






Synthesis of Methanol and Acetic Acid from Biomass and Waste Tyres: An Algebraic Targeting Approach

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Abstract. This study employed a process targeting technique to evaluate thermodynamic, environmental and economic feasibility of the synthesis of methanol and acetic acid (AA) from waste tyres and forestry waste (pinewood waste). The results revealed that the synthesis of methanol from waste tyres and pine wood produced CO₂ and was constrained by the change in enthalpy whereas the synthesis of AA was constrained by the change in Gibbs energy and did not produce CO₂. Additionally, the carbon efficiency, atom economy and economic gross potential (EGP) for the synthesis of methanol from waste tyres and pinewood waste co-feed were determined to be 69.17%, 62 % and \$ 0.245 million per year, respectively. In contrast, these metrics for AA synthesis were 100% ,100% and \$ 1.878 million per year, respectively. It was further determined that 1 mole of methanol can be co-produced with approximately 1.19 mole of AA from waste tyres, while 2.719 mole of AA can be co-produced with 1 mole of methanol from pinewood waste without any CO₂ emissions.

Keywords: Algebraic targeting approach, atom economy, carbon efficiency

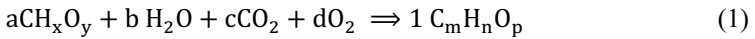
1 Introduction

Sustainable waste biorefineries aim to convert low value waste materials, such as waste tyres and forestry waste, into valuable products by effectively utilizing these resources, reducing energy demands, and environmental emissions, while enhancing profitability. Numerous alternative designs can be generated within a waste biorefinery, making the design a complex process. Applying targeting methods at the conceptual design level can not only help in selecting optimum alternatives but also determine the process performance without requiring detailed process flowsheets [1]. However, current studies on waste tyre and biomass waste conversion systems [2-4] often overlook this crucial step of establishing performance targets and instead directly proceed into detailed designs. Directly proceeding to detailed design can often be time consuming and lead to an inefficient process. Patel et al. [5,6] demonstrated that performance targets for chemical processes can be determined at the of a conceptual design stage by employing mass, energy, and entropy balances. Peduzzi et al.[7] extended the targeting approach by considering both biomass and coal for the co-synthesis of bio-methane and succinic

acid. While their study evaluated the system from a thermodynamic point of view, it did not address the environmental and economic implications. Evaluating the feasibility of a process not only from a thermodynamic point of view but also from an environmental and economical perspective is essential prior to a detailed design. Therefore, the current study aims to integrate these three performance indicators to evaluate the sustainable conversion of waste tyres and biomass waste into methanol and acetic acid (AA) at the conceptual design level.

2 Targeting Approach

This study applies the concepts of the first and second laws of thermodynamics in conjunction with material balances to establish performance targets for synthesis of methanol and acetic acid from two types of waste, prior to a detailed design. It is assumed that both feed and product streams enter and exit the process at ambient conditions (298.15K, 1 atm). The material balance, based on the input-output structure, quantifies the amount of waste feedstock required for the synthesis of the product (s). It also gives an indication of the amount of CO₂ that can be generated from the process. An overall process for the conversion of waste into product (methanol or AA) is described by equation 1.



Where (a), (b), (c), and (d) represent the molar quantities of typical waste, water, carbon dioxide and oxygen, respectively, whereas C_mH_nO_p denotes methanol or acetic acid (AA). By performing an atomic balance, the molar quantity of (b), (c), and (d) can be expressed in terms of (a), as shown in equation 2.

$$b = \frac{1}{2}(n - ax), c = m - a, d = \frac{1}{2}a\left(2 + \frac{x}{2} - y\right) + \frac{1}{2}p - \frac{n}{4} - m \quad (2)$$

From equation (2), the molar quantity of waste material required to produce 1 mole of methanol/AA can be determined by solving the system of linear equations. Furthermore, performing an overall energy balance enables the evaluation of whether the process produces or consumes energy in terms of ΔH and ΔG. By substituting equation 2 into equation 1, the overall difference in ΔH and ΔG can be expressed by equation 3

$$\Delta i_{\text{process}} = \Delta i_{i(\text{C}_m\text{H}_n\text{O}_p)}^{\circ} - a\Delta i_{i(\text{CH}_x\text{O}_y)}^{\circ} - \frac{1}{2}(n - ax)\Delta i_{f(\text{H}_2\text{O})}^{\circ} - (m - a)\Delta i_{f(\text{CO}_2)}^{\circ} \quad (3)$$

Where Δi_f^o represent the enthalpy or Gibbs energy of formation for all components involved in the study and Δi_{process} the change in enthalpy or Gibbs energy of the process. The enthalpy and Gibbs energy formation for waste tyres and pinewood waste were calculated using a correlation from [8]. To simplify the calculations, mass and energy balance linear equations can be solved simultaneously, either analytically or graphically. This approach enables rapid determination of performance targets that meet specific conditions. Once the mass and energy targets are established, the sustainability and economic viability of the process can be addressed using metrics such as

carbon efficiency (C_{eff}), atom economy (AE) [6], and economic gross potential (EGP) [1]

$$C_{\text{eff}} = \frac{\text{moles of C in } C_m H_n O_p}{\text{moles of carbon in feed}} \times 100\% \quad (4)$$

$$AE = \frac{\text{mass of } C_m H_n O_p}{\text{mass of feed}} \times 100\% \quad (5)$$

$$EGP = \sum n_i P_{\text{product},i} - \sum n_j P_{\text{feed},j} \quad (6)$$

Where n and P are the stoichiometric coefficient and price of a chemical species, respectively. For a process to be economically viable, EGP must be positive.

3 Results and discussions

3.1 Single product from single feedstock

Figure 1 shows the mass and energy targets for the synthesis of 1 mol of methanol from either waste tyres (point A) or biomass waste (point B). This process is constrained by ΔH , and for thermodynamically feasibility, operation on the $\Delta H=0$ line, as defined in equations 7 & 8, is necessary. It is evident that biomass produces more CO_2 compared to waste tyres for the synthesis of one mole of methanol. This is due to the higher oxygen content in biomass, which exit the process as CO_2 . When operating on the CO_2 zero line ($c=0$), the process requires both heat and work for it to be feasible, regardless of the waste type. Additionally, methanol production from waste tyres results in lower CO_2 emissions while achieving higher C_{eff} and AE. This is attributed to the lower oxygen content in waste tyres compared to biomass waste. However, the process requires more H_2O and O_2 in the feed. Furthermore, it is observed that the production of methanol from pinewood waste yields an EGP of nearly equal to that of waste tyres.

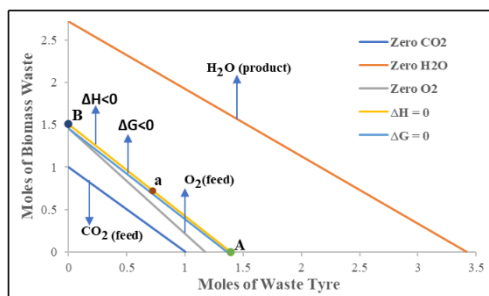
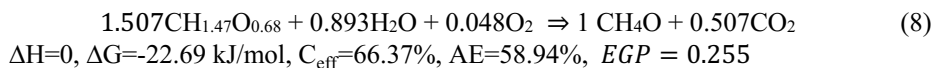
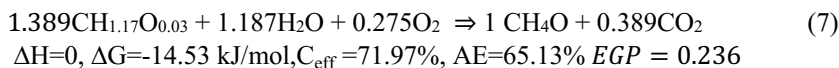
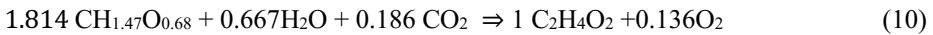


Fig. 1. Methanol synthesis from waste tyre and biomass

Figure 2 illustrates the mass and energy targets for the synthesis of 1 mole of acetic acid from waste tyres (point A) and biomass waste (point B). To avoid CO₂ production, operation should occur below the zero CO₂ line, which requires the utilization of O₂ and H₂O as feed. Under these conditions, the processes (point A and B) will require both heat and work. Operating on the zero O₂ (d=0) line, both processes still require heat and work to achieve feasibility. It is also evident that both processes (A and B) are constrained by ΔG. Operating on the ΔG = 0 line demonstrates that both processes utilize CO₂ as a feed and produce energy (equation 9 and 10). Additionally, the synthesis of AA from biomass produces O₂ whilst waste tyre utilizes O₂. Additionally, AA production from pinewood waste achieves a higher EGP compared to waste tyres. When comparing the production of AA with methanol, it is observed that AA achieves an EGP that is 7.9 times higher than methanol when waste tyres are used as a raw material. Similarly, when pinewood waste is used, AA synthesis yields an EGP about 7.4 times greater than methanol.



$$\Delta H = -10.25 \frac{\text{kJ}}{\text{mol}}, \Delta G = 0, C_{\text{eff}} = 100\%, \text{AE} = 100\%, \text{EGP} = 1.860$$



$$\Delta H = -0.31 \frac{\text{kJ}}{\text{mol}}, \Delta G = 0 \frac{\text{kJ}}{\text{mol}}, C_{\text{eff}} = 100\%, \text{AE} = 99.59\%, \text{EGP} = 1.884$$

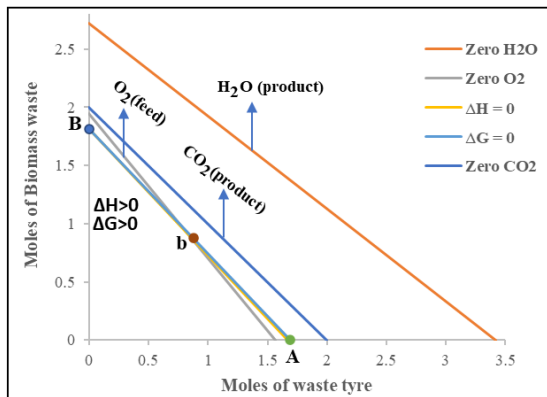
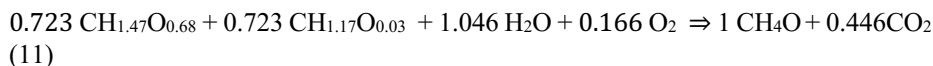


Fig. 2. Synthesis of Acetic acid from waste tyre and biomass

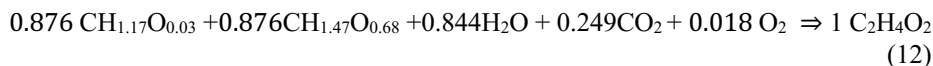
3.2 Single products from multiple feedstocks

If operating on the ΔH zero line, the co-feed of waste tyres and biomass waste for the synthesis of 1 mole of methanol (Fig. 1) can be located anywhere between point A and B. The process (co-feed) will still produce CO₂ and a small amount of work (ΔG < 0). For instance, with a co-feed ratio of 1:1 as shown by point a in figure 1, the overall process can be algebraically summarized by equation 11. It is noticed that the C_{eff}, AE, ΔH or ΔG, and EGP lie between those of single feedstocks.



$$\Delta H = 0 \frac{\text{kJ}}{\text{mol}}, \Delta G = -18.44 \frac{\text{kJ}}{\text{mol}}, C_{\text{eff}} = 69.17\%, \text{AE} = 62\%, \text{EGP} = 0.245$$

Point b in figure 2 shows a co-feed ratio of 1:1 for the synthesis of acetic acid and is summarized by equation 12.



$$\Delta H = -5.454 \frac{\text{kJ}}{\text{mol}}, \Delta G = 0 \frac{\text{kJ}}{\text{mol}}, C_{\text{eff}} = 100\%, \text{AE} = 100\%, \text{EGP} = 1.878$$

3.3 Multiple products from single feedstocks

Figures 3 and 4 show the material and energy targets for the co-production of methanol and acetic acid from waste tyre and biomass waste, respectively. The amount of waste tyre or biomass waste was plotted against the amount of acetic acid by considering one mole of methanol. Acetic acid (AA) was considered as feed when the overall material and energy balance was established, thus a negative value of AA in figure 3 and 4 corresponds to product. Operating somewhere above the CO₂ zero line, the process will be thermodynamically feasible but at the expense of significant amount of CO₂ being emitted (figure 3). To avoid CO₂ emissions, one should operate at point T (on the ΔH zero line).

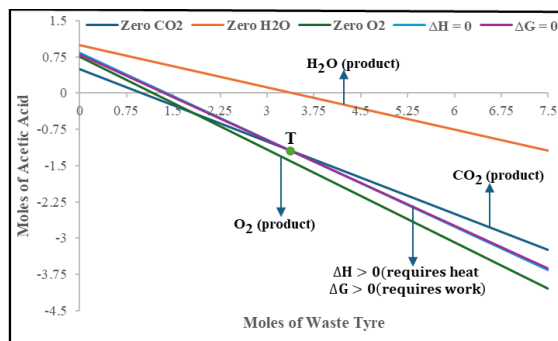
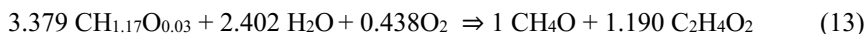


Fig. 3. Co-production of methanol and acetic acid from waste tyres

The overall mass and energy target at this point is summarized in equation 13. Interestingly, one can co-produce AA and methanol from waste tyres without emitting CO₂ and the overall process will still be feasible from both thermodynamic and economic perspectives.



$$\Delta H=0 \frac{\text{kJ}}{\text{mol}}, \Delta G=-2.49 \frac{\text{kJ}}{\text{mol}}, C_{\text{eff}}=100\%, \text{AE}=100\%, \text{EGP} = 4.08$$

Operating at point U (adiabatic process), as depicted in figure 4, the process neither produces nor requires any CO₂. Operating on the zero CO₂ line, the process is thermodynamically infeasible until the point where this line converges with ΔH and ΔG zero lines. Additionally, it is evident that the process will produce oxygen at point U. The overall mass and energy targets at point U are summarized in equation 14.



$$\Delta H=0 \frac{\text{kJ}}{\text{mol}}, \Delta G=-21.85 \frac{\text{kJ}}{\text{mol}}, C_{\text{eff}}=100\%, \text{AE}=95.27\%, \text{EGP} = 7.680$$

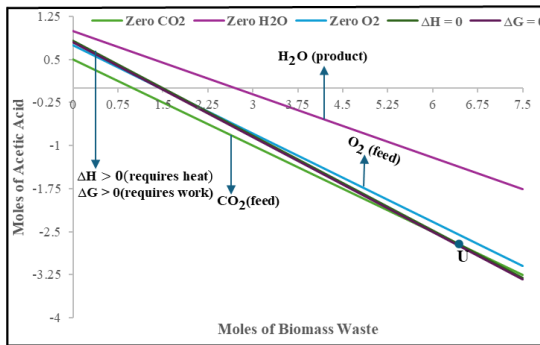


Fig. 4. Co-production of methanol and acetic acid from biomass

Operating the process adiabatically, 1 mole of methanol is co-produced with 1.19 mole of AA from waste tyres, generating approximately 2.49 kJ/mol of work is generated. This process does not produce any CO₂. When using biomass waste, 1 mole of methanol can be co-produced with approximately 2.719 mole of AA, generating 21.85 kJ/mol of work; however, the AE is reduced due to the production of O₂. It is evident that the co-production of methanol and AA requires a higher water input compared to the production of a single product. Additionally, the co-production of methanol and AA achieves a higher EGP than the production of a single chemical, though it demands more feed-stock.

4 Conclusion

This study extended the application of mass, energy, and entropy balance to graphically evaluate the synthesis of methanol and acetic acid (AA) from waste tyres and pinewood waste from environmental, thermodynamic and economic perspectives. It was observed that the synthesis of 1 mole of methanol from waste tyres and biomass waste generated

0.39 mole and 0.51 mole of CO₂, respectively. The C_{eff}, AE, and EGP were found to be 71.97%, 65.13% and 0.236 million /year for the synthesis of methanol from waste tyres. In comparison, using biomass waste resulted in C_{eff}, AE and EGP of 66.37%, 58.94% and \$ 0.255 million/year, respectively. In contrast, the synthesis of acetic acid from waste tyres or biomass waste did not produce any carbon dioxide. For waste tyre this resulted in 100% carbon conversion efficiency and 100% atom economy and EGP of \$ 1.80 million per year. which increased the C_{eff}, AE and EGP to 100% and \$1.860/year million for waste tyre, 100%, 93.28% and \$1.884 million /year for biomass waste. It was determined that the synthesis of methanol from waste tyre and biomass was constrained by ΔH , whereas the synthesis of AA was limited by ΔG . Additionally, the C_{eff}, AE, ΔH or ΔG , and EGP from the co-feed of waste tyre and biomass for the synthesis of methanol and AA lie between those of single feedstocks. The co-production of methanol and AA was also evaluated, revealing that such a process neither requires nor produce CO₂ but achieved higher a EGP than the synthesis of a single product.

Acknowledgments. This work was funded by the University of South Africa (UNISA)

Disclosure of Interests. The authors declare that they have no competing financial interests or personal relationships that could have appeared to alter this work

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