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Beyond Yield: Assessing Reaction System Performance using Economics

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ABSTRACT

Early stage exploration of reaction systems, including catalyst selection, operating conditions' specifications, reactor design, and optimization, is critical in the engineering field. It is general practice in the reaction engineering field to explore systems against certain performance metrics, of which yield is one of the most commonly utilized objectives. While the yield provides a quantitative measure of how efficiently reactants are converted into target product(s), its definition is ambiguous, particularly in the presence of side/ incomplete reactions, and multiple products. Most of the yield definitions focus on a specific target product; however, conditions within the reactor search space that provide a maximum yield for one product may not be the same as those for another. Moreover, the presence of other undesired products that are not considered may reduce the overall efficiency of the system. This necessitates the utilization of a more holistic metric that encompasses the value of all the generated products. Attempts to address this consider lumping components into a total yield metric. However, this assumes equal weights on all components without adequately capturing their individual significance on the actual performance. This study proposes the utilization of an "economic-value yield" objective that captures all the products' value by using the market price as a weight factor. The traditional yield metric for the various products is contrasted against the economic one to highlight its ability of providing insight into regions within the reactor search space that are associated with high-value products that are otherwise not observed in the conventional definition. This is illustrated with a case study utilizing propane as a feedstock in the novel piston reactor technology.

Keywords: Reaction, Technoeconomic Analysis, Reaction Engineering, Propane

INTRODUCTION

The development of optimized and novel reactors is key for sustainable technology design and development [1] . Early-stage exploration and design of reaction systems is of paramount importance in reaction and chemical engineering for a plethora of reasons including the identification and screening of promising reactions, selection of raw materials and catalysts, understanding reaction mechanisms, optimization of reaction conditions, and assessing the overall feasibility of a reaction system. It is general practice in the catalysis and reaction engineering field to study reaction systems against certain performance metrics that assist in evaluating the efficiency of reactors and chemical reactions. Various objectives are utilized to evaluate reactors, depending on the characteristics of the reaction and nature of the process. Some of the most commonly used metrics include conversion, selectivity, and yield.

While the yield is a fundamental and widely used metric in chemical engineering and reaction optimization, there is no universally agreed upon definition for such a term. it remains associated with limitations including the ambiguity of its definition, as it can refer to conversion yield, selectivity yield, total yield, or other variations that may result in misinterpretations. Moreover, most of the yield definitions focus primarily on the desired product without accounting for the formation of by-products or undesired side reactions that can be crucial for assessing the system's overall performance. For instance, a reaction with high yield may be deemed undesirable if it results in the production of substantial amounts of

unwanted by-products. Maximizing the yield for one product may not result in the conditions that reflect optimum performance. A more holistic approach is required to account for the contribution of multiple products in a reaction system. Attempts to address this issue consider lumping the components into a total yield term [2]. However, this assumes equal weights on all the generated products. A proper weighted yield term is required to account for the contribution of multiple products in a reaction system based on their significance.

The concept of economics can serve as a powerful tool to practically evaluate chemical reactions. This study proposes the utilization of an "economic-value yield" (EVY) metric, by assigning weights to the various components based on their market price, and contrasts it against traditional yield metric definitions to highlight its ability of providing insight into regions within the reactor search space that are associated with high-value products. To the authors' knowledge, there are no peer-reviewed publications utilizing metrics that capture the economics of the reaction products when assessing reaction chemistries. Such a metric is particularly helpful in the assessment of novel reactor technologies.

One of the emerging novel reactor concepts is the piston reactor technology, which is essentially a repurposed internal combustion engine that focuses primarily on the production of chemicals, in addition to the power and heat associated with the conventional combustion engine. Its advantages include high temperature and pressure conditions at short residence times, thereby enhancing the performance of numerous chemical reactions. The cyclic nature of the reaction system offers a novel mode of carrying out chemical reactions, where the fast temperature quench enables a target non-equilibrium state where the desired product could be generated at optimal yield and efficiency [3].

In this study, the EVY objective is utilized to assess the performance of the piston reactor technology to screen chemistries using propane as a feedstock to determine economically attractive regions within the reactor search space. Results are contrasted against the traditional yield metric, highlighting the importance of utilizing economics when assessing the performance of reactor systems.

CONVENTIONAL YIELD METRICS

There is no universally agreed upon definition for the "yield" concept [4] as it is applied in numerous contexts, and its definition varies depending on the application, or process. Table 1 depicts a summary of the most common definitions of yield used in the literature. The presence of multiple descriptions for the yield metric introduces uncertainty, particularly when studies fail to explicitly define the parameter utilized in their evaluations. This lack of terminology hinders the comparability of research results and findings within the reaction and engineering fields. Most of the published studies use the "overall reactor yield" term, on a molar basis, to define the reactor's yield [5]. In this case, the yield is defined as the ratio of the target product formed to the reactant fed. This is observed in numerous studies including methanol formation from syngas [6], naphthalene oxidation to phthalic anhydride [7], and hydrogen production from methane reforming [8], to name a few.

The issue with such a definition, and its variations in Table 1, is highlighted when there are multiple products formed, as these common definitions neglect the impact of formation of by-products and undesired products. Conditions representing a high yield of one product are not the same as those for another product, leading to a misrepresentation of the actual conditions that pertain to the reactor's optimal performance. Moreover, a high yield of a certain component does not necessarily guarantee a high overall performance efficiency particularly if substantial amounts of undesired components are formed.

To alleviate this issue, some studies lump certain components together to formulate a total yield term, as in the case of oxidative coupling of methane (OCM). In OCM, methane, co-fed with oxygen, react to produce primarily ethane and ethylene [2]. Since both ethane and ethylene are the main products, a "C_2 Yield" term is utilized to account for the formation of the two products by summing up the yield of each component. In other studies, a C_{2+} yield term is utilized, corresponding to the total yield of ethane and ethylene, in addition to propane and propylene [9]. While this takes into consideration the formulation of other products, it automatically assigns equal weights to them, potentially overlooking the variations in their significance, thereby also leading to a misrepresentation of the overall results.

Moreover, such definitions cannot be applied in situations where the target product is not known from the offset. This is particularly highlighted in the technology assessment and chemistry screening cases phases of early-stage reaction exploration, such as the case of the piston reactor.

ILLUSTRATION: PISTON REACTOR

As an illustration, the concept of yield is applied on screening chemistries within the piston reactor. The piston reactor is essentially a repurposed internal combustion engine (ICE) that is utilized primarily as a reactor to produce chemicals, in addition to the electricity and heat associated with the conventional ICE [10]. The piston reactor operates in a cyclical manner by

Table 1: Common Definitions for the Yield Metric

	Definition	Formula	Ref.
Overall reactor yield	Overall reactor efficiency in converting the reactants to target products	$Y = \frac{Target\ product\ formed\ (mol)}{Reactant\ fed\ (mol)}$	[17]
Reaction Yield	Ratio of actual amount of product formed to the maximum amount that could be generated (theoretical yield)	$Y_{th} = \frac{Actual\ amount\ of\ product\ made\ (mol)}{Theoeretical\ yield\ (mol)}$	[18]
Yield	Amount of desired product generated to the amount formed if there were no by-products and main reaction reached completion	$Y = \frac{Desired\ product\ generated\ (mol)}{Products\ generated\ (no\ byproducts)\ (mol)}$	[19]
Overall fractional Yield	Ratio of all the products formed to the reactants that have reacted	$\Phi = \frac{All\ product\ formed\ (mol)}{All\ reacted\ reactant\ \ (mol)}$	[20]
Instantaneous Fractional Yield	Rate of generation of a desired product relative to rate of consumption of a key reactant	$\varphi = \frac{Rate\ of\ product\ generation}{Rate\ of\ reactant\ consumption}$	[7]
Weight Yield	Mass of target product as percentage of total reactant mass	$Weight\ Yield = \frac{Target\ product\ (mass)}{Total\ reactant\ (mass)}$	[21]
Total Yield	Ratio of total products formed to the reactor fed	$Total\ Yield = \frac{Total\ products\ formed}{Reactant\ \ fed}$	[9]

compressing the feed gas and expanding within short time-frames in the order of milli-seconds [11]. The compression phase results in elevated temperatures and pressures that enhance the efficiency of certain reactions, whereas the expansion results in a rapid quenching of the mixtures enabling the formation of products at optimal conditions [12].

We illustrate the metrics for the case of exploring propane conversion in the piston reactor, based on the piston reactor results of Abousrafa et al. [13]. There are multiple variables that can be explored for a piston reactor applied to propane conversion such as the impact of co-feeding the propane with both O_2 and CO_2 as performed by Abousrafa et al. [13]. Adding O_2 to the reaction promotes the autoignition of propane, resulting in heat generation that can be utilized to co-generate power from the piston reactor. As for CO_2, in addition to the environmental benefit of utilizing it as a feedstock, CO_2 addition facilitates the occurrence of several reactions such as dry reforming and oxidative dehydrogenation. This analyzes data for an intake temperature and pressure of 773K, 1 bar, and an RPM of 3000 [13]. Products from the reaction include H_2, CO, C_2H_4, CH_4, C_3H_6, C_2H_2, C_6H_6, and C_4H_6. At complete propane conversion, the impact of co-feeding O_2 and CO_2 on the overall reactor yield of the major generated species is shown in Figure 1 (a-d). For the four main components formed in the piston reactor, H_2, CO, C_2H_4, and CH_4, maximum yields are obtained at CO_2/C_3H_8 and O_2/C_3H_8 ratios of 0 and 1.5, 2 and 1.5, 2 and 0.5, 0 and 0.5, respectively. To account for all the components, a total yield metric, similar to the one utilized in the OCM studies [9], is calculated, and the results are illustrated in Figure 1e. The figures show that the yield maxima for all four species and also the total yield are different, highlighting the difficulty in using yield as a performance metric for the optimal search of reactions systems with multiple potentially desired species formed as products. The total yield metric considers all formed species; however, the metric assumes each product with equal weight.

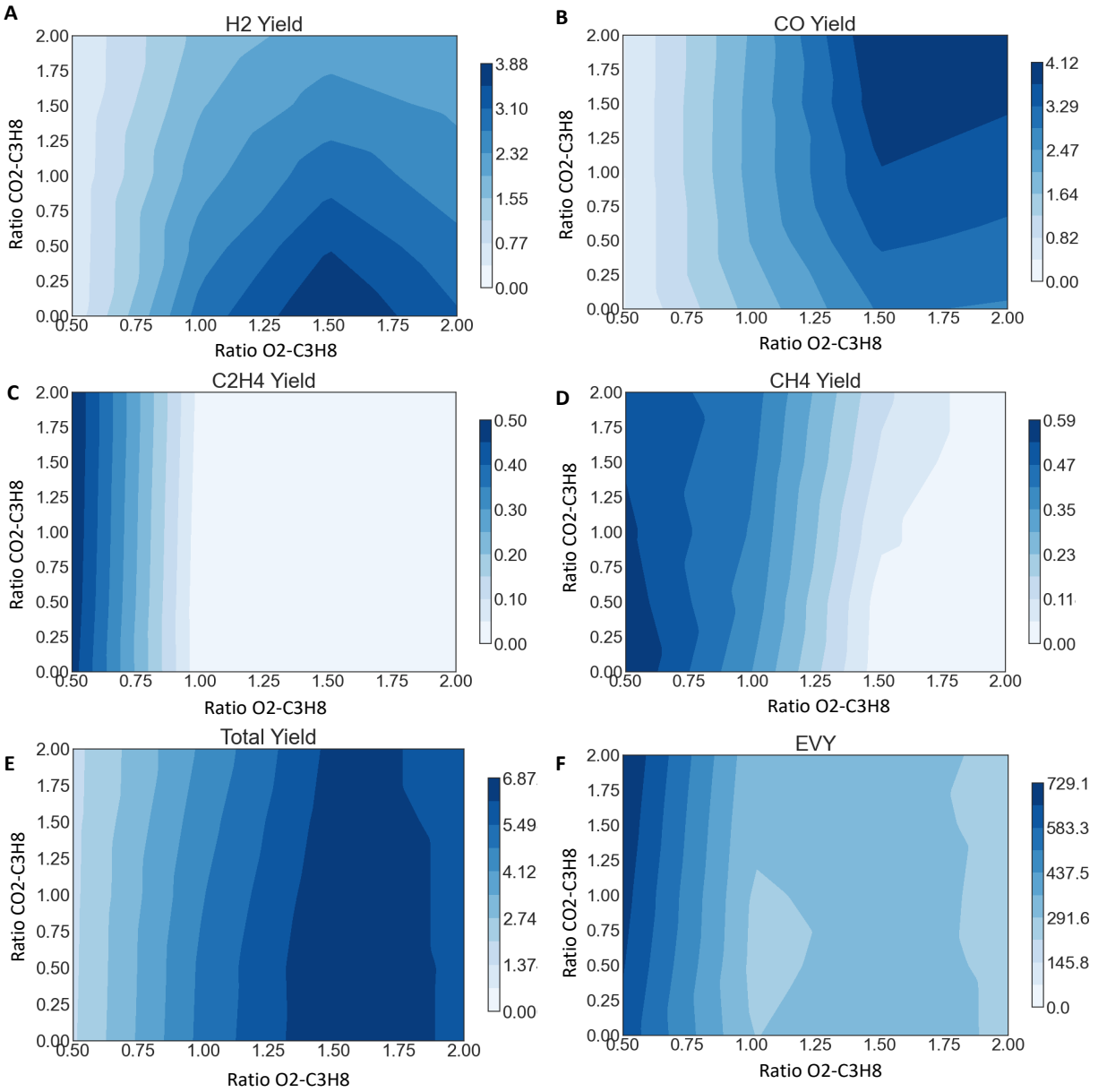

Figure 1: Effect of Co-feeding O_2 and CO_2 on H_2, CO, C_2H_4, and CH_4 yields

Table 2: Price assumptions for the EVY calculation

Component	Formula	Price($/t)	Ref.
Hydrogen	H_2	1,200	[14]
Carbon Monoxide	CO	55	[15]
Methane	CH_4	278	[16]
Ethylene	C_2H_4	882	[16]
Acetylene	C_2H_2	1313	[16]
Benzene	C_6H_6	865	[16]
Propene	C_3H_6	1488	[16]
Butadiene	C_4H_6	1357	[16]

Economic-Value Yield

Rather than assuming equal weighted total yield or individual component yields as objectives, a differently weighted yield metric that considers the formation of multiple valuable reaction products would be preferred. Considering that the implementation of most production systems is to a large extent based on the value of products formed from raw materials, this work proposes the utilization of an economic-value yield metric for the reactor performance that uses the product prices as a weight

factor to obtain an overall reactor-yield metric:

$$EVY = \sum_j P_j \times WY_j \quad (1)$$

Where:

- EVY is the economic-value yield ($/t feed)
- P_j is the market value, or price, for product j ($/t product)
- WY_j is the weight yield of the product j as percentage of the total reactant weight (t product/ t reactant)

Table 2 contains the prices of the chemicals produced in the piston reactor. Figure 1f shows the results for EVY at various O_2/C_3H_8 and CO_2/C_3H_8 ratios. Results show that the EVY profile does not match any of the individual yield components. It also shows opposite trends to those observed in the total yield metric (Figure 1e). The maximum total yield is observed at CO_2/C_3H_8 and O_2/C_3H_8 ratios of 0.5 and 1.5, whereas maximum EVY is at CO_2/C_3H_8 and O_2/C_3H_8 ratios of 2 and 0.5. However, these results assume equal weights for all those four main components. Although the maximum EVY is in line with maximum C_2H_4 yield, there are regions within the C_2H_4 figure that show zero yield, yet are associated with substantial value, highlighting the importance of utilizing a properly weighted total yield metric to obtain more representative conclusions. Another important observation is the presence of trace components including C_3H_6, C_2H_2, C_6H_6, and C_4H_6 that have a substantial contribution to the EVY. Although they are present in concentrations <2 mol%, and are associated with overall reaction yields <0.1, there are cases where they result in double the EVY. These results further emphasize the importance of adding appropriate weight, in terms of product value, to the conventionally utilized yield terms.

CONCLUSIONS

It is general practice in the reaction engineering field to evaluate reactions based on certain performance metrics, of which reaction yield is one of the most utilized objectives. There is no universal definition for the yield metric, resulting in challenges including lack of consistency, and results comparability. Moreover, most of the definitions focus on a single desired product without taking into consideration the formation of other undesired or by-products. This leads to difficulty in pinpointing regions of optimal reactor performance, as the yields of one component are associated with different conditions than another. Moreover, the presence of undesired products that are not considered could lead to an inefficient overall performance. A more comprehensive metric is required to account for the contribution of all the generated products in a reaction system. Some studies attempt to alleviate these issues by lumping the components into a total yield term. However, the assumption of equal weights of components may not be representative of actual performance. This necessitates the utilization of a proper weighted yield term to account for the contribution of all the generated products in a reaction system. This study proposes an "economic-value yield, EVY" metric, where the prices are utilized as weight factors. In addition to its simplicity, using chemical prices reflects actual market value, thereby indicating the relative contribution, or importance, of each generated component. The piston reactor technology is used as an illustration to contrast the EVY results against the traditional yield metric. Results showed that regions within the reactor search space that are associated with high-values do not match the individual yield results, nor the conventional total yield metric. Moreover, the contribution of elements that are associated with low-yield, yet high value, are not shown in the traditional calculations. This highlights the importance of utilizing economics when assessing the performance of reactor systems.

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