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Perspectives on exploiting near-critical fluids for energy-efficient catalytic conversion of emerging feedstocks

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ABSTRACT

Near-critical fluids possess unique tunability of the physical and transport properties for performing resource-efficient catalysis (i.e., conserving feedstock and energy) characterized by process intensification, high product selectivity, enhanced safety and facile separation steps. Alternative technology concepts for energy-intensive and waste-generating megaton industrial processes (such as ethylene and propylene epoxidations, *p*-xylene oxidation and olefin hydroformylations) that employ gas-expanded liquids or supercritical fluids to demonstrate such process attributes are highlighted. In particular, continuous or flow processes that employ either homogeneous or supported ionic liquid phase (SILP) catalysts are emphasized. Economic and LCA analyses based on plant-scale simulations reveal clear potential for practical viability and lowered environmental impacts of these alternative processes (relative to the conventional technologies). The emerging biomass and shale gas based chemical industry, where new catalytic technologies are needed to make equivalent petrochemical intermediates, may be receptive to adopt and implement such new resource-efficient technologies.

1. Introduction

The United States chemical industry output is estimated to reach 3.4 trillion US$ by 2020, nearly double the 2010 value of 1.8 trillion US$ [1]. Plant-based biomass and C_1—C_5 hydrocarbons (from shale gas extraction) have emerged as alternative feedstock sources to meet this rapidly increasing demand for chemicals. However, new chemistries and resource-efficient catalytic technologies (that conserve feedstock and energy) are needed to produce petrochemical equivalents from these emerging feedstocks. This challenge not only provides exciting R&D opportunities for chemists and chemical engineers but could also rejuvenate the US chemical industry as a major manufacturing sector and exporter. *The development of resource-efficient technologies is also being increasingly recognized as a good business strategy while promoting sustainability* [2].

The chemical manufacturing industry is energy-intensive. Fig. 1 shows the top 18 chemicals whose annual global production capacities are on the order of megatons and cumulatively account for nearly 80% of the overall energy consumed by the industry [3]. Fig. 1 also shows the greenhouse gas (GHG) emissions (in terms of CO_2 equivalent) contributed by each of the chemicals based on the fact that the energy required for their production is almost exclusively derived from fossil fuels. The global GHG emissions attributed to chemical and petrochemical processes amounts to 1.24 $GtCO_2$-eq annually. In contrast, the 2010 GHG emissions attributed to the transportation industry is roughly 7.2 $GtCO_2$-eq [4].

The 18 large-volume chemicals account for 0.96 $GtCO_2$-eq (or approximately 75% of the total annual amount). Ethylene and propylene, major feedstocks of the chemical industry, are near the top of this list. Both involve energy intensive production from the corresponding alkane stemming from the endothermic nature of the catalytic dehydrogenation step as well their separation from the corresponding alkanes of nearly identical volatility. Ethylene and propylene are also major precursors for a variety of chemicals listed in Fig. 1, including ethylene oxide, ethylene glycol, and propylene oxide. Terephthalic acid production from *p*-xylene is also on the energy-intensive list. Though not on the list, hydroformylations of alpha olefins to produce nearly 4000 kton of linear alcohols or acids are also energy-intensive processes.

Consistent with the theme of the 2013 workshop on supercritical fluids and energy in Campinas, Brazil, this 'perspectives' article highlights integrated approaches in which non-traditional reaction media such as near-critical carbon dioxide and near-critical hydrocarbons may be partnered with conventional organic

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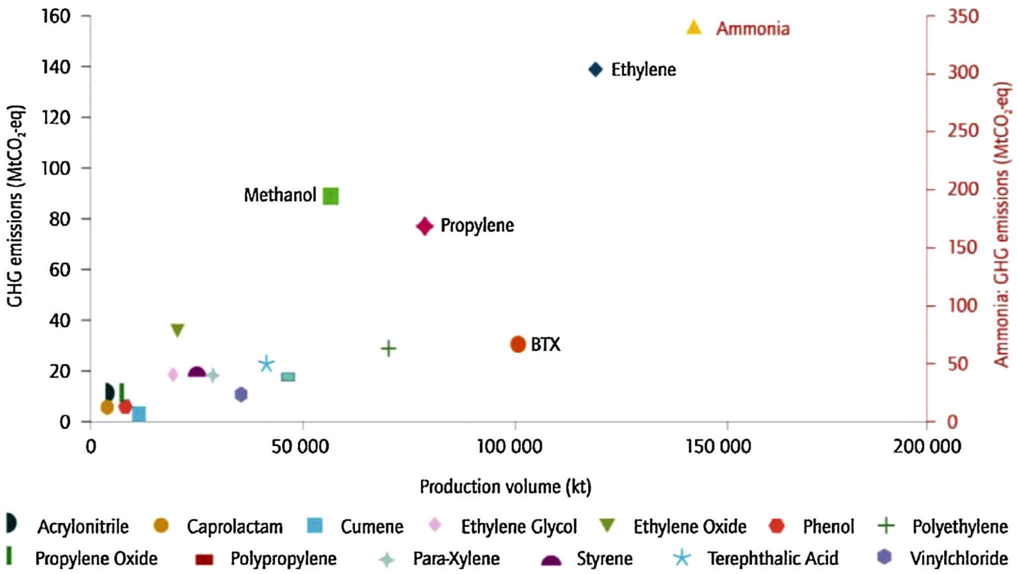

Note: GHG emissions for olefins in this figure represent that of the steam cracking process. Ammonia is presented on a different axis on the right.

Fig. 1. Global GHG emissions of top 18 large-volume chemicals, 2010. Taken from Ref. [3].

solvents and ionic liquids to develop energy-efficient and practically viable catalytic technologies. The reduced energy intensity also decreases GHG emissions from these processes. The focus is on applications that specifically target some of these top-18 chemicals (such as ethylene oxide, propylene oxide, terephthalic acid, hydroformylated olefins). Continuous processing, economic analysis and cradle-to-gate LCA are emphasized to provide insights into the practical viability of the alternative processes and the extent of reduction of energy and GHG emissions. It must be emphasized that there is no attempt to present an exhaustive review of the field. Such reviews are already available [5–16].

2. Benign solvents for multiphase catalysis

The use of alternative solvents in multiphase catalysis may be found in recent reviews [5–8]. Examples of benign solvents include supercritical CO_2 ($scCO_2$) [9], water [10], gas-expanded liquids (GXLs) [11,12], ionic liquids (ILs) [13,14] and switchable solvents [15,16]. Alternative solvents should ideally retain the beneficial aspects of traditional solvents (polarity, catalyst/reactant solubility) while also being environmentally benign. In addition, they should also facilitate energy-efficient separation post-reaction, enhance process safety, and allow operation at mild operating conditions. In general, conventional organic solvents and ionic liquids (ILs) are either selected and/or designed (in the case of ILs) for a particular reaction. The physical and transport properties of single liquid solvents are usually fixed and not easily tunable with moderate changes in pressure and/or temperature. However, when partnered with a near-critical gas (that is typically between 0.7 and 1.3 T_c of the gas at reaction temperature) that is miscible in these solvents, the so-called gas-expanded liquids (GXLs) are generated. As shown in Table 1, gases such as carbon dioxide (CO_2) and light hydrocarbons (such as propylene and ethylene) are between 0.7 and 1.3 T_c at ambient temperature. When CO_2 ($P_c = 72.8$ bar, $T_c = 304.1$ K) is used as the partnering gas, a CO_2-expanded liquid (CXL) results.

The physical and transport properties of near-critical gases are sensitively tuned with pressure. As the gas pressure is increased across its critical pressure, the density becomes liquid-like while transport properties remain intermediate between that of a gas and a liquid [11]. The liquid-like densities enable these gases to dissolve freely in conventional organic solvents, with equilibrium solubilities ranging from a few mol% at relatively moderate pressures to tens of mol% at near-critical pressures and beyond. Such phenomenon is not observed when the gases are far removed from their critical temperature where they behave like ideal gases and, as such, the pressure-dependence of physicochemical properties is not as sensitive. Under such conditions, gas dissolution in the liquid phase is governed by Henry's law and varies linearly with the partial pressure of the gas.

Table 1
Properties of some near-critical gases at ambient temperature ($T = 298$ K).

Gas	T_c (K)	T/T_c	P_c (bar)
CO_2	304.2	0.98	73.8
Ethylene	282.5	1.05	50.4
Propylene	365.2	0.82	45.9

The physicochemical properties of the GXLs are continuously tunable with gas pressure, depending on the extent of gas dissolution in the liquid phase. Upon gas dissolution, the density of the GXL phase decreases, viscosities are lowered and diffusivities enhanced [11]. Table 2 summarizes reported enhancements in such physicochemical properties of GXLs. The miscibility of permanent gases (O_2, H_2, CO etc.) can be uniquely pressure-tuned in GXLs. At similar partial pressure, the permanent gas solubility in a CXL can be higher compared to that in the neat solvent as shown by the positive values of solubility enhancement in Table 2 [17–19]. In certain cases, the gas solubility has been reported to be greater than that of the pure gas at the same total pressure [20,21]. GXLs also possess enhanced transport properties (lower viscosities and higher diffusivities) compared to liquid solvents [22,23].

The enhanced solubilities of gases have been exploited to develop catalytic technologies that eliminate gas starvation in the liquid phase, intensify reaction rates and enhance product selectivity. This article highlights specific examples of how GXLs have been exploited to develop energy-efficient catalytic technology concepts for some of the energy-intensive processes such as