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DOI
10.1016/B978-0-443-15274-0.50386-3

Publication date
2023

Document Version
Final published version

Published in
Computer Aided Chemical Engineering

Citation (APA)
Stepchuk, I., Pérez-Fortes, M., & Ramírez, A. R. (2023). Impacts of defossilising downstream derivatives in petrochemical clusters – MTBE case study. In *Computer Aided Chemical Engineering* (pp. 2429-2434). (Computer Aided Chemical Engineering; Vol. 52). Elsevier. https://doi.org/10.1016/B978-0-443-15274-0.50386-3

Antonis Kokossis, Michael C. Georgiadis, Efstratios N. Pistikopoulos (Eds.)
PROCEEDINGS OF THE 33rd European Symposium on Computer Aided Process Engineering (ESCAPE33), June 18-21, 2023, Athens, Greece
http://dx.doi.org/10.1016/B978-0-443-15274-0.50386-3

Impacts of defossilising downstream derivatives in petrochemical clusters – MTBE case study

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Abstract

Using alternative carbon sources (ACS) to produce downstream derivatives (DDs) is a promising option for defossilising the chemical industry. However, the potential consequences of using ACS in interconnected petrochemical clusters are generally overlooked. This paper aims to develop a methodological approach for systematically analysing defossilisation impacts at the value chain level. For this, a single value chain for producing methyl-tert-butyl-ether (MTBE) was used as a case study. The individual components of the value chain were modelled in Aspen Plus v12. Both ACS- and fossil-based value chains were compared in terms of (i) changes in the structure of the value chain and (ii) the magnitude of the impacts. The results show that the defossilisation of a single value chain causes additional impacts at the cluster level.

Keywords: Industrial defossilisation, downstream derivatives, interconnected cluster.

1. Introduction

The chemical sector is highly dependent on the usage of fossil carbon as feedstock for the production of chemicals (Nesbitt 2020). The launch of the EU chemicals strategy for sustainability has triggered the chemical industry to look for innovative solutions toward a green transition. One of the possible solutions is to defossilise the chemical industry by replacing fossil-based feedstock with alternative materials (EC 2020). Alternative carbon sources (CO_2, biomass, waste) are increasingly considered as alternative feedstocks for bulk chemicals production (i.e. ethanol, methanol, ammonia). However, there is less research on the potential of defossilising downstream derivatives (DDs) (Moncada, Posada, and Ramírez 2015). DDs are the chemicals present at the end of value chains before they are distributed to potential customers, for instance, styrene, acetone, or polyvinyl chloride (Kramer et al. 2017).

DD's value chains are usually integrated into large petrochemical clusters (Porter 1998), through symbiotic relationships inside and between value chains within the clusters (Chertow 2000). The defossilisation of one DD process will likely affect other processes inside the value chain and within the cluster. Thereby, making uncertain what the total impact on the performance of the value chain and cluster could be. The goal of the current work is to develop and test a methodology to analyse how using alternative carbon materials for defossilising a single DD value chain can affect its existing interactions and performance in a petrochemical cluster. For this paper, MTBE (methyl tert-butyl ether) was selected as a case study.

2. Methodology

This paper departs from an in-house model of a representative petrochemical cluster. The model mimics a real petrochemical cluster and it is based on the 6 industrial sites of the Port of Rotterdam (PoR) petrochemical cluster (Ramirez-Ramirez 2019). The model includes a total of 22 plants with the production of 52 chemicals classified in 9 subclusters. Each plant was modelled in Aspen Plus v12, and the interconnections are modelled in an interface. The subclusters are chlorine, methanol, ethylene, propylene, ammonia, aromatics, olefins, bio-based and other chemical-based subclusters.

The representative cluster contains a diverse range of chemicals. In this paper, chemicals produced in the cluster are presented as follows (Figure 1): feedstock (F), auxiliary chemicals (AC), chemical building blocks (CBBs), commodity chemicals (CCs), and downstream derivatives (DDs). All these chemicals are interconnected by mass, energy and or waste flows. The connectivity of the value chain is represented by the number of mass flows interconnections within value chain boundaries (i.e. horizontal connections) and the number of subclusters involved in the production of a single DD (i.e. vertical connections). The methodology contains four main steps which are discussed below.

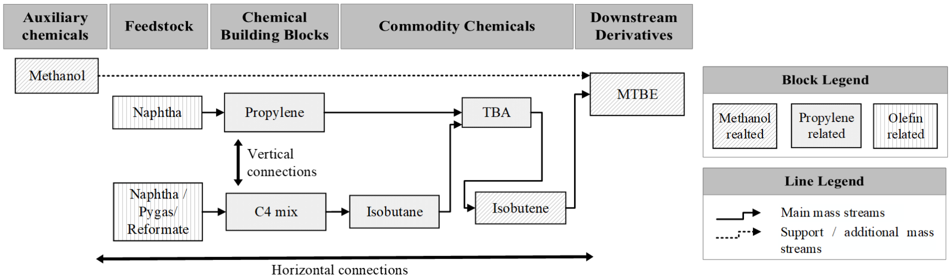

Figure 1: Schematic representation of MTBE value chain with existing mass flow interconnections.

2.1. Selection of key downstream derivatives

The representative cluster contains 13 DDs but not all of them have a large potential for defossilisation. Therefore, the selection of the most promising DDs was made based on three criteria: (i) embodied carbon, (ii) connectivity of the components in the value chains and (iii) availability of data of the ACS-based routes in the literature.

First, the amount of embodied carbon was assessed for each DD to identify the most promising derivatives for defossilisation. Embodied carbon (EC) is defined as the elemental carbon embodied in material flows of chemicals entering specific stages of production to meet process needs (Eq.(1)). For the assessment of embodied carbon, data was collected from each DDs' Aspen Plus model of the representative petrochemical cluster. The embodied carbon of each DD was calculated as follows:

$$EC_{DD} = \sum_{i=1}^{n} M_i * C_{wt\%_i} \qquad (1)$$

where $i = (1 \dots n) -$ number of material flows entering the production process of the DD; $M_i -$ inlet capacity of particular material flow, ktonne/year; $C_{wt\%_i} -$ weight percent of fossil-based carbon embodied in the chemical, %.

The next step involved identifying the existing connectivity of mass flows within value chains and representative clusters. This was done by mapping the network, i.e., identifying the interconnections (i.e. mass flows) between chemicals, and the connectivity of each value chain was assessed in terms of horizontal and vertical interconnections.

Last, a literature screening was performed to identify ACS-based production routes (i.e. from CO_2, waste, biomass). Information was collected for each ACS-based route with a technology readiness level (TRL) of 4 or higher.

Based on three selection criteria, potential DDs were selected for further research. To evaluate the available defossilisation pathways (i.e. ACS-based routes) and develop the methodology to assess subsequent impacts at the value chain level, first, a single DD value chain (i.e. case study) was selected.

2.2. Selection of ACS-based route for the case study

This step involved the selection of the most promising ACS-based production routes for the case study. Routes were further screened in terms of data availability (i.e. the more data, the better), type of options (i.e. thermochemical, electrochemical, biochemical and the process conditions, e.g., mild conditions were preferred over stringent conditions), complexity (i.e. the number of process steps, the fewer steps the better), and scalability. The routes were then ranked and the most promising option was selected for further study.

2.3. Process modelling of ACS-based route

The selected ACS-based route was then modelled at the scale (i.e. capacity) and purity of the current fossil process. Here it is assumed that the alternative route will replace one-to-one the amount of product produced by the fossil-based route. For this, the development of the process flow diagram and Aspen Plus v12 model was done based on data collected for the selected ACS-based route. The model was assumed to be in continuous mode with a whole year of operation (i.e. 8000 hours per year). Properties for biomass components were introduced into Aspen Plus simulation by the usage of biomass property databases developed by the National Renewable Energy Laboratory (NREL).

2.4. Defossilisation impacts analysis

Value chains can be represented graphically as a network, with nodes and links. Nodes refer to chemical processes involved in the value chain, while links represent material, waste and or energy flows between the nodes. Networks were developed for fossil- and ACS-based value chains of the case study, which allow to study changes that would occur when replacing a fossil-based process, a node, in the network with ACS-based process. Structural changes in nodes and links were categorized, as (i) removed - no longer required, (ii) affected - required, but capacities are changed, (iii) unchanged - required, capacities remain the same, and (iv) added – required, to be added (i.e. new chemicals/flows).

It is expected that structural changes in the value chain will affect its total performance. To quantify the magnitude of these impacts the following techno-economic and environmental KPIs were selected: (i) production rates, (ii) fossil-based carbon offset (i.e. the amount of fossil embodied carbon replaced by alternative carbon), and (iii) additional investment needed. Based on these indicators, the ACS-based value chain of the case study was assessed and compared to the fossil-based counterpart.

3. Results and discussion - MTBE case study

3.1. Selection of case study – MTBE

Based on the methodology for the selection of DDs presented in Section 2.1, 6 DDs were selected (see Table 1). First, priority was given to DDs with embodied carbon of

> 40 ktonne/year. Then, chemicals were examined in terms of connectivity and availability of ACS-based routes. DDs with a higher number of vertical connections were preferred because changes in the value chains of those DDs will more likely result in a higher probability of impacts at the cluster level. MTBE was selected as a case study. As can be seen from Table 1, it has high EC, is highly interconnected within the value chain and cluster, and has a wide range of ACS-based routes present in the literature.

Table 1: Key downstream derivatives.

Downstream Derivatives	EC*	Connectivity		ACS-based routes			Research
name	*kt/y*	*vertical*	*horizontal*	*CO_2*	*biomass*	*waste*	*selected*
Styrene	914	3	11	-	+	+	+
Methyl tert-butyl ether (MTBE)	281	2	8	+	+	+	+
Polyvinyl chloride (PVC)	181	2	6	+	+	+	+
Polyethylene terephthalate (PET)	155	2	8	+	+	+	+
Carbon Black	132	0	1	+	+	+	-
Phthalic anhydride	71	0	3	-	+	-	-
Propylene glycol ether (PGE)	58	4	14	+	+	+	+
Polyols	44	4	13	+	+	-	+
Dimethyl ether (DME)	35	0	2	+	+	+	-
Acetone	33	0	4	+	+	+	-
Biodiesel	4	0	4	n.a.	n.a.	n.a.	-
Hydrochloric acid (HCl)	0	0	8	n.a.	n.a.	n.a.	-
Bioethanol	0	0	2	n.a.	n.a.	n.a.	-

**secondary data for calculations is taken from Aspen models*

3.1.1. Fossil-and ACS-based MTBE

MTBE is used in the fuel industry as an additive to increase the octane number. Conventionally, it is produced from a chemical reaction of methanol and isobutene. In the representative cluster, MTBE is produced in the amount of 400 ktonne/year. For its production, methanol and C4 mix are purchased from outside the cluster. Propylene is obtained from the cluster's olefin plant. Isobutane and tert-butyl alcohol (TBA) are produced within the propylene subcluster of the representative cluster (Section 2).

From the literature, the biomass-to-isobutanol-to-MTBE synthesis process was selected based on economic and technical constraints. The process involves different stages: (i) conversion of biomass to sugars through ethanol-based organosolv, (ii) enzymatic hydrolysis and fermentation of isobutanol, (iii) dehydration of isobutanol to isobutene, and (iv) conversion of isobutene to MTBE (Moncada, Posada, and Ramírez 2017). Ethanol is required as a solvent in a quantity of 5 L per kg of dry biomass and is completely recycled in the process. Simplified block diagrams of both fossil- and ACS-based value chains of MTBE are presented in Figure 2.

3.2. Defossilisation impacts analysis

Figure 2 shows a qualitative comparison of major changes in the structure of mass flows of MTBE value chain after defossilisation. Nearly 60% of the structure of MTBE value chain is changed. TBA, isobutane, C4 mix, and propylene are no longer required inside value chain and therefore their use is reduced by 100%. However, an additional chemical, ethanol, is needed as a solvent for isobutanol production. Although the quantity of ethanol is high, it is fully recovered within the value chain. Here, it was assumed that it does not affect the value chain carbon offset rate. The fossil-based carbon offset was calculated as the amount of alternative carbon replacing fossil embodied carbon of MTBE. The latter is a sum of fossil-based carbon embodied in material flows of isobutene and imported methanol entering the MTBE process. The fossil-based carbon offset is 80 %, as fossil-based isobutene is completely replaced by an alternative one. Economic performance is also affected. Based on ongoing modelling work, additional investment is roughly 15% of the bare equipment costs of MTBE fossil-based value chain.

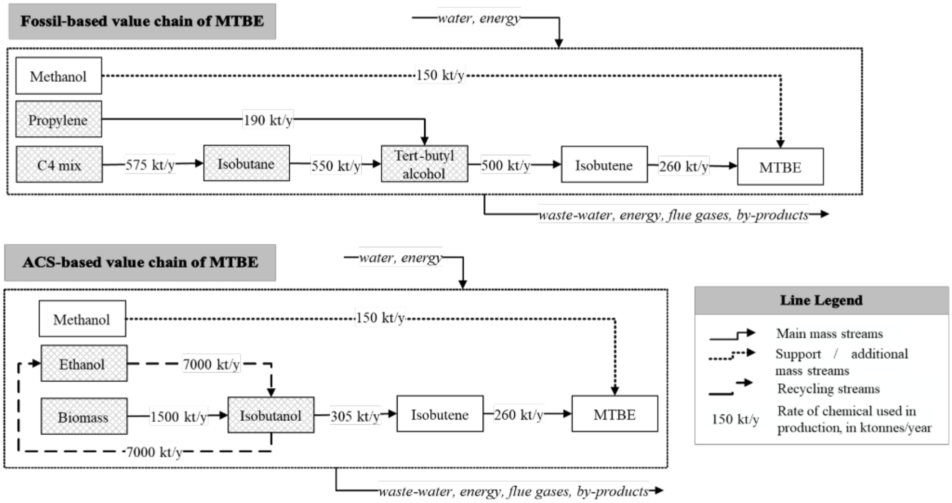

Figure 2: Simplified MTBE value chains with main mass flow interconnections for the production of 400 ktonne/year.

The majority of chemicals involved in fossil-based MTBE production are currently produced within the cluster and are involved in the value chains of other DDs (Table 2). Therefore, structural changes in the MTBE value chain will affect other value chains. For instance, tert-butyl alcohol is derived as a coproduct of propylene oxide production, requiring both C4 mix and propylene as feedstock materials. The defossilisation of the MTBE value chain will therefore affect the amount of C4 mix imported into the cluster as well as the isobutane and propylene capacities. Thereby impacting other DDs, such as styrene, and propylene glycol ether which also require propylene. The latter are highly interconnected within the cluster, resulting in further propagation of defossilisation impacts.

Table 2: Structural changes at the value chain and cluster level.

Chemical	Present in the cluster				Required for MTBE value chain		Defossilisation impacts	
					fossil	ACS	*value chain*	*cluster*
name	*yes/no*	*	**	*kt/y*	*kt/y*	*kt/y*	*change*	*change*
Methanol	yes	B	no	150	150	150	unchanged	unchanged
Propylene	yes	P	yes	497	190	-	removed	affected
C4 mix	yes	B	yes	575	575	-	removed	affected
Isobutane	yes	P	yes	550	550	-	removed	affected
Tert-butyl alcohol	yes	P	no	603	500	-	removed	affected
Isobutene	yes	P	no	260	260	260	unchanged	unchanged
Biomass	yes	B	yes	2000	-	1500	added	affected
Ethanol	no	B	no	-	-	7000	added	added
Isobutanol	no	-	-	-	-	305	added	added

**B –is bought from the market, P- is produced within the representative cluster;*
*** involved in value chains of other DDs, yes/no.*

The impact assessment in this paper was done based on the changes in mass flows. However, to develop the full picture of potential impacts, it is crucial to also include impacts on energy and water flows due to defossilisation. This is part of the current research, which will be available at the time of the conference.

4. Conclusions and future work

The defossilisation of a single DD can significantly have impacts beyond the process itself, especially in highly interconnected petrochemical clusters. This paper proposed a novel methodology for systematically analysing defossilisation impacts at the value chain level. The findings highlight the need for methodologies to be able to assess changes at the value chain level and their consequences at the cluster level (e.g. impacts on fossil-based carbon offset of other DDs due to defossilisation of MTBE). In future work, the ACS-based MTBE value chain will be assessed in terms of changes in energy and water flows and the methodology will be further developed to identify where the largest impacts in terms of defossilisation can be obtained in different DD value chains.

Acknowledgements

This publication is part of the project “Unravelling the impacts of using alternative raw materials in industrial clusters”, project number VI.C.183.010 of the research programme VICI which is financed by the Dutch Research Council (NWO).

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