Atom Economy, Expanding Boundaries to Incorporate Upstream Reactions

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Abstract

In this work, we address one of the overall shortcomings of atom economy and the limited scope of the boundaries chosen. While atom economy is not the only measure of a process' sustainability, it is a valid comparison from a materials usage view. With this in mind, many publications in green chemistry focus on atom economy as a method for estimating the environmental impacts of a reaction scheme to reach a desired product.

The choice of which reactions are considered in the atom economy analysis, or the system boundaries, plays as great of an importance as it does in performing life cycle assessments. Most applications of atom economy begin their analysis with manufactured intermediates and follow a short chain of reactions to the final products. This ignores any upstream processing that was done to create the intermediates and may skew results to incorrectly favor one of the proposed reaction schemes. Here, we develop a simple expression for atom economy that aggregates overall reaction stoichiometries for a chain of reactions leading from raw materials to the final products. We find that by expanding the boundaries to incorporate upstream manufacturing of raw materials, the overall atom economy changes substantially. In order to fully utilize atom economy, system boundaries must encompass upstream reactions in order to prevent sub-optimal materials usage.

In this paper, we calculate the overall atom economy of two reaction schemes for synthesizing 1,3-propanediol. This system was chosen as a case study to highlight the choice of system boundaries. By implementing the aforementioned equation to include the upstream processing reactions it is found that the atom economy of each process is no longer 100% as had been reported previously.

Introduction

Most chemists have traditionally measured the efficiency of a reaction by the percentage yield [1]. In an effort to foster awareness of the atoms of reactants that are incorporated into the desired product and those that are wasted (incorporated into undesired products), the concept of atom economy (AE) was first developed by Barry Trost in 1991[2]. There are many papers on atom economy [3-6] that only address the atom economy of reactions within a limited system boundary. By limiting the scope of the calculation, atom economy can falsely identify favorable reaction synthesis routes. Due to the numerous different routes that can be utilized to produce a single product, a more thorough atom economy calculation should be used. Fig.1 depicts an expanded version of typical atom economy calculations. Many atom economy calculations calculate only either the final or last two steps of a synthesis in order to prove that one route is more favorable than another. However, using a boundary that encompasses all of the reactions, it can be seen that exanding the boundaries could lead to different results. In the case where only the last two steps for each synthesis are considered, the bottom route in Fig. 1 appears more favorable,

but the answer could change by moving to expanded boundaries as shown. Although this is a simplified example, it highlights the problem of non-optimal choices that can be made by limiting system boundaries.

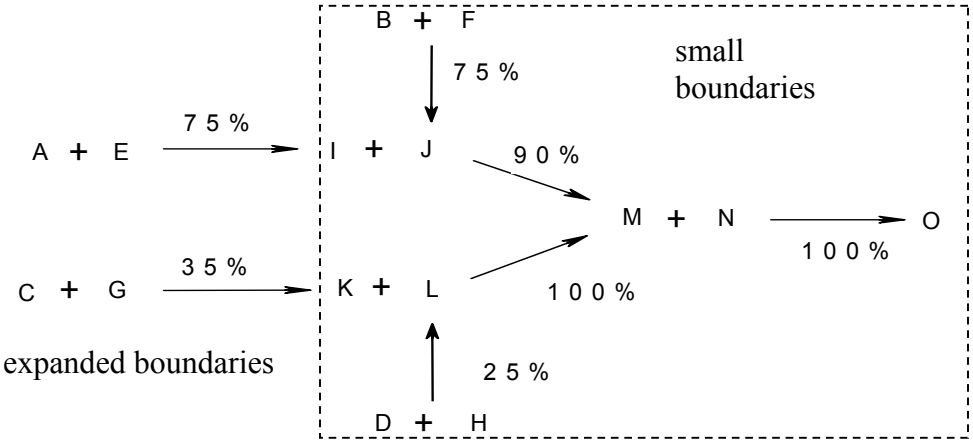

Fig.1 expanded version of typical atom economy calculations

Case Study

The product synthesized in each reaction scheme examined in this paper is 1,3-propanediol. This chemical is a key component in the production of many polymers used to produce polyesters[7]. It is also used to make diamino propane and malonic acid, which can be used in a variety of applications.

Two reaction schemes that lead to the same product have been chosen in order to:
a) show the difficulty of using only a small reaction scheme boundary in an analysis,
b) expand atom economy in order to account for all reactants, and
c) formulate an equation that will incorporate all upstream reactants without the need of calculating a total atom economy.

The two parallel reactions chosen to synthesize 1,3-propanediol were the Shell process[8] and the Degussa process[9]. The Shell Process begins with a mixture of ethylene oxide, carbon monoxide, hydrogen, non-phosphine-ligated cobalt (as a catalyst), and lipophilic tertiary amine promoter (as a catalyst) in methyl-t-butyl ether to form 3-hydroxypropanal. Next, an aqueous solution is added to the mixture and the 3-hydroxypropanal is allowed to separate into the aqueous solution, leaving most of the catalyst in the organic phase. The aqueous phase is removed and mixed with hydrogen and a hydrogenation catalyst to make 1,3-propenediol. Lastly, the 1,3-propenediol is separated and some of the catalysts are recycled [8].

The Degussa method of 1,3-propanediol synthesis begins with a mixture of acrolein and water that undergoes a hydration reaction creating 3-hydroxypropionadehyde. Any unreacted acrolein is removed and the remaining mixture is catalytically hydrogenated to create 1,3-propenediol. The 1,3-propenediol has a lower boiling point than the rest of the byproducts in the solution so it can be easily distilled from the mixture. Then, 3-3'-oxybis-1-propanal is separated from the byproducts. The 3-3'-oxybis-1-propanal is then mixed with an acid solid catalyst in an aqueous solution to cleave the 3-3'-oxybis-1-propanal and form 1, 3 propanediol. The additional 1,3-propanediol from the resulting mixture can be separated by distillation[9].

From a traditional point of view, each process has an atom economy of 100% since all steps of the two reactions are addition reactions. However, since both reactions have different starting materials, it cannot be assumed that the entire reaction schemes for both methods have the same atom economies. In order to determine which method is truly superior by atom economy standards, each process must be taken to their elementary starting materials. In both cases, this turns out to be water, methane, and propane.

The expanded set of elementary reactions for the Shell process are shown in Fig. 2.

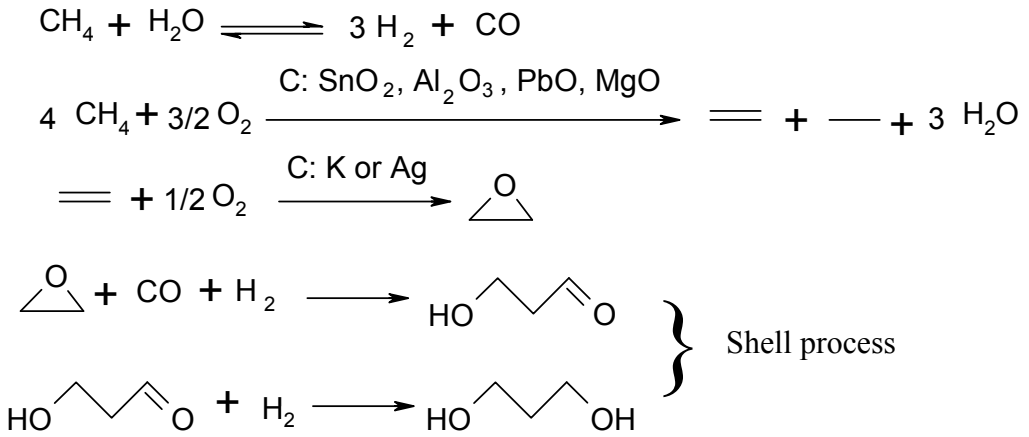

Fig. 2 Shell Process

As shown in Fig.2, the last two reactions are the Shell process. More upstream reactions have been included for the reactants and the intermediates. The Shell reaction is shown again in Fig. 3 with the overall reaction flow and stoichiometries. Altogether, five molecules of methane, one molecule of water, and four oxygen molecules are needed to produce one molecule of the final product. The raw materials extracted from the environment, such as methane, water and oxygen, are used to produce the intermediates, reactants, and in turn, the final product. This flow sheet is the basis for calculating the individual or overall atom economy of the cradle-to-gate process.

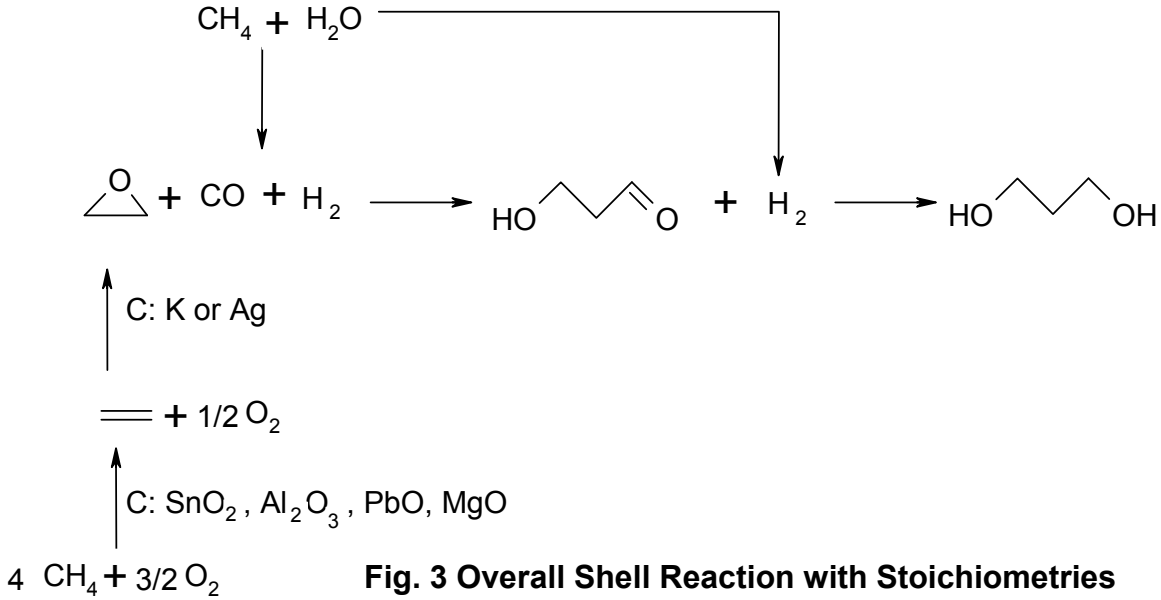

Fig. 3 Overall Shell Reaction with Stoichiometries

The AE for each individual step and overall AE for the Shell process are given in Table 1.

Table 1: Atom Economy for Shell Process

Equation	Desired Products	MW	Reactants	MW	Atom Economy
$CH_4 + H_2O \leftrightarrow 3H_2 + CO$	$2H_2$ + CO	32	CH_4+H_2O	34	94.12%
$4CH_4 + \frac{3}{2}O_2 \rightarrow H_2CCH_2 + C_2H_6 + H_2O$	H_2CCH_2	28	$4CH_4$+$3/2O_2$	112	25.00%
$H_2CCH_2 + \frac{1}{2}O_2 \rightarrow C_2H_4O$	C_2H_4O	44	C_2H_4+$1/2O_2$	44	100%
$C_2H_4O + CO + H_2 \rightarrow HO(CH_2)_2CHO$	$HO(CH_2)_2CHO$	74	C_2H_4O+CO+H_2	74	100%
$HO(CH_2)_2CHO + H_2 \rightarrow HO(CH_2)_3OH$	$HO(CH_3)_3OH$	76	$HO(CH_2)_2CHO$+H_2	76	100%
Overall	$HO(CH_3)_3OH$	76	$5CH_4$+H_2O+$4O_2$ +C_2H_4	162	46.91%

The AE can be calculated by taking the ratio of the mass of the utilized atoms to the total mass of the atoms of all the reactants and multiplying by 100%. As shown below, the reaction of the second step is 25.00%, while the overall AE is 46.91%. The second step atom economy is:

$$\%\ \text{Atom Economy} = \frac{(\text{MW of Desired Products})}{(\text{MW of All Reactants})} \cdot 100\% = \frac{(28)}{(112)} \cdot 100\% = 25\%$$

Assuming the second reaction proceeds to completion, only 25% of the mass of the reactants are incorporated into the desired product while the rest of the mass would form unwanted side products. Using standard practice from life cycle assessment techniques, in order to calculate the overall atom economy of the process, the MW of the raw materials back to the first step must be known. Later in this work, an equation to calculate the overall atom economy using individual steps AE is derived to simplify the overall calculation.

The complete Degussa process is given by the following reaction scheme in Fig. 4.

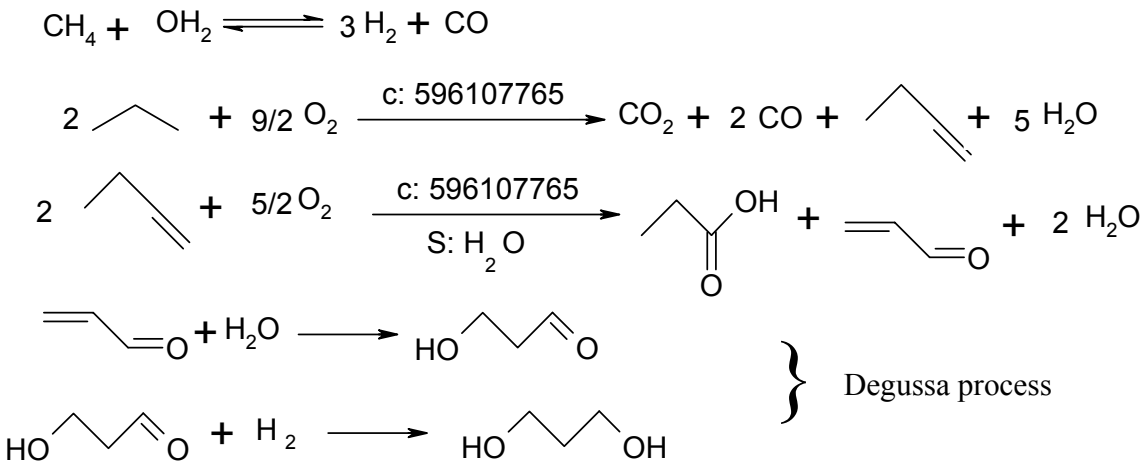

Fig. 4: Degussa Process

As shown, the last two reactions produce 1,3-propanediol. More upstream reactions have been tracked to produce the reactants and the intermediates, such as acrolein, propene, and H_2. Altogether, five reactions are needed to complete the process. Fig.5 shows a stoichiometrically balanced overall reaction flow for the Degussa process. Four molecules of propane, 23/2 molecules of O_2, one methane molecule and two molecules of water are needed to produce one molecule of the final product. Acrolein and H_2 have been produced as the reactants for the 1,3-propanediol production from methane, water, oxygen and propane. These four can be extracted from nature, thereby they are initial raw materials.

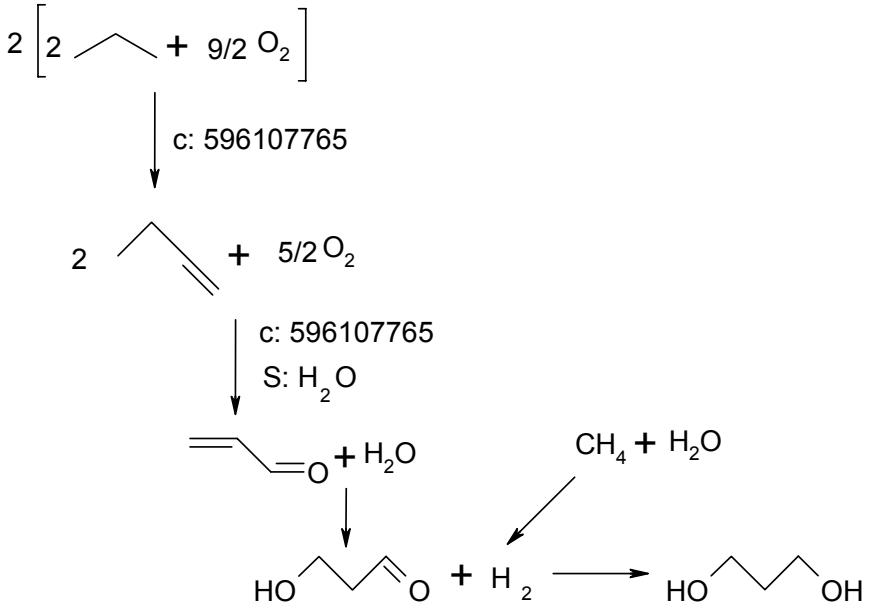

Fig. 5: Overall Degussa Reaction with Stoichiometric Coefficients

Table 2 lists the AE for the individual and overall reactions. For instance, the overall atom economy is 12.75%.

Table 2: Atom Economy for Degussa Process

Equation	Desired Products	MW	Reactants	MW	Atom Economy
$CH_4 + H_2O \leftrightarrow 3H_2 + CO$	H_2	2	CH_4+H_2O	34	5.88%
$2C_3H_8 + \frac{9}{2}O_2 \rightarrow CO_2 + 2CO + C_3H_6 + 5H_2O$	C_3H_6	84	2*(2C_3H_8+9/2O_2)	464	18.10%
$2C_3H_6 + \frac{5}{2}O_2 \rightarrow C_2H_3COOH + C_3H_4O + 2H_2O$	C_3H_4O	56	2C_3H_6+5/2O_2	164	34.15%
$C_3H_4O + H_2O \rightarrow HO(CH_2)_2CHO$	$HO(CH_2)_2CHO$	74	C_3H_4O+H_2O	74	100%
$HO(CH_2)_2CHO + H_2 \rightarrow HO(CH_2)_3OH$	$HO(CH_3)_3OH$	76	$HO(CH_2)_2CHO$+H_2	76	100%
Overall	$HO(CH_3)_3OH$	76	4C_3H_8+23/2O_2+ CH_4+2H_2O	596	12.75%

Proposed formula for calculating the overall atom economy

As previously stated, in order to calculate the overall atom economy of the process, it takes a while to map a complete reaction scheme with all of the reactions stoichiometrically balanced to the final product. For instance, balancing the Degussa process for the overall reaction to arrive at 23/2 moles of O_2 is tedious. Therefore, an equation was devised to integrate the atom economy of individual steps so that a database of equations can be set up for calculating overall atom economy.

The equation is given as:

$$\frac{1}{\varepsilon_{overall}} = 1 + \sum_{i=1}^{N} \frac{P_i}{P_N}\left(\frac{1}{\varepsilon_i} - 1\right)$$

where i=1,2…N are the synthesis steps in order, N is the final product, P_i is the molecular weight of the products for each synthesis step, P_N is the molecular weight of the final product, and ε_i is the atom economy of each synthesis step.

Using this equation, the atom economy of the two routes producing 1,3-propanediol can be calculated using the AE of each step in Table 1 and Table 2. Note that each reaction in the table has been balanced to produce 1 mole of the desired product.

For the Shell process:

$$\frac{1}{\varepsilon_{overall}} = 1 + \left[\frac{32}{76}\left(\frac{1}{0.9412} - 1\right) + \frac{28}{76}\left(\frac{1}{0.2500} - 1\right) + \frac{44}{76}\left(\frac{1}{1} - 1\right) + \frac{74}{76}\left(\frac{1}{1} - 1\right) + \frac{76}{76}\left(\frac{1}{1} - 1\right)\right]$$

Therefore, $\varepsilon_{overall}$ of this process is 46.91%, which matches what was obtained with hand calculations using aggregation of all upstream raw materials.

For the Degussa Process:

$$\frac{1}{\varepsilon_{overall}} = 1 + \left[\frac{2}{76}\left(\frac{1}{0.0588} - 1\right) + \frac{84}{76}\left(\frac{1}{0.1810} - 1\right) + \frac{56}{76}\left(\frac{1}{0.3415} - 1\right) + \frac{74}{76}\left(\frac{1}{1} - 1\right) + \frac{76}{76}\left(\frac{1}{1} - 1\right)\right]$$

Therefore, $\varepsilon_{overall}$ of this process is 12.75%, which is also the same as from previous hand calculations using integration of all the upstream raw materials. This may seem trivial for simple reactions with few intermediate steps, but as reactions become more complicated, hand calculations can become very difficult and tedious, as in the case of products such as pharmaceuticals.

Discussion

Atom economy is becoming more and more recognized as another important criterion for measuring the efficiency of a reaction [10]. It goes beyond the calculation of the yield of a reaction and is more accurate by taking into account the utilized and unutilized atoms of the reactants. The percentage atom economy allows for a quantitative comparison of one reaction (or synthesis) to another. Clearly, based on the calculations shown in this work, the overall atom economy changes as upstream boundaries are changed to include raw materials extracted from the environment. When only the last two steps cited in Degussa and Shell processes are calculated, the atom economies are both 100%. After including the upstream reactions, the atom economy of the Shell process is much higher than that of the Degussa Process. This means that upstream manufacturing routes should be assessed for a product's reaction scheme in order to truly understand the total chemical picture.

As the boundary system is enlarged to include the raw materials, the calculation of overall atom economy becomes increasingly complicated. In order to avoid this problem, we developed a formula which uses the atom economy of each step to calculate an overall atom economy. With this formula, it is possible to build up an atom economy database for any desired reaction scheme. The SciFinder database already provides multiple synthesis steps for desired products. With these synthesis steps and the proposed equation, calculating the overall atom economy for multiple routes would take a fraction of the time of hand calculations.

Marco Eissen, *et al.,* also recently developed an equation for the overall atom economy that includes upstream reactions[11]. However, their formula does not treat the upstream reactions as independent equations, thus causing increased calculational demands in the way the analysis must be done. Their formulation also requires that one aggregate information from the end point (product) without being able to isolate individual sub-reaction schemes for analysis easily.

Fig.6 and Fig.7 depict another way to represent large synthesis routes. As shown by the figures, the final product in our case study is traced back to the environmentally extracted materials. Each of these chemicals is reacted to form intermediates, which are later reacted to form more intermediates until the final product is reached. This is similar to the representations given by Overcash[12]. This layout can help in the proposed database building we have mentioned for doing the calculation of yield, atom economy, and other criteria. We are currently working on automating the analyses through computational methods using this type of representation.

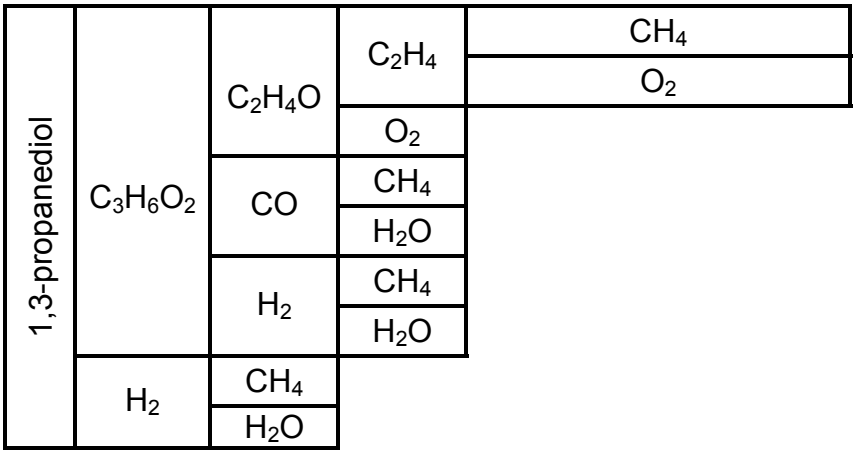

Fig. 6: Graphical representation of Shell Process

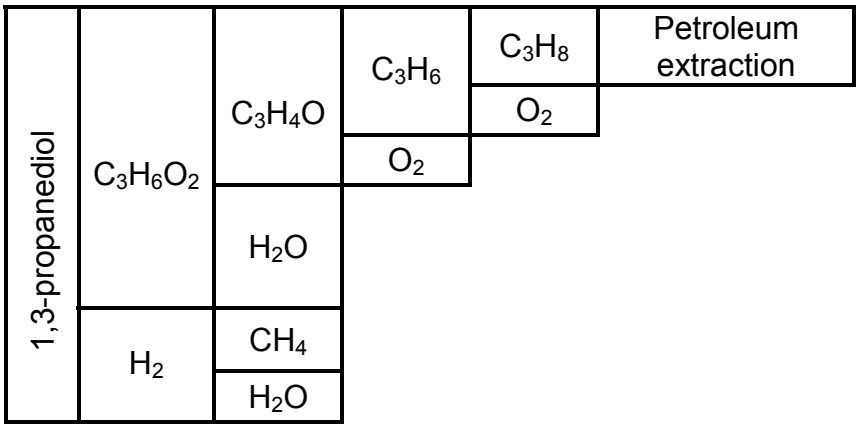

Fig. 7: Graphical representation of Degussa Process

As a final note, there exists a serious limitation of AE in that it does not consider the inherent qualities of the reactants or wastes, such as toxicity or affect on acidification or global warming. For example, the Degussa process requires the extraction of petroleum which does not enter into the AE calculations. This route, then, would incur some environmental impacts during the generation of the initial raw materials that is not included in the AE examination. These effects will also be incurred during any separation processes to purify products from their byproducts. Perhaps a better measure of the efficiency of a reaction scheme other than AE alone is to consider both the AE and yield through a deeper analysis. Of course, in assessing the environmental suitability of a reaction (or synthesis), one should not only consider the efficiency of the reaction but also other factors such as toxicity, the use of auxiliary substances, energy requirements, feedstock origins, and catalytic vs. stoichiometric reagents. More work is needed to develop these ideas into an elegant and robust analysis tool.

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