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Polygeneration of fuels and chemicals

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Research advances in the rapidly growing field of polygeneration are highlighted. Although ‘polygeneration’ has had many meanings, the chemical engineering community has overwhelmingly settled on a meaning which describes a process that co-produces at least two products: electricity, and at least one chemical or fuel via a thermochemical route that does not rely on petroleum. The production of syngas is almost always the primary intermediate for energy conversion, but the feeds, products, technologies, and pathways vary widely. However, the choice of the most optimal polygeneration system is highly dependent on circumstance, and often results in systems with only one fuel or chemical co-produced with electricity. Conversely, the synergistic use of multiple types of feedstocks can have important profitability benefits.

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Introduction

In polygeneration, several different kinds of chemical processes are tightly integrated together into one larger process. By doing this, certain synergies can be exploited which makes the resulting process more efficient, more economical, and/or more environmentally friendly than independent, stand-alone processes. For example, in the production of chemicals such as methanol from syngas, there are often waste gases of which only some can be recycled to synthesis reactors and the rest must be purged. For a standalone methanol plant, it makes sense to have very high recycle rates in order to maximize the production of its only product. However, because recycling has diminishing returns, it may make more economic sense to simply recycle less (or nothing!) and instead use the waste gases for electricity production, thus resulting in a plant which co-produces methanol and a net surplus of electricity in large quantities. Or, if a company has a need for several particular different kinds of chemicals or fuels, a polygeneration process which uses the same supply of syngas (a blend of carbon monoxide and hydrogen) to produce all of the chemical or fuel products may make economic sense because the syngas generation steps required for the various products can be integrated all into one. Whatever the case, the idea is to gain some advantage by the integration of the different process sections.

Terminology and scope

The word ‘polygeneration’ is very broad since many kinds of processes can produce more than one product simultaneously (e.g. petroleum refining). Although the idea of co-producing multiple products had been understood for some time, the term ‘polygeneration’ first appears in the open engineering literature in 1982 (to the best of the authors’ knowledge) through studies at NASA [1••] and General Electric [2]. Although those works and almost all other early works focused on systems using only coal gasification, researchers now use the term more broadly to apply to systems which use natural gas, biomass, and nuclear energy. Of all academic literature using the term ‘polygeneration’ (that could be identified) published between January 2013 and April 2015 [3,4••,5,6•,7,8,9•,10•,11•,12,13,14•,15••,16•,17,18,19,20,21,22,23•,24,25,26•,27,28,29,30,31•,32,33•,34,35•,36,37,38,39,40,41,42,43,44,45,46•], none apply it with respect to crude oil, and in every case in which the term is used except one [25], electricity is a co-product.

Two seminal works from 1982 represent the genesis of two different meanings of the term developed over the past three decades. The NASA usage [1••] helped lead to an understanding of the term in the context of two or more co-products in total where one is a chemical or fuel. The General Electric usage [2] helped lead to an understanding of the term in the context of municipal utilities, where polygeneration is the natural extension of well-understood terms such as ‘co-generation’ (electricity and heat), and ‘tri-generation’ (electricity, heat, and cooling). In the latter context, polygeneration typically means a tri-generation system with more utility products such as drinking water, or secondary forms of heat or cold (e.g. steam, refrigeration, air conditioning, etc.). However, the former definition has won over. All works that the authors can identify in the engineering literature which use the term ‘polygeneration’ since 2013 includes at least one chemical or fuel as a co-product in addition to electricity, except for the works of a few research groups [21,28,32,47]. In addition, all research groups except one [9•,20] apply the term to a thermochemical process as opposed to a biochemical one. This represents a shift in the cultural use of 'polygeneration' strongly in favour of the former meaning. Therefore, based on the overwhelming consensus of the terminology in the literature, the authors propose the following definitions for use in chemical engineering contexts:

- **Co-generation**: A process with electricity and heat (usually in the form of either steam or hot water) as products. Also called 'combined heat and power.'
- **Tri-generation:** A process with electricity, heat (usually in the form of either hot water or steam), and cooling (such as air conditioning services or chilled water) as products.
- **Polygeneration:** A thermochemical process which simultaneously produces at least two different products in non-trivial quantities, but is not a petroleum refining process, a co-generation process, or a tri-generation process, and at least one product is a chemical or fuel, and at least one is electricity.

The term also overlaps with the term 'biorefinery', which can be explained as follows:

- **Biorefinery:** A process for converting biomass into value-added products, including electricity, fuels, chemicals, food, and proteins. This can include thermochemical routes such as gasification, or biochemical routes such as fermentation or digestion. See [48] for a review of the term.
- **Thermochemical biorefinery:** A process which is both a polygeneration process and a biorefinery (thus via the thermochemical route).

As a final note, the scope of this review was limited to processes which self-identify as 'polygeneration'. The reader is referred to [49,50] for recent reviews of biorefineries, which include thermochemical biorefineries and hence, polygeneration.

The syngas route

In almost all studies examined in this work, polygeneration utilizes the 'syngas route,' as summarized in Table 1. The general strategy is to first produce syngas of some variety, usually containing a mix of H_2 and CO (the valuable parts), along with wastes such as CO_2 and H_2O (arising through oxidation of fuels), and impurities such as sulphurous compounds. The syngas has to then be modified to balance the molar ratio of H_2 to CO to some optimum value, based on the stoichiometry of the reaction. Typically, slightly more than twice as much H_2 as CO is optimal for most downstream fuel and chemical conversion processes, such as Fischer–Tropsch synthesis, or methanol synthesis. In some cases, an equimolar ratio is optimal, such as in the case of direct DME conversion. Additionally, the syngas must be cleaned to remove CO_2, H_2O, and impurities that may harm catalysts or cause problematic emissions or inefficiencies. However, the order of these steps varies from process to process. Once the clean, 'balanced,' syngas is produced, it can be split and fed to several different synthesis trains in parallel, since they often require very similar syngas compositions. Often, a portion of the unreacted syngas is recycled to the synthesis reactor, depending on the economics of the process. However, nearly always, the remaining off-gas is sent to power generation since syngas has a high heating value, even when it contains a large amount of diluents like H_2O and CO_2. The result is often a large net-excess of power produced arising from this configuration.

Syngas production and balancing

On key characteristic that distinguishes a polygeneration process is the manner in which 'balanced' syngas is produced. Figure 1 outlines a polygeneration superstructure of all processes surveyed in this work. Each box in this figure is optional to some degree, as is many of the feed streams, stream splits, recycle, or stream merges. There are many levels of detail inside each of the boxes which are not shown for simplicity, and not all interconnections between them are shown either. However, the general strategies are prevalent.

Coal and biomass can be converted to syngas through gasification technologies, of which there are many different types. In most cases, this requires the use of high-purity O_2 produced by an air separation process, which is expensive, energy intensive, and a major source of inefficiency. Typically, this produces 'H_2-lean' syngas, meaning that the syngas needs to be upgraded to a higher H_2 content suitable to the desired downstream molar ratio. Common strategies for this include using a water gas shift reactor, blending in high purity H_2 produced by some other means, or blending in 'H_2-rich' syngas which has a high H_2/CO molar ratio, such that the blended mix has the desired balance. Each method has its own special challenges and trade-offs.

Syngas can also be produced by the reforming of natural gas, of which many strategies are possible. Gas reforming strategies differ mostly in the amounts of steam, CO_2, and O_2 which are fed (not all are required), the types of catalyst used, and how heat is supplied since the reforming reactions are quite endothermic. This allows the system designer much control over the H_2/CO ratio produced. For example, it may make sense to either directly produce the appropriate H_2/CO ratio (e.g. about two) in the reformer, or alternatively produce an H_2-rich syngas that can either be blended with something else, or downgraded using a reverse water gas shift reactor. The heat requirement can be provided by placing the reformer in a furnace, direct oxidation inside the reactor, or by integrating with something highly exothermic such as a