



Thermodynamic appraisal of the gas phase conversion of ethylene or ethanol to propylene



Tino Lehmann^{a,*}, Andreas Seidel-Morgenstern^{a,b}

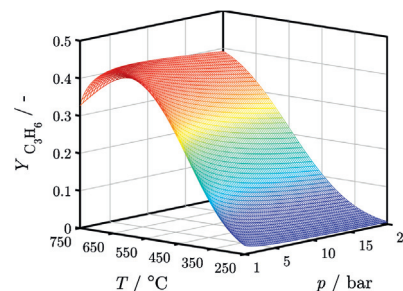
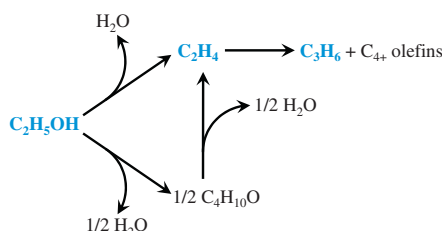
^aOtto-von-Guericke-University, Institute of Process Engineering, Universitätsplatz 2, 39106 Magdeburg, Germany

^bMax-Planck-Institute for Dynamics of Complex Technical Systems, Sandtorstr. 1, 39106 Magdeburg, Germany

HIGHLIGHTS

- Chemical equilibria with up to 32 components were investigated.
- Non-ideal behavior was rigorously implemented and found to be negligible.
- No significant propylene generation below 250 °C.
- Optimal propylene yields of 42% at 1 bar and 600 °C (ethanol) or 650 °C (ethylene).
- Lower temperatures can compensate yield effects of water in the reactor feed.

GRAPHICAL ABSTRACT



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ABSTRACT

Propylene production from current sources will not suffice in the long run to meet market requirements. The transformation of either ethylene or ethanol into propylene is hence an interesting alternative to conventional production routes. These two chemical processes were thermodynamically analyzed employing Gibbs energy minimization. Investigated process parameters included system pressures ranging from 1 to 20 bar and reaction temperatures between 250 and 750 °C. Regarding initial compositions, pure ethylene or ethanol feeds were considered as well as binary mixtures of aqueous ethanol containing water mass fractions up to 95%. The effect of catalyst-caused shape selectivity on the product spectrum was accounted for by using different species lists. Non-ideal behavior was incorporated using the virial equation but found to be negligible. Both ethanol and ethylene feeds gave a maximum propylene yield of approximately 42% (carbon atom basis) at a system pressure of 1 bar. Optimal reaction temperatures were found at 600 °C (ethanol feed) and 650 °C (ethylene feed), respectively. In addition, chemical equilibria revealed room for improvement as far as currently available catalysts are concerned. The results of this study are thus useful as a benchmark for future catalyst developments. The potential attractiveness of ethylene- or ethanol-based propylene production is pointed out from a general thermodynamic point of view.

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1. Introduction

Propylene is one of the central base chemicals in the petrochemical industry, second only to ethylene. The market for

* Corresponding author. Present address: Integrated Lab Solutions GmbH, Max-Planck-Str. 3, 12489 Berlin, Germany. Tel.: +49 391 6758644; fax: +49 391 6712028.
E-mail address: tino.lehmann@integratedlabsolutions.com (T. Lehmann).

propylene has experienced an increased demand pull in the last decades primarily due to its consumption in polypropylene manufacture [1]. This is a challenging development because production of propylene is still heavily dependent on petrochemical processes in which it is reduced to the status of a co-product. The most important example is steam cracking of various hydrocarbon streams which is mainly performed to generate ethylene. Propylene yields are in this case primarily determined by the feed slate. The increasing utilization of lighter feedstocks like ethane is

Nomenclature

b_h	$= \sum_{i=1}^N \beta_{hi} n_{i,0}$, molar amount of element h	p_c	critical pressure
ε	energetic parameter	$Q_{\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}}$	molar feed ratio of water to ethanol
B	second virial coefficient	\mathcal{R}	gas constant
F	total volumetric feed flow rate	S_i	carbon-based selectivity of species i
G	total Gibbs energy	T	system temperature
\bar{G}_i	partial molar Gibbs energy of species i	T_c	critical temperature
$\Delta_f G_i^\circ$	standard Gibbs energy of formation of species i	T_r	$=T/T_c$, reduced temperature
$\Delta_f G_{C,i}^\circ$	carbon-normalized standard Gibbs energy of formation of species i	W	mass of catalyst
$\Delta_f G_I^\circ$	standard Gibbs energy of formation of isomer group I	y_i	mole fraction of species i
k_{ij}	binary interaction parameter for molecule pair i – j	Y_i	carbon-based yield of species i
L	number of elements	X_k	fractional conversion of key component k
n_i	mole number of species i	Greek Symbols	
n_t	$= \sum_{i=1}^N n_i$, total mole number	β_{hi}	number of atoms h in species i
N	total number of species in the system	ζ_{kl}	k – l group interaction parameter
N_I	number of species in isomer group I	θ_{ki}	surface area fraction of group k in molecule i
N_i^G	number of groups composing molecule i	λ_h	Lagrange multiplier for element h
p	total system pressure	φ_i	mixture fugacity coefficient of component i
p°	standard-state pressure, 1 bar	ω	acentric factor

therefore quite detrimental regarding propylene supply, since these feedstocks give only minor propylene quantities [2]. In addition, there is only limited opportunity to enhance propylene yields by adjusting cracking conditions: higher propylene/ethylene ratios are usually traded off for lower total amounts of short-chain olefins [3] which is economically undesirable. This situation – and the fact that demand growth rates for propylene are exceeding those for ethylene – has led to the investigation of various on-purpose technologies for propylene production [1].

One of the possible options for such an on-purpose process is the direct conversion of the cracker main product ethylene to propylene. Several catalysts have been reported for this reaction within the last seven years. These include acidic materials – SAPO-34 [4–6] and ZSM-5 [7] – as well as supported nickel catalysts [8–13]. A potential application could focus on a downstream reactor unit shifting the cracker product spectrum towards higher propylene yields. Such a scenario clearly calls for opportunistic olefin economics, i.e., the price of ethylene must be less than the market value of propylene. However, there are also situations when ethylene is in excess supply. It is in these two cases that an ethylene-to-propylene reaction can make sense.

A closely related process is the conversion of ethanol to propylene. Development of such a production route is potentially very attractive both from an economic and ecological point of view. The reason is that ethanol can be readily derived from various biomass feedstocks via fermentation (so-called bio-ethanol) [14]. Future use of lignocellulosic biomass in particular holds great promise for generation of bio-ethanol [15]. It could therefore serve as a basis for the production of propylene and polypropylene from renewable resources [16,17].

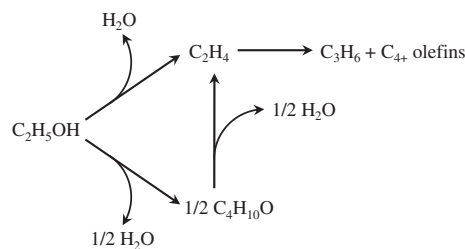
Against this background, significant research efforts have been carried out regarding the transformation of neat ethanol into propylene. A literature survey reveals the pre-eminent role of the ZSM-5 catalyst in this context, which is employed either in undoped [18,19], metal-loaded [20–28] or phosphorus-promoted [29–33] form. Other catalyst systems have been investigated as well [5,34–42]. Studies on the conversion of water-containing (bio-)ethanol to light olefins in general and propylene in particular constitute another research focus in the published literature [43–50].

The purpose of this paper is an in-depth equilibrium assessment of propylene generation from either ethanol or ethylene feeds.

Such a more general perspective is currently missing in the pertinent literature where publications mainly deal with specific features of the various catalysts. The present focus is deliberately not on mechanistic or kinetic issues. Instead, thermodynamic process limits are delineated considering for the most part industrially relevant feed conditions, i.e., focusing on concentrated systems without inert diluent. The influence of system pressure and temperature on attainable propylene yields is investigated. Identifying optimal process conditions in this respect is a major goal of this study. Moreover, the effect of water on the conversion of aqueous ethanol is elucidated. Co-fed water has been already shown to have a tremendous influence on important kinetic aspects (product distribution, deactivation behavior) when bio-ethanol is converted to light olefins like propylene [43,51–55]. Here we will take a closer look at the thermodynamic impact of varying fractions of water in the reaction feed.

2. Methodological approach**2.1. Definition of species lists**

Choosing species assumed to be present at equilibrium is an important step prior to any thermodynamic calculation. The selection of chemical components typically requires specifying the reactions taking place which is essentially a kinetic issue. This is difficult for catalytic processes where the mechanistic details of



Scheme 1. Simplified reaction network for the conversion of ethanol to propylene. Details of C₃+ olefin formation may vary for different catalysts according to the particular reaction network postulations.

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