated to the developer, and the user can contribute possibly correct the design, leading to a newer version to enable a community of the freeware users record better efficiency in their different project deployment of the software.

Otherwise, such bugs identified in the usage of the simulator can be taken up as a research project by an individual or a group to help address any potential future challenge encountered during their usage, rather than going back to the old practice of utilizing commercial simulators for different applications.

6 Conclusions

This study was able to explore the deployment of freeware process simulators like DWSim and COCO in comparison with using a process simulator (Aspen HYSYS) to evaluate the prediction accuracies of the simulators for a set of thermodynamic properties in contrast with the existing experimental reports. The properties include heat capacity, specific enthalpy, standard entropy, density, thermal conductivity, and molar internal energy. Properties predicted by most of the simulators do show a good level of agreement with the experimental data, especially for ones indicated by the COCO process simulator, which has proven its potential to model process systems and predict systems' behavior accurately, following its high level of agreement with experimental data compared within the study. They suggest that COCO as freeware is reliable and trustworthy for any dedicated research.

In some cases, like the specific heat capacity, entropy, and enthalpy prediction, the COCO simulator (with discrepancy of –1.58, –0.06, and +0.16 % for Cp, SF, and HF from the experiment) showed better performance

compared to other simulators evaluated, including the commercial simulator (with a discrepancy of +1.70, –0.40, and +58.87 % for Cp, SF, and HF from the experiment), concerning the reference experimental results.

In addition, the consistency of the predictions from the freeware simulators with commercial simulator predictions for the product distribution of butane dehydrogenation was evaluated. The study of the dehydrogenation process at 700 °C shows that a low pressure of 0.1 MPa favors a 1, 3-butadiene yield of 8.00, 17.30, and 16.50 %.

In contrast, the change in the pressure to 1.0 MPa raises the 1, 3-butadiene yield to 16.9, 16.8, and 14.4 % for the simulation in DWSim, COCO, and AH simulators, respectively. Among the freeware evaluated, the study confirms that the COCO simulator shows better reliability due to its better agreement with the Aspen HYSYS simulator across the product distribution at low and higher pressure.

Therefore, this study confirms that COCO can be chosen as a reliable tool or process simulator for thermodynamic modeling of Butane dehydrogenation.

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