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Future Opportunities and Challenges in the Design of New Energy Conversion Systems

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Abstract

In this perspective, an overview of the key challenges and opportunities in the design of new energy systems is presented. Recent shifts in the prices of natural energy resources combined with growing environmental concerns are creating a new set of challenges for process design engineers. Due to the massive scale and impact of energy conversion processes, some of the best solutions to the energy crisis lie in the design of new process systems which address these new problems. In particular, many of the most promising solutions take a big-picture approach by integrating many different processes together to take advantage of synergies between seemingly unrelated processes. This paper is an extended version of a paper published as part of the proceedings of the 8th International Conference on the Foundations of Computer-Aided Process Design (FOCAPD 2014) in Computer-Aided Chemical Engineering Vol. 34 (Adams TA II, Challenges and opportunities in the design of new energy conversion systems, July 2014, pages 5-14).

Graphical Abstract: [none]

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1. Introduction

The current “energy crisis” is the result of the sum of human activity, which essentially is to make and use energy. This crisis is the result of several trends crashing together: the rise in population, the rise in global standards of living (measurable by energy consumption), the depletion of finite energy and water resources, the emission of greenhouse gases, and the sheer massive scale of these activities. Complicating matters are geopolitics, the uneven distribution of resources, social and political opinions, the complexity of global trade, and seven billion people making independent decisions about their own best interests. It is a global problem with no easy solution.

One good approach is the design of new energy conversion process systems. There is a significant need to design new systems which not only take into account recent advances in technology and shifts in resource availability and demand, but also consider sustainability as an integral part of the design methodology. This means that any new candidate process systems should not only be environmentally sustainable, but also economically sustainable, as well as politically or socially sustainable. A process which satisfies all three categories meets what is called the “triple bottom line” of sustainability (Elkington, 1997). In other words, the best processes are those that are a good economic choice for a company to make willingly without overly large government involvement; that have a minimally negative (or even positive) environmental impact; and that the general population is either supportive of or at least not vocally opposed to the activity. Processes that satisfy the triple bottom line are the most likely candidates to help deal with issues related to the energy crisis because they are the most likely to be commercialized at meaningful scales, and they simultaneously are better for the environment than the status quo. Because of the sheer size of many energy conversion processes, even small improvements to efficiency or emissions can have a massive effect when applied to the global scale. This summarizes the grand challenge of the process design engineer.

A convenient way of understanding the energy challenge is to examine the energy return on energy invested (EROEI) for many common energy conversion processes in use today and in the past, as shown in Fig. 1. The EROEI is computed by taking the energetic content of the product delivered divided by the energy required to produce it. Ideally, the energy required for production includes the “cradle-to-gate” energy expenditures along the entire supply chain leading up to the production of that product over the entire life time of that supply chain. This includes the direct energy consumed during regular production of the product, but also the indirect energy consumption associated with aspects further up the supply chain (Poisson & Hall, 2013). This includes transportation fuels required to transport intermediate products from place to place, resource extraction, and the energy consumed during construction, commissioning, and decommissioning of each stage (where significant). The reader is referred to Murphy et al. (2011) for a full description various EROEI methodologies.

For example, in the 1930s, the EROEI of oil production was about 100, meaning that about 100 barrels of oil could be produced by consuming 1 barrel of oil (equivalent) to power the oil pumping and related processes. In the 1970s, this dropped to 30 and is around 14 starting in the 2000s. Unconventional oil is worse, with tar sands and shale oil at 4-5. Essentially, all of the “low hanging fruit” has been plucked, not just for oil, but for all natural resources as reserves deplete, forcing upstream recovery to move to deeper waters and more extreme climates. This is also reflected in renewable technologies, where we are currently developing (quite necessarily) areas such as biofuels and solar thermal to prepare for an eventual low-resource future. Unfortunately, the processes seen as most promising also have the most abysmal EROEIs at just above one (anything below one is mathematically unsustainable for fuel production). We are gradually moving toward lower and lower EROEIs for energy conversion in general, which is why quality process design is such a critical component of the global solution.

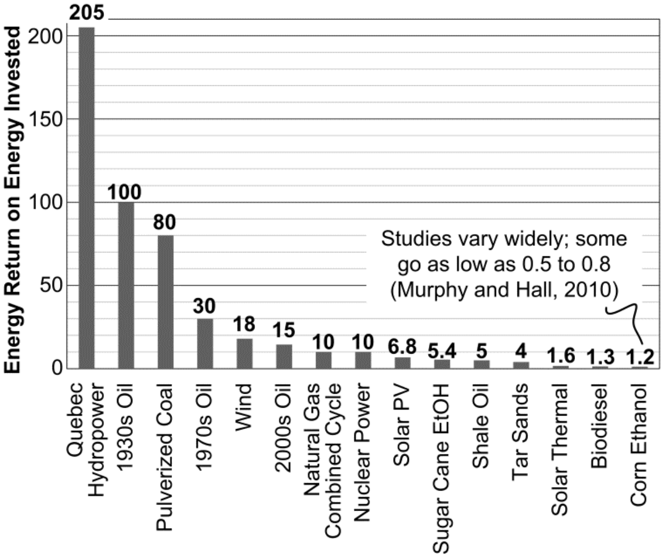

Figure 1: The energy return on energy invested for selected energy conversion processes. Data are approximate and can vary for each specific process and application. All data from Murphy & Hall, 2010, except Tar Sands (Poisson & Hall, 2013), and Hydropower (Gagnon, Bélanger, & Uchiyama 2002).

In this perspective article, a brief overview of the state of natural resources are presented, followed by a discussion of the new design challenges and opportunities that result. Several energy conversion process opportunities are identified which have the potential for significant global impact, either through the design of new processes which take advantage of new or emerging unit operations, or by the innovative integration of existing technologies into new processes. The scope is restricted to thermochemical conversion of non-renewable resources with a North American perspective.

2. What We Have to Work With

2.1 Non-Renewable Resources

It is helpful to examine the current state of our limited resources in order to understand our options for future processes. Recently, a significant price disparity has arisen between oil and gas, as shown in Fig. 2. Prior to the energy crisis of 2008, gas and oil had approximately the same price on an energy-content basis. However, in 2009, discoveries of shale gas reserves and advances in recovery technologies sent a price shock from the sudden new supply of gas. As a result, the oil price is currently 3.2 times the price of natural gas on an energy-content basis (on Nov 26, 2014), even though the price of crude has tumbled by almost $30 per barrel in the past five months. This price disparity is driving a rush of new interest into using natural gas as a raw material to create energy products traditionally produced by oil, which will be discussed in section 4.

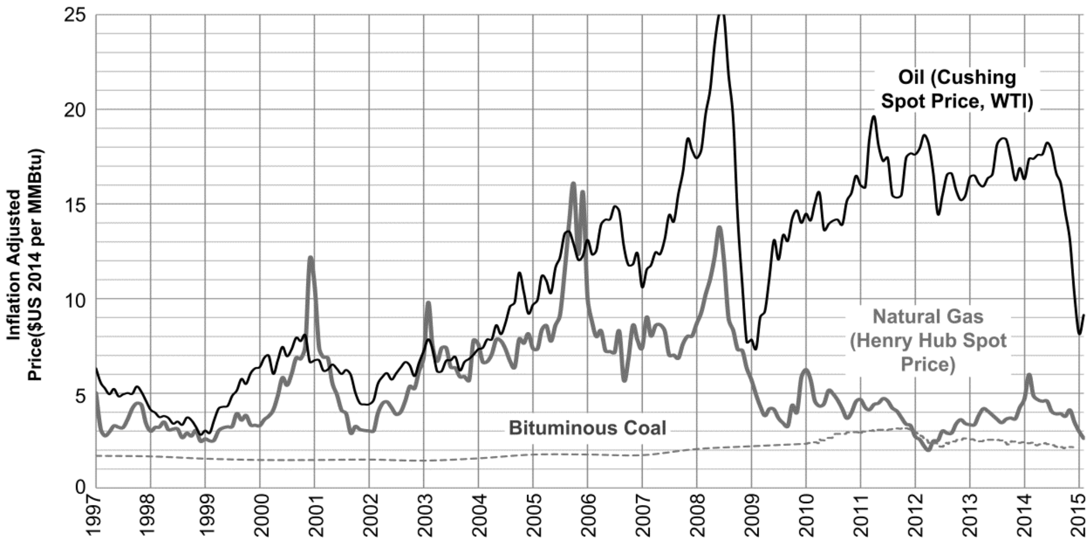

Figure 2: Approximate average US prices of oil (monthly, from EIA, 2014a), natural gas (monthly, from EIA, 2014b), and coal (from EIA, 2013a yearly prior to 2010, from EIA 2014b biweekly after 2010), on an energy basis, adjusted for inflation to January 2014 US Dollars. Data were computed assuming 5.8 MMBtu/barrel of WTI crude and adjusting for inflation using the consumer price index (Bureau of Labor Statistics, 2014). Bituminous coal prices after 2010 use a weighted average of coal prices from the Central Appalachian and Uinta basins to approximate the weighting used to compute prices prior to 2010.

Based on the ratio of reserves to production, there is enough supply of petroleum to meet current demand for 53 years. This number should not be taken literally since it has actually been rising as more oil becomes discovered or technically recoverable. In fact, in 1984, the world oil supply was only at about 35 years (BP, 2014). Nevertheless, as shown in the gradually diminishing EROEI in Fig. 1, oil is becoming increasingly more difficult to obtain as recovery shifts more toward tar sands, deep waters, and polar regions. The quality of oil is also diminishing; the average API gravity refined in the US has steadily declined by about 2° over the past thirty years (Bacon & Tordo, 2005).

Conventional natural gas has a similar supply of about 55 years with almost no change in this number from 1984-2014 (BP, 2014). However, technically recoverable shale gas reserves are roughly just as large (EIA, 2013b), bringing the total combined reserve to around 109 years at present usage rates. Moreover, the future of fossil methane will not likely end there, since there could be as much as 10×10^{12} t of carbon (as CH_4) locked into gas hydrates located deep in rock beds offshore and in polar areas (Hester & Brewer, 2009). Although it is not yet economical to unlock these deposits, it makes sense to transition toward an increased use of gas now, expecting to eventually replace the conventional and shale gas sources with gas hydrates.

Coal is cheap and available, with a 113 year world supply (BP, 2014). For the range shown in Fig. 2, the cost of bituminous coal has essentially always been cheaper than oil or gas on a per-energy basis by a significant margin, and enjoys a much reduced variability. Despite the lower fuel prices, coal-based processes are generally much more expensive in terms of capital due to the difficulty of solids handling, contaminants, and higher carbon content per Joule, which results in generally more CO_2 produced than gas in most cases. Nevertheless, despite the dirtier nature of coal, several new energy conversion processes have the potential to use coal wisely such that all three aspects of the triple bottom line are satisfied.

Uranium, a non-fossil but non-renewable resource, is also relatively abundant in economic quantities, with about an 80 year world supply and rising (World Nuclear Association, 2012). Although its primary (peaceful) use is for electricity production and growth in this area is slowing, it is possible that new energy systems will be able to economically exploit its energy content for other forms of energy production, which is discussed in section 4.3. Similarly, thorium is about three times as abundant as uranium, and may be used as well, though this has not yet been widely commercialized (World Nuclear Association, 2014).

2.2 Renewable Resources

Theoretically, renewable solar resources (which include wind, biomass, and hydroelectric) may be able to provide for all current world energy needs of about 17 TW for all sectors including electricity, heat, industry, and transportation, (de Castro et al., 2011). Although estimates vary widely, wind energy could supply as much as 38 TW (de Castro et al., 2011), hydroelectric up to 1.6 TW, and direct solar (photovoltaic and concentrated solar thermal) as much as 580 TW (Jacobson & Delucci, 2011). Although this means it is still possible that humanity can exist at its present size and standard of living using only renewables, this will not be possible for many decades. For example, even though it is growing very quickly (about 25% annually), only about 0.05 TW of wind energy is in use today, meaning that it will take 15 years to reach just 1 TW (de Castro et al., 2011). Direct solar sources have more potential but come with the negative impact of blocking the light from whatever hopes to live underneath. However, at present, the combined total production by wind, solar, and hydroelectric makes up only about 3% of the total world energy use.

Biomass will also play an important role, but with a significant trade-off as growing biomass for energy purposes too often competes directly with food and wildlife for land, with many resulting unintended consequences. Sustainable forestry and sustainable agriculture techniques can be used to limit these effects, but such development is ongoing and the trade-off can never be completely prevented. However, using energy from biomass waste sources, such as pulp and paper industry wastes, municipal solid wastes, or discarded food products has the distinct advantage of very limited competition with land and wildlife. For example, one can convert waste cooking oil from deep fryers at restaurants into a useable fuel (Zhang et al, 2003), and it makes little sense to grow potatoes just to collect the waste oil from making fries. In fact, a secondary environmental benefit may be realized from diverting waste biomass away from landfills or treatment centres. Although helpful, the total potential global energy production from waste bioenergy is estimated at about 0.5 TW, or only about 3% of current global energy use (Gregg 2010).

This illustrates the grand challenge for the energy conversion systems community. We must develop new and better processes which use our non-renewable resources in a more efficient and environmentally friendly way so that we can safely and affordably transition to a fully renewable world within the next century. We can do this by developing new systems which incorporate existing and/or research-level technologies which provide energy while satisfying the triple-bottom-line of sustainability, and by identifying and developing new technologies or chemical unit operations (that do not exist yet) which enable better systems. Some areas of opportunity for these are discussed in the rest of this article. Eventually, we will have to figure out how to meet world energy needs perpetually on a fixed upper bound renewably supply of about 620 TW.

3. Design Opportunities in Electric Power Generation

3.1 Post-combustion CO_2 capture

Some of the most near-term opportunities for power generation are in the area of solvent-based CO_2 capture from traditional power plants (either pulverized coal or natural gas, see Wang et al., 2011 for an extensive review). Typical flue gas exhaust contains a high concentration of nitrogen and a comparatively small concentration of CO_2, despite the massive quantities of CO_2 produced from fossil fuel combustion. This results in a CO_2/N_2 separation problem, which is very energy-intensive to overcome. Amine-based systems using solvents like monoethanolamine or diglycoalamine/morpholine mixtures can be effective, although many other kinds of solvents can be used (Adams, Nease, & Khojestah Salkuyeh, 2014). Solid sorbents, often amine-based are also a possibility, and an area of active research.

Finding better ways of CO_2 capture from flue gas has important near-term implications because it can be retrofitted (in theory) to most of the existing power plants in use today, as long as the associated CO_2 transport and storage mechanisms are provided. Indeed, the first major scale implementation and regular operation of carbon capture and sequestration went online in 2014 at a SaskPower coal-fired plant in Saskatchewan, Canada (SaskPower, 2014). It uses Shell's proprietary amine-based CANSOLV process retrofitted to the plant, with the CO_2 sent for enhanced oil recovery.

Although post-combustion capture is quite useful for the retrofit of existing plants as in this case, the design of the system itself is fundamentally quite poor as far as low-CO_2 power production is concerned because the CO_2/N_2 problem will always exist. Small improvements achieved from advances in better solvents and sorbents for CO_2/N_2 separation are important for the near term because they will help reduce the energy penalties for these retrofit cases, and there is no shortage of existing power plants that could benefit. However, to make substantial gains, any new power plants that are constructed with the purpose of low-CO_2 power from fossils need a complete system level redesign to specifically avoid the CO_2/N_2 problem. Four up and coming technologies that do this are presented in the remainder of this section. These technologies, particularly the last three, are the areas which provide some of the best future opportunities in energy conversion system design.

3.2 Integrated Coal Gasification Combined Cycles

Coal gasification can be used in the integrated gasification combined cycle (IGCC) power plant, shown in Fig. 3 (see Weil, 2010 and Sahraei et al., 2014 for detailed reviews of IGCC). The general strategy is to gasify coal into syngas (a mixture of CO, H_2, H_2O, and CO_2), convert it to a mixture of H_2 and CO_2 using the water gas shift reaction and a variety of cleaning steps, remove about 90% of the CO_2 via a solvent-based process, and then combust the H_2 in a gas combustion turbine. CO_2 can be pipelined for use in enhanced oil recovery or CO_2 sequestration. With this strategy, the CO_2/N_2 separation problem has been avoided and replaced with two smaller problems: O_2/N_2 separation from air, and CO_2/H_2 separation from syngas. However, this is more efficient than traditional coal combustion with CO_2 capture but only somewhat less expensive (NETL, 2007). However, there remain some serious implementation challenges such as the multi-billion dollar capital cost, the uncertainty in CO_2 sequestration technology, and social opinions discouraging the use of coal in general.

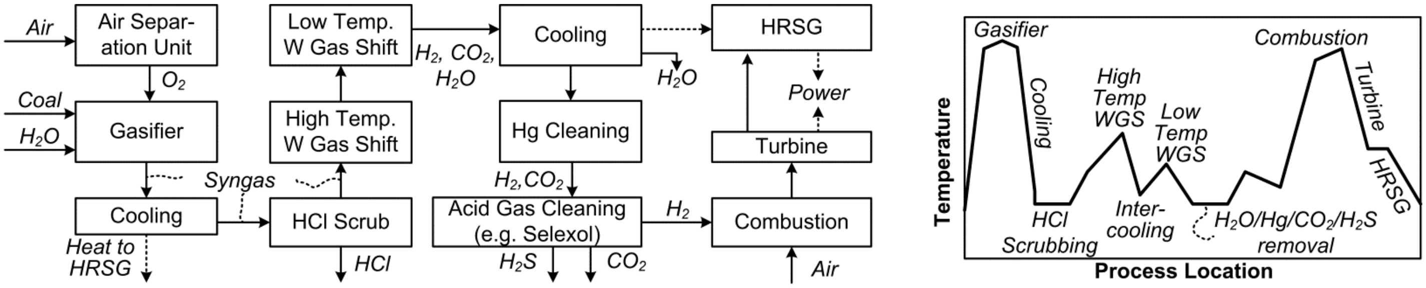

Figure 3: (left) Brief overview of the IGCC process. (right) Temperature profile of the process gas. See Field and Brasington (2011) and NETL (2007) for process examples and stream data.

Many of these challenges arise from the poor exergy efficiency of IGCC, due partly to the fact that the system temperature rises and falls frequently and significantly throughout the process, as sketched in Fig. 3 (right) for one example process. Therefore, the greatest opportunities for improvement lie in the design of gas clean-up processes (removal of HCl, H_2O, Hg, CO_2, H_2S) that can be operated at more uniform and higher temperatures. This problem is known as “warm syngas cleanup". In addition, there is a significant amount of energy lost through the production of the high purity O_2 required in the gasifier. The development of more efficient ways of obtaining the necessary O_2 would provide some useful improvements, with ionic transport membranes (Shelly, 2009) and ceramic autothermal recovery (Gray, Salerno, & Tomlinson, 2004) technologies being the most promising. However, these are not yet mature, and while they would help increase the efficiency of the process, the system-level problems associated with syngas cleanup and absorption-based CO_2 recovery remain.

3.3 Chemical looping combustion

In CLC, gaseous fuel is combusted using a metal oxide instead of air as shown in Fig. 4a (see Fan et al., 2015 for an extensive review)..Solid metal particles (such as Ni or Fe) are oxidized in air, forming metal oxides which are separated out of the exhaust via a cyclone. The metal oxides are then reduced via a reaction with natural gas or syngas, separated by gravity, and recycled. Both reactors operate at high pressures and are exothermic; the resulting high pressure air exhaust spins a turbine for electricity, and waste heat from both exhausts power a bottoming cycle for the generation of additional power. The fuel exhaust stream contains only H_2O and CO_2, which can be separated relatively easy via a condensation-based process. The concept can be applied not only for electricity (Adanez et al., 2012) but also for H_2 production (Cormos, 2012) or coal gasification (Tong et al. 2014).

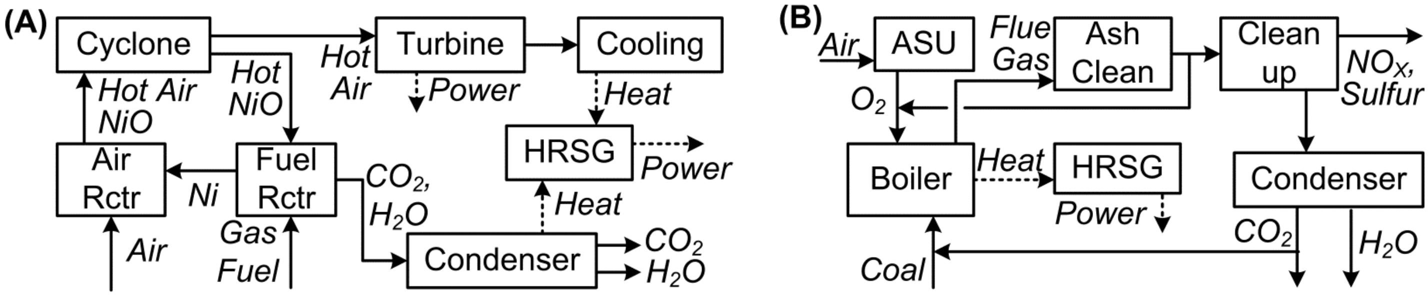

Figure 4. Simplified sketches of (a) CLC for natural gas or syngas, (b) the coal oxyfuel process.

In this way, the CO_2/N_2 separation problem has been transformed into a metal oxide/N_2 separation problem and a CO_2/ H_2O separation problem. The first two steps together require low energy consumption since gas-liquid separations in a cyclone are quite efficient. Similarly, the CO_2/H_2O separation problem requires less energy than solvent-based CO_2/N_2 separation by roughly an order of magnitude. Although this means that high efficiencies can be realized, many other system level challenges remain associated with solids handling and heat management issues.

3.4 Oxyfuel combustion

Oxyfuel combustion is similar to traditional coal or natural gas combustion, except that the fuel is combusted in the presence of high purity O_2 instead of air, as shown in Fig. 4b (the reader is referred to Scheffknecht et al., 2011 and Habib et al., 2011 for detailed reviews). The heat produced is used to generate steam for a steam power plant. The waste products are, again, primarily CO_2 and H_2O for low-cost separation. Thus, this plant transforms the CO2/N2 problem into an O_2/N_2 separation problem and a CO_2/H_2O separation problem. However, the primary disadvantages of oxyfuel combustion are the very high energy requirement for producing high purity O_2 (since significantly more O_2 is needed per kg of coal than IGCC), and the very high temperatures produced by combustion in a pure oxygen environment. As a result, the flue gas or CO_2 must be recycled in large quantity to keep temperatures at reasonable levels. Current predictions show that it is at present only economical (compared to IGCC) to reduce CO_2 emissions by about 90% using this technique (Hadjipaschalis, Kourtis, & Poullikkas, 2009). A 90% capture rate is the goal of FutureGen 2.0, the first large-scale oxyfuel combustion and carbon sequestration project that began construction in 2014 (Folger, 2014). However, future improvements in materials and process designs may allow very high capture rates, especially regarding the air separation unit.

3.5 Solid oxide fuel cell systems

SOFCs are high temperature fuel cells that transport $O^{=}$ ions through a solid electrolyte. Since fuel is electrochemically oxidized, the cell is not thermodynamically limited to a Carnot cycle and thus has a high electrical efficiency. The electrolyte also acts as a N_2/O_2 separator, providing N_2-free oxidation of many kinds of gaseous fuels. From a systems perspective, the ability to have separate anode and cathode exhaust streams is beneficial because, after a fuel completion step, the exhaust gas consists of just CO_2 and H_2O which can again be separated with low energy expenditures similar to CLC and oxyfuels. A simple example is shown in Figure 5 (see Adams et al., 2013 for a review). As an extra benefit, the cathode exhaust can be integrated with compressed air energy storage systems, allowing for zero emissions, high-efficiency “peaking” power using either natural gas (Nease & Adams, 2013) or coal (Nease & Adams, 2014). As in the oxyfuel case, the SOFC approach transforms the CO_2/N_2 separation problem into an O_2/N_2 separation problem and a CO_2/H_2O separation problem, similar to the oxyfuel case. However, no cryogenic air separation techniques are required for the O_2/N_2 separation since it occurs in the SOFC, resulting in a high efficiency.

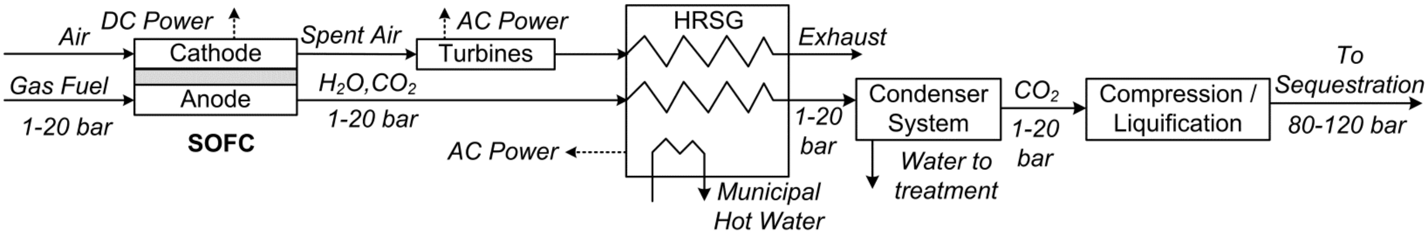

Figure 5. An example SOFC power generation system with 100% CO_2 capture. Heat recovered in the HRSG can be used for the generation of process steam, steam for turbines, or municipal hot water or heating as desired. SOFC and fuel pressures can theoretically operate up to 20 bar (pressure drops not shown for brevity).

3.6 Environmental benefits for advanced power generation systems

The chemical looping, oxyfuel, and SOFC systems share some common traits in terms of their potential environmental benefits. For example, these systems can capture a significant amount of water; a 700 MW coal-based SOFC system can actually <u>produce</u> 1 GL/y of high-purity water, compared to IGCC which would consume 1.6 GL/y (using dry cooling tower technology for each (Adams & Barton, 2010)). Note that each of the three advanced systems has near-zero CO_2 emissions whether the fuel is natural gas, coal, or biomass. For biomass, this means that a biomass-driven process which includes CO_2 sequestration would actually have net-negative CO_2 emissions when factoring in the entire lifecycle, since the net effect is to remove CO_2 from the air (via photosynthesis) and eventually sequester it in the ground.

Since these three systems can have very low CO_2 emissions, the majority of emissions will arise from upstream resource recovery and transport. On average, producing and transporting natural gas actually has about 2.3 times the global warming potential than mining and delivery of coal per unit of energy delivered (NETL, 2011). This is due in large part to gas flaring (see section 4.5) and CH_4 leaks during gas production and pipelining, and because CH_4 has 7.6–72 times the global warming potential of CO_2 per mole (typically 25 is used, (Forster et al., 2007)). This aspect is often neglected, but is starting to gather attention. For example, a recent joint academic/government study considering new CH_4 leak data concluded there is no clear GHG benefit to the environment by replacing gasoline with natural gas, while replacing diesel with natural gas may actually be worse (Brandt et al., 2014).

Although the global warming potential of system lifecycles (or at least the gate-to-gate portion thereof) is now increasingly considered as a part of a system design analysis, other environmental impacts such as acidification, eutrophication, photochemical oxidation, resource depletion, ecotoxicity, water depletion, and human toxicity are much less commonly studied, especially by the process systems engineering community. In fact, in many cases, a system designed to decrease the global warming potential by using a CO_2 capture strategy may end up causing additional damage in the other categories.

For example, several studies have shown that for traditional natural gas power, adding solvent-based post-combustion CO_2 capture might reduce the total cradle-to-grave lifecycle global warming potential by 50-75% but increase all of the other categories by roughly 10-50% (Zapp et al, 2012). The cumulative impact of the other categories may significantly offset the reductions in global warming potential, meaning that the total environmental impact is only somewhat reduced (Nease & Adams, 2015) or possibly even worse than business as usual

(Petrakopoulou & Tsatsaronis, 2014). IGCC shows a similar behaviour in most studies, where the use of IGCC with pre-combustion capture is worse than the status quo in most categories except global warming potential (Schreiber, Zapp, & Marx. 2012). Although results vary widely from study to study, there is a general agreement that the severe energy penalty associated with CO_2 capture causes other significant environmental impacts throughout the entire supply chain.

However, the three advanced power systems show more promise, with oxyfuel reducing impacts compared to the status quo in most categories (Zapp et al, 2012), and SOFC systems reducing impacts in all of them (Nease & Adams 2015). The benefits of chemical looping are less clear and less well studied, but in general there appears to be some overall environmental benefit compared to the status quo (Petrakopoulou & Tsatsaronis, 2014). In the end, it is not clear which of these power generation options are the best, considering the balance of technical, economic, or environmental issues. However all three show great promise for a more sustainable, long term future use of fossil fuels.

Overall, multi-impact cradle-to-grave life cycle analyses (LCAs) of these and many other energy conversion processes are rare and inconsistently applied. Similarly, systems engineers too often focus on local system level development without looking at the bigger environmental picture, either neglecting environmental impacts altogether or looking only at global warming potential (the author is often guilty of this as well). Therefore, this is one major area of opportunity for the systems community because there is a great need for big picture LCA studies to accompany each potential energy conversion system or associated technological innovation to determine if the concept is ultimately worth pursuing, and how much impact it could have.

4. Design Opportunities in Fuels and Chemicals

4.1 Natural gas and shale gas processes to replace petroleum

With the new, sustained price gap between oil and gas (Fig. 1), there is now a great incentive to re-examine synthetic petrochemical processes. For example, the Shell middle distillate synthesis process converts natural gas into syngas with an appropriate H_2/CO ratio and then converts syngas to synthetic gasoline and diesel using a Fischer-Tropsch catalyst (Leckel, 2009). Gas-derived syngas can also be used to produce methanol, which may be converted to dimethyl ether (a clean-burning diesel substitute), gasoline, olefins, or simply used as a fuel or stock chemical. Methanol can be pipelined, so there are potentially significant environmental opportunities by producing methanol near shale gas wells and pipelining it to distant refineries, thereby avoiding CH_4 leaks from gas pipelines and compressor stations, thus potentially reducing lifecycle GHG emissions. This has not been well-explored to the best of my knowledge. The production of olefins such as ethylene (a major precursor to the polymers industry) from gas-derived methanol is particularly promising but often overlooked. However, in many cases, the biggest opportunities lie in integrating fuel and/or chemical production with power production in a polygeneration system. (Khojasteh Salkuyeh & Adams, 2014), as shown in section 5.

4.2 Integrated resource systems with coal and gas

It is possible to get efficiency and environmental benefits by designing processes which integrate two or more fuels together. For example, coal gasification is exothermic and good for producing syngas with a low H_2 content, while natural gas is endothermic and good for producing H_2-rich syngas. Most liquid fuel synthesis routes from syngas, however, require H_2/CO molar ratios between the H_2 contents of the syngas derived from either fuel. Traditional routes using only one resource require extra steps which either upgrade the H_2 content by adding steam (for coal), or by increasing the CO content by adding CO_2 or O_2 (for gas), each with an energy penalty. Instead, syngas from both coal and gas can be used without modifying the H_2 or CO content by blending the syngas streams to achieve the right balance, thereby avoiding those energy penalties. In many cases, this is economically preferable as well (Adams & Barton, 2011). Even higher efficiencies are possible by directly integrating the two, using the heat produced from coal gasification to drive the endothermic gas reforming reaction (Ghouse & Adams, 2014). There are many opportunities for design advances since this concept is relatively new and could be integrated with a great variety of processes.

4.3 Integrated systems with nuclear energy

With plentiful domestic supplies of uranium, it makes sense to exploit it for chemical production in addition to electricity, assuming that social acceptance and related cost challenges can be surmounted. For example, H_2 could be produced through electrolysis and then either used as a fuel or mixed into coal-derived syngas to achieve a blend suitable for Fischer-Tropsch synthesis. Alternatively, newer high-temperature reactors such as the modular helium reactor or molten salt reactor could be used to provide the endothermic heat required for natural gas reforming, which can then be used to produce fuels or chemicals. Such an approach avoids fossil fuel combustion for process heat purposes. Depending on the system, using nuclear energy as the heat source for synthetic fuel processes can help result in a remarkable 79% reduction in process CO_2 emissions (even without CO_2 capture) compared to traditional synthetic fuel production strategies using coal. An interesting result is that about 20% of the energy contained in the diesel/gasoline product originates from the uranium (Khojestah Salkuyeh & Adams, 2013). This provides a new way of exploiting uranium reserves for the export of energy products without proliferation concerns. This area has many opportunities for the design of new processes since it can be applied to many different applications.

4.4 New applications of petroleum coke

Petroleum coke or “petcoke” is a waste product from the refining of heavy crude oil. As mentioned previously, the supply of light crudes is diminishing with heavy crude refining growing rapidly, especially in Canada where the oil sands industry has been experiencing explosive growth. As a result, the production of petcoke is about 150 million tonnes per year and is expected to grow by another 46% by next year (Murthy et al., 2014). Petcoke is potentially very useful because it has a high energy content, but unfortunately it often also has a high sulphur and vanadium content. As such, petcoke combustion is greatly limited or restricted by environmental regulations in many areas. In fact, Canada’s oil producing province of Alberta requires oil sands facilities to stockpile their petcoke in anticipation of future processes which might be able to unlock the energy stored within in an environmentally acceptable way (Government of Alberta, 2008).

Although petcoke has a high carbon content, it is a waste product, and so using it for energy conversion has the potential to actually yield significant environmental benefits. Whereas the status quo is to dispose of the waste, using it to make fuels helps to mitigate the use of other fossil fuels, thus having a net benefit to the environment. Our rough estimates show that if the petcoke wastes produced from a traditional Canadian refinery were gasified and converted to

Fischer-Tropsch liquids, the hydrocarbons produced would be sufficient to increase the output of the refinery by around 1-3%. Alternatively, for the same production rate this would reduce crude oil consumption by roughly 300,000 – 1,200,000 barrels per year per major refinery. Although a 1-3% reduction in crude oil consumption will not solve the energy crisis, when applied at the global scale it can certainly provide an important contribution.

Therefore, this is an excellent opportunity for the development of new processes. It is not yet clear what the best strategies for petcoke utilization will be. Gasification will most likely be the key enabling technology, which can be used in a way similar to coal. Petcoke or mixtures of coal and petcoke can be gasified into syngas, which can then be used for electricity, synthetic fuel, alternative fuels, alcohols, ethers, olefins, or any of the myriad of integrated process options that result from syngas production. Petcoke is very carbon intensive, so in most cases hydrogen upgrading will be needed, such as with natural gas reforming, water gas shift reactions, or the injection of H_2 arising from electrolysis or other methods. There are currently ten active petcoke gasification plants using a variety of gasification technologies (Murthy et al., 2014), so there is enough experience to expect sufficiently rapid adaptation in the future.

4.5 New applications in flare gas

Gas flaring and venting is currently a common occurrence during oil production, where unwanted associated gas with some energy content is flared or released because it cannot be captured economically. This practice causes considerable environmental damage since it releases particulate soot, sulphur dioxide, methane (which has a global warming potential roughly 25 times worse than CO_2 per pound depending on the metric), and lots of CO_2 itself, with up to 281 million tonnes per year released worldwide (Johnson & Coderre, 2012). This is a significant portion of emissions: for example, flaring and venting accounts for over 2% of Alberta's total CO_2 emissions (Hussain et al, 2014). Although 2% may seem small, when compounded globally, reduction efforts in this area could make an important impact.

This occurs because capture and conversion of the flare gas is usually not economic, despite its energy content. Although the sum total of flaring worldwide is quite large, flaring at individual sites is relatively small compared to the recovered product, and collection and transport of the gas spread out over a vast area can be quite expensive, especially where infrastructure is scarce. Developing nations are particularly susceptible to this problem. As a result it is quite difficult to make a business case for converting the collected gases into a saleable product (Johnson & Coderre, 2012). For example, if one were to invest in a gas-to-liquids plant (see section 4.1), it would be significantly less risky and probably more profitable to make such a plant using conventional pipeline natural gas instead of flare gas. Therefore, there is a significant opportunity for process engineers to come up with better systems that can exploit this waste resource in a more cost effective way. A large part of the problem is at the systems level, where the best solutions are likely to involve changes along the entire supply chain of the flare gas, and will likely also require synergies with the associated petroleum and gas recovery supply chains as well.

5. Design Opportunities in Polygeneration

5.1 Polygeneration for co-production of chemicals and electricity

Many liquid fuel production processes produce high-energy waste gases. For example, this often results from incomplete conversion of various catalysts which convert syngas to hydrocarbon liquids, alcohols, and olefins. The unconverted gases (“off-gases”) can only be partially recycled due to limits on reactor feed concentration or the buildup of inert species. Traditionally, these purged gases are combusted for either heat or power production and can be a major source of direct CO_2 emissions. However, this purge stream can be used as a fuel for one of the three advanced power generation systems described in section 3, and the waste heat from power production is used for the heat needs of the fuel section. As a result, it is possible to design a completely self-sufficient polygeneration process from fossil fuels (meaning no energy utility imports) with nearly zero direct process CO_2 emissions. In addition, the co-production of power often helps the profitability of a process. For example, due to diminishing returns, it may be more economical to avoid the recycle of unreacted reagents entirely and instead co-produce electricity in about equal amounts as chemicals. This has been proposed for chemical looping (Khojestah Salkuyeh & Adams, 2015a) and SOFC systems (Adams et al., 2013) for various products and scenarios. However, there are many opportunities for discovery since there are many potential applications which are still unexplored (See Floudas et al. 2012 for an extensive review).

There is also substantial growth potential in this area for small scale applications as well. For example, there is a rising interest in mobile technologies which can co-produce chemicals and electricity. One such application is in the conversion of shale gas or flare gas into useful products. Mobile applications are particularly relevant because many flare gas and shale gas sites are distributed, remote, and in small quantities. In addition, because production changes over time, the amount of useful gas from one particular drilling site may deplete after only a year or two in some cases.

Rather than constructing pipelines and transportation infrastructure to each of these locations, mobile “polygeneration on a truck” facilities can be driven to the sites where they recover and convert recovered gases into other energy products. They can then be redeployed to new locations once production depletes. For example, ChemBioPower is producing mobile facilities which co-produce electricity and dimethyl ether from natural gas (Anselmo & Sullivan, 2014). Pioneer Energy (USA) is also developing mobile polygeneration systems which co-produce electricity and methanol (Hussain et al., 2014). In either approach, the electricity and some of the fuels can be used locally for wellhead operations, which may have some secondary value associated with the difficulty of providing remote wellhead operations with energy in the form it is needed for operation. Similarly, both methods can be used to reduce transportation costs associated with product recovery of waste gases by converting gases to chemicals which are less costly to transport. In either case, the co-production of electricity and fuels is an important for the economics of the system, which is often more economic than just the fuel production.

5.2 Polygeneration for the flexible co-production of products

One key potential advantage is the exploitation of market variations by changing feedstocks and/or products to respond to yearly, seasonal, or even daily market prices and demands. One way is to produce syngas at a steady rate, then divide it between different processing trains depending on market prices, whether it be fuels, chemicals, or power. Again, off-gases can be diverted to one of the three advanced power generation systems to achieve near-zero process

CO_2 emissions for any product portfolio (Fig. 6). However, this is quite complex since it involves many unit operations integrated together dynamically, with interactive effects that may not even be foreseeable until actual construction. It is not yet clear how much flexibility can actually be implemented; experimental flexibility studies of SOFC systems show that the change in fuel quality that can be tolerated as a result of dynamic shifting is limited by several complex factors (Harun, Tucker, & Adams, 2014). There are also many design challenges going forward, since many of the dynamic models necessary to simulate flexible plant performance do not exist. Even so, simulating and optimizing the dynamics of the entire plant in detail can be difficult if not impossible given current computational power. However, the potential rewards may be significant enough to justify working on this challenge; in one flexible coal-and-biomass-to-liquids polygeneration study, a 50% daily flexibility in process capacity could provide a 17% net present value increase, with up to a 62% increase in value with complete flexibility (Chen et al., 2011). Another study which also considered coal-and-biomass-to-liquids through different routes found similar results, concluding that even in current market prices, a flexible facility which was able to exploit changes in electricity price by varying product portfolios on an hourly basis was more profitable than a stand-alone, static plant (Meerman et al, 2012).

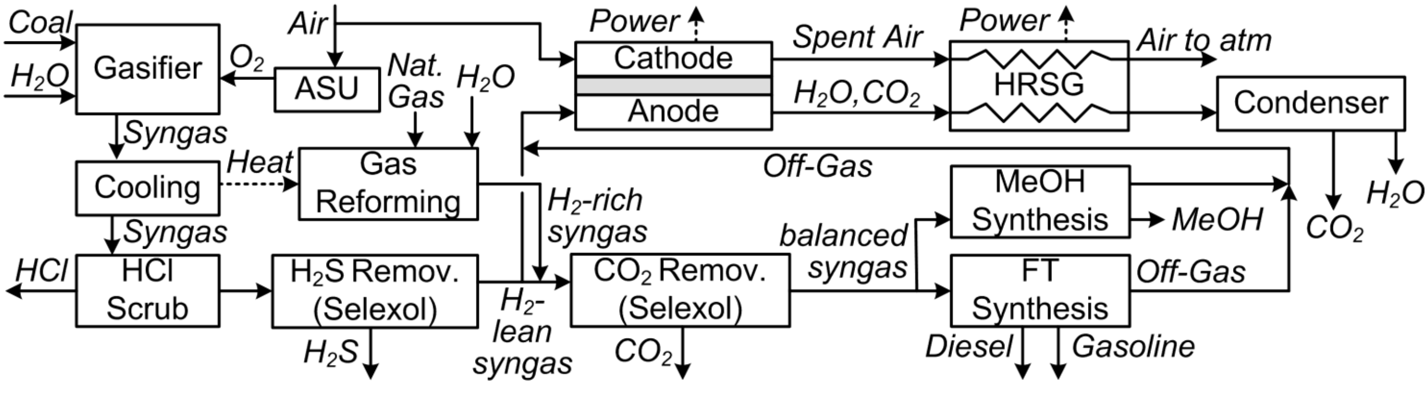

Figure 6. An example simplified process using SOFCs to co-produce power and fuels with zero direct CO_2 emissions, using both coal and natural gas. Based on Adams et al. (2013).

5.3 Barriers and challenges in polygeneration

Although the proposed systems suggested in this perspective look very promising from a theoretical and technical perspective, some significant challenges associated with the societal/political aspect of the triple bottom line of sustainability need to be overcome before widespread adoption can take place. One key issue is that the more kinds of systems are integrated together, the more involvement by government regulations and regulatory agencies are required. In some cases there may be little to no experience or precedent for these agencies to work together, which could create logistical or bureaucratic issues in terms of getting the necessary licenses and permits.

For example, a company that has experience in natural gas reforming may not want to consider the addition of a nuclear reactor to improve the process despite the potential technical and economic benefits, because of the additional overhead and challenge to that company associated with a new relationship with a nuclear regulatory agency. Similarly, a company which will now be co-producing electricity in large quantities for sale to the grid in a flexible way, may find barriers in the way electric grids are regulated, power contracts are handled, and the perpetual bidding systems that can take place several times every hour. Or, a company which is in the business of producing one class of chemicals may not want to consider the co-production of a different class of chemicals if the company has little experience in the new safety, training, and regulatory issues that might result. Furthermore, it can be difficult for a company who may want to co-produce something that requires them to sell it to markets in which they have no brand presence, experience, or relationships. And finally, community opposition to any major novel chemical process may present its own challenges, as is the case with the FutureGen 2.0 project in Illinois (Zeman, 2014 and Talbot, 2014),

Another challenge with polygeneration systems is that market conditions can significantly affect the business choices around which the "best" processes can be made. Many studies have highlighted this for a variety of applications, such as polygeneration systems which co-generate Fisher-Tropsch liquids and methanol products (Adams & Barton, 2010 and Khojestah Salkuyeh & Adams, 2013), i-butene and ethanol (Martín & Grossmann, 2014), methanol and dimethyl ether (Khojestah Salkuyeh & Adams, 2014), and olefins and fuels (Khojestah Salkuyeh & Adams, 2015b), each with electricity as an additional major product. In each of these cases, the average lifetime market prices of the products strongly impacted the optimal product portfolios, such that the optimal balance of co-products can change significantly. The impact of the oil price can have an equally important effect. For example, high oil prices make the alternative strategies presented in this perspective look more attractive, whereas low oil prices favour the status quo, and due to the strong influence of the oil price on world economies, it can be a very powerful influence. Thus, there is a considerable risk associated with the speculation of what future market prices will be over the long term.

In order to help overcome these challenges, process system engineers can demonstrate that the added value obtained by the extra complexity is sufficiently large enough to offset the costs of overhead, bureaucracy, and uncertainty/risk associated with it. In addition, by working closely with those involved in the non-technical and business side of the process, engineers can attempt to incorporate these issues during the synthesis phase of the design.

6. Future challenges and opportunties for CAPE tools

Most of the computer-aided process engineering (CAPE) tools in existence today are intended for use with specific areas of application. However, in order to achieve the grand challenge put forth in this perspestive—that is, the design of more sustainable chemical processes which help improve the triple bottom line—this requires expertise across a wide range of disciplines and applications ranging from very big picture society-level impacts to very detailed unit operation simulations. As a result, the process system engineer's task is to conceive of a process, design it, simulate it, improve it, optimize, it, study it, evaluate its economics, determine the effects of its uncertainty, understand its links to politics and society, and assess its life cycle impacts on the environment. These steps are often achieved in stages using different CAPE tools over a relatively long period of time.

Existing chemical process simulators such as Aspen Plus, Pro/II, ProMax, gProms, ChemCADm and Aspen HYSYS do a very good job of allowing the engineer to combine many of these steps, such as providing the linkages between steady-state and dynamic simulations, and the incorporation of detailed capital and utility cost estimates. However, there is little available within the existing suite of commercial software to connect the results of simulations with life cycle analyses (LCAs) in an impactful way. Some software has acknowledged the growing interest in environmental impact studies. For example, Aspen Plus has features which make accounting for CO_2 emissions and energy streams easier by allowing the user to map CO_2 emissions associated with commonly used utilities. The WAste Reduction (WAR) algorithm, which can be used to assess the relative potential environmental impacts of emissions released by a chemical plant can be used in ChemCAD or via any CAPE-OPEN interface, or imported from Aspen Plus into a stand-alone softare package (US EPA, 2011). The Environmental Fate and Risk Assessment Tool (EFRAT) performs a similar function within Aspen Hysys by identifying potential environmental impacts associated with emissions from the plant or accidental releases of chemicals contained within (Shonnard et al.). While these are very useful tools, their intended purpose is limited to the scope of the simulation, which is typically restricted to the local process. Thus, these features are not intended for use in big-picture cradle-to-grave LCAs, and contain no easy connectivity with common LCA software or tools such as GaBi, SimaPro, GreenScope, or OpenLCA. Additionally, they each are limited to certain subsets of environmental factors and methodologies.

There is a rapidly growing community of academic, industrial, and government researchers who are building life cycle inventory databases of many common steps in industrial supply chains. LCA software takes advantage of these databases by making it relatively fast and easy to grab and connect these stages together in a simulator, creating supply chains (or product systems as they are known in that community) for analysis in a relatively short time. However, it is tedious to connect common chemical process simulators with these LCA software packages, and is mostly done through manual data entry. It is just as difficult to incorporate the results of LCA software into cheimcal process simulators as feedback. Part of the reason for this is that the LCA and process design communities are traditionally not linked. Although some chemical engineering programs in North America incorporate some environmental or “green design” concerns into their curriculum, it is not common for process design courses to include LCA considerations in the same way that techno-economic and HAZOP analyses are considered. For example, the AICHE Student Design Competition problem has never included an LCA component. However, interest and need is growing quickly.

Significantly improved research productivity and impact could be achieved if these two types of software were interconnected. At present, the conceptual process designer has the ability to very rapidly determine how changes in design options and parameters affect the big picture economic view since rather rigorous capital and operating cost estimates can be determined in real time and displayed right in the flowsheet simulator. However, what is needed is the ability to quickly and easily see how changes in design parameters affect the big picture cradle-to-grave life cycle. The integration of process simulation software with LCA software should be substantially aided by the existence of open format standards for data exchange, in the form of CAPE-OPEN for process simulation data and SPOLD for LCA data.

Although being able to see the impact immediately in external software in some automated way is useful, having it available in the same framework as the process simulator would allow the designer to utilitze valuable tools already available in the simulation software like optimization, sensitivity analyses, and so on. This in turn would increase the likelihood for process designers to consider LCA as an integral part of their investigations because having access to the information in an environment with which they are already familiar helps to overcome the associated learning curve and information gap. Educators will be able to incorporate LCA into design and simulation courses more readily and rapidly, thus encouraging growth in the practice.

7. Conclusions

The energy crisis can be combatted in no small part by the careful, considerate design of new energy conversion systems. In particular, systems using CLC, oxyfuel, and SOFC technologies have significant future promise both as stand-alone power generation systems and as important parts of complex, integrated polygeneration facilities. Key opportunities for chemical and liquid fuel production are emerging, especially in the production of chemicals from natural gas and shale gas to displace petroleum, the utilization of uranium for liquid fuels production, and the integration of multiple fuel processing steps together. However, devising optimal designs for these complex systems is quite difficult, especially when considering the entire supply chain.

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References

Adams, T.A. II, & Barton, P.I. (2010). High-efficiency power production from coal with carbon capture. *AIChE Journal*, *56*(12), 3120-3136.

Adams, T.A. II, & Barton, P.I. (2011). Combining coal gasification and natural gas reforming for efficient polygeneration. *Fuel Processing Technology*, *92*(3), 639-655.

Adams, T.A. II, Nease, J., Tucker, D., & Barton, P.I. (2013). Energy conversion with solid oxide fuel cell systems: A review of concepts and outlooks for the short- and long-term. *Industrial & Engineering Chemistry Research*, *52*(9), 3089-3111.

Adams, T.A. II, Khojestah Salkuyeh, Y., & Nease, J. Processes and Simulations for Solvent-based CO_2 Capture and Syngas Cleanup. In: Shi, F. (editor). Reactor and Process Design in Sustainable Energy Technology. Amsterdam: Elsevier; 2014. p. 163-231.

Adanez, J., Abad, A., Garcia-Labiano, F., Gayan, P., & de Diego, L.F. (2012). Progress in chemical-looping combustino and reforming technologies. *Prog Energy Comb Sci*, *38*(2) 215-282.

Anselmo, A., & Sullivan, J. (2014). DME: The fuel of the future is here today (2014). *ChemBioPower White Paper*, 2 June 2014.

Bacon, R. & Tordo, S. (2005). Crude oil price differentials and differences in oil qualities: A statistical analysis. *ESMAP Technical Paper of The World Bank,* 081 (October 2005).

BP (2014). Statistical review of world energy 2014. Corporate report.

Brandt, A. R. , Heath, G. A., Kort, A., O'Sullivan, F., Pétron, G., Jordaan, S. M., Tans, P., Wilcox, J., Gopstein, A. M., Arent, D., Wofsy, S., Brown, N. J., Bradley, R., Stucky, G. D., Eardley, D., & Harris, R. (2014). Methane leaks from North American natural gas systems. *Science*, *343*, 733-735

Bureau of Labor Statistics (2014). CPI Detailed report Data for January 2014, online publication.

de Castro, C., Mediavilla, M., Migual, L.J., & Frechoso, F. (2011). Global wind power potential: physical and tchnological limits. *Energy Policy, 39*, 6677-6682.

Chen, Y., Adams, T.A. II, & Barton, P.I. (2011). Optimial design and operation of flexible energy polygeneration systems. *Industrial & Engineering Chemistry Research*, *50*(8), 4553-4566.

Cormos, C.-C. (2012). Evaluation fo syngas-based chemical looping applications for hydrogen and power co-generatino with CCS. *International Journal of Hydrogen Energy*, 37(18), 13371-13386.

Elkington, J. (1997) Cannibals with forks – The triple bottom line of 21st century business. *Captsone Publishing, Ltd.* Oxford.

Energy Information Administration (2012). Form EIA-860 detailed data (government database). Data for Generators as of 2012.

Energy Information Administration (2013a). Annual Coal Report 2013

Energy Information Administration (2013b). Technical recoverable shale oil and shale gas resources: An assessment of 137 shale formations in 41 countries outside the United States. 2013, government publication.

Energy Information Administration (2014a). Cushing, OK WTI Spot price FOB, online database updated Nov 26, 2014.

Energy Information Administration (2014b). United States Natural Gas Henry Hub Spot Price, online database updated Nov 26, 2014.

Energy Information Administration (2014c). Coal Markets Archive, database updated Nov 26, 2014.

Environmental Protection Agency (2011). Environmental Optimization using the WAste Reduction Algorithm (WAR). EPA 600-F11027.

Environmental Protection Agency (2012). Standards of performance for greenhouse gas emissions for new staionary sources: Electric utility generating units. *Federal Register*, *77*(87), 26476-26477.

Environmental Protection Agency (2014). Standards of performance for greenhouse gas emissions for new stationary sources: Electric utility generating units. *Federal Register*, *79*(14), 3557-3558.

Fan, L.-S., Zeng, L., Luo, S. (2015) Chemical-looping technology platform. *AIChE J, 61*(1), 2-22.

Field R.P., & Brasington, R. (2011). Baseline flowsheet model for IGCC with carbon capture. *Industrial & Engineering Chemistry Research, 50*, 11306-11312.

Floudas, C.A., Elia, J.A., Baliban, R.C. Hybrid and single feedstock energy processes for liquid transportation fuels: A critical review. *Computers & Chemical Engineering¸41*, 24-51.

Folger, P. (2014). The FutureGen carbon capture and sequestration project: A brief history and issues for Congress. *Congressional Research Service*, report 7-5700

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J., Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M. & Van Dorland, R. (2007). Changes in Atmospheric Constituents and in Radiative Forcing. *In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Gagnon, L., Bélanger, C. & Uchiyama, Y. (2002). Life-cycle assessment of electricity generation options: The status of research in year 2001. *Energy Policy, 30*, 1267-1278.

Ghouse, J. & Adams, T.A. II (2014). Hybrid radiant syngas cooler and steam methane reformer. US patent application.

Government of Alberta (2008), Alberta's Provincial Energy Strategy, ISBN 978-0-7785-6332-7, December 2008.

Gray, D., Salerno, S., & Tomlinson, G. (2004). Current and Future IGCC Technologies: Bituminous Coal to Power. Mitretek Technical Report MTR-2004–05, 2004.

Gregg, J.S. National and regional generation of municipal residue biomass and the future potential for waste-to-energy implementation. *Biomass & Bioenergy, 34,* 379-388.

Gupta, A.K., & Hall, C.A.S. (2011). A review of the past and current state of EROI data. *Sustainability, 3,* 1796-1809.

Habib, M.A., Badr, H.M., Ahmed, S.F., Ben-Mansour, R., Mezghani, K., Imashuku, S., Ia O, G.J., Shao-Horn, Y., Mancini, N.D., Mitsos, A., Kirchen, P, Ghoneim, A.F. (2011). A review of recent developments in carbon capture utilizing oxy-fuel combustion in conventional and ion transport membrane systems. *International Journal of Energy Research*, *35*, 741-764.

Hadjipaschalis, I., Kourtis, G.,& Poullikkas, A. (2009). Assessment of oxyfuel power generation technologies. *Renewable & Sustainable Energy Reviews*, *13*, 2637-2644.

Harun, N.F., Tucker, D., & Adams, T. A. II (2014). Fuel composition transients in fuel cell turbine hybrid for polygeneration applications. *Journal of Fuel Cell Science and Technology*, *11*(12), 061001-1—061001-7.

Hester, K.C. & Brewer, P.G. (2009). Clathrate hydrates in nature. *Annual Reviews in Marine Science*, *1*, 303-327.

Hussain, D., Dzombak, D.A., Lowry, G.V., Zubrin, R.M., Malliaris, S., & Adams, T.A. II (2014). Reducing greenhouse gas emissions through mobile systems for methanol production, electricity generation, & CO_2-enhanced oil recovery utilizing North America's flare gas resources. *13th Annual Conference on Carbon Capture, Utilization, and Storage*, April 28-May 1, 2014, Pittsburgh, PA.

Jacobson, M.Z. & Delucci, M.A. (2011). Providing all global energy with wind, water, and solar power, Part I: Tehnologies energy resources, quantities and areas of infrastructure, and materials. *Energy Policy, 39*, 1154-1169.

Johnson, M.R., & Coderre, A.R. (2012). Opportunities for CO_2 equivalent emissions reductions via flare and vent mitigation: A case study for Alberta, Canada. *International Journal of Greenhouse Gas Control*, 8, 121-131.

Khojestah Salkuyeh, Y., & Adams, T. A. II (2013). Combining coal gasification, natural gas reforming, and external carbonless heat for efficient production of gasoline and diesel with CO_2 capture and sequestration. *Energy Conversion & Management*, *74*, 492-504.

Khojestah Salkuyeh, Y., & Adams, T.A. II (2014). A new power, methanol, and DME polygeneration process using integrated chemical looping systems. *Energy Conversion and Management*, 88, 411-425.

Khojestah Salkuyeh, Y., & Adams, T.A. II (2015a). A novel polygeneration process to co-produce ethylene and electricity from shale gas with zero CO_2 emissions via methane oxidative coupling. *Energy Conversion and Management*, 92, 406-420.

Khojestah Salkuyeh, Y., & Adams, T.A. II (2015b). Co-production of olefins, fuels, and electricity from conventional pipeline gas and shale gas with near-zero CO_2 emissions; Part II: Economic performance. In press: *Energies*, 8, doi:10.3390/en80x000x.

Leckel, D. (2009). Diesel production from Fischer-Tropsch: The past, the present, and new concepts. *Energy & Fuels 23*(5), 2342-2358.

Martín, M., & Grossmann, I.E. (2014) Optimal simultaneous production of i-butene and ethanol from switchgrass. *Biomass & Bioenergy 61*, 93-103.

Meerman, J.C., Ramírez, A., Turkenburg, W.C., & Faaij, A.P.C. (2012) Performance of simulated flexible integrated gasification polygeneration facilities, Part B: Economic evaluation. *Renewable and Sustainable Energy Reviews*, *16,* 6083-6102.

Murphy, D.J.R. & Hall, C.A.S. (2010) Year in review—EROI or energy return on (energy) invested. *Ann NY Acad Sci, 1185*, 102-118.

Murphy, D.J.R., Hall, C.A.S., Dale, M., & Cleveland, C. (2011) Order from Chaos: A preliminary protocol for determining the EROI of fuels. *Sustainability*, *3*(10) 1888-1907.

Murthy, B. N., Sawarkar, A. N., Deshmukh, N. a., Mathew, T., & Joshi, J. B. (2014). Petroleum coke gasification: A review. *Canadian Journal of Chemical Engineering, 92*(3) 441–468.

National Energy Technology Laboratory (2007). Cost and performance baseline for fossil energy plants: Bituminous coal and natural gas to electricity final report; DOE/NETL-2007/1281.

National Energy Technology Laboratory (2011). Life cycle greenhouse gas inventory of natural gas extraction, delivery, and electricity production. DOE/NETL-2011/1522.

Nease, J., & Adams, T. A. II (2013). Systems for peaking power with 100% CO_2 capture by integration of solid oxide fuel cells with compressed air energy storage. *Journal of Power Sources*, *228*, 281-293.

Nease, J., & Adams, T. A. II (2014).Coal-fuelled systems for peaking power with 100% CO2 capture through integration of solid oxide fuel cells with compressed air energy storage. *Journal of Power Sources, 251*, 92-107.

Nease J., & Adams T.A. II (2015). Life cycle analyses of bulk-scale solid oxide fuel cell power plants. *Canadian Journal of Chemical Engineering,* in press, CJCE-14-0460.R1 (2015).

Petrakopoulou, F., & Tsatsaronis, G. (2014). Can carbon dioxide capture and storage from power plants reduce the environmental impact of electricity generation? *Energy & Fuels 28,* 5327-5338.

Poisson, A., & Hall, C.A.S. (2013). Time series EROI for Canadian oil and gas. *Energies*, 6, 5940-5959.

Sahraei, M.H., McCalden, D., Hughes, R., Ricardez-Sandoval, L.A. (2014) A survey on current advanced IGCC power plant technologies, sensors, and control systems. *Fuel 137*, 245-259.

SaskPower (2012). Boundary Dam Integrated Carbon Capture and Storage Demonstration Project. Corporate Publication, April 2012.

Scheffknecht, G., Al-Makhadmeh, L., Schnell, U., and Maier, J. (2011). Oxy-fuel coal combustion—A review of the current state-of-the-art. *International Journal of Greenhouse Gas Control 5S*, S16-S35.

Schreiber, A., Zapp, P., & Marx, J. (2012). Meta-analysis of life cycle assessment studies on electricity generation with carbon capture and storage. *Journal of Industrial Ecology* S1:S155-S168.

Shelly, S (2009). Oxygen and nitrogen: onward and upward. *Chemical Engineering Progress, 105,* 1.

Shonnard, D., Lindner, A., Nguyen, N., Ramachandran, P.A., Fichana, D., Hesketh, R., Slater, C.S., Engler, R. (2007) Green Engineering-Integration of Green Chemistry, Pollution Prevention, and Risk-Based Considerations. In: Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology, Vol 1. Ed: Kent, J.A. Springer Science+Business Media: New York.

Seider, W., Gani, R., Chen C.-C., El-Halwagi, M., Towler, G., Shonnard, D., Crowl, D. Biegler, L.T., Grossmann, I., Reklaitis, G.V., Shaeiwitz, J., & Turton, R. (2012) Guide to teaching design with internet links, 2nd ed. *CACHE Learning Resource Center*.

Talbot, D. (2014) Construction begins at a carbon-capture plant, but will it ever be completed? *MIT Technology Review*

Tong, A., Bayham, S., Kathe, M.V., Zeng, L, Lui, S., & Fan, L.-S (2014). Iron-based syngas chemical looping process and coal-direct chemical looping process development at Ohio State University. *Applied Energy*, 113, 1836-1845.

Wang, M., Lawal, A., Stephenson, P., Sidders, J., & Ramshaw, C (2011). Post-combustion CO_2 capture with chemical absorption: A state-of-the-art review. *Chemical Engineering Research & Design*, 89, 1609-1624.

Weil, K.S. Coal gasification and IGCC technology: A brief primer (2010). *Proceedings of Institution of Civil Engineers: Energy, 163*(1), 7-16.

World Nuclear Association (2012). Supply of Uranium. http://www.world-nuclear.org/info/Nuclear-Fuel-Cycle/Uranium-Resources/Supply-of-Uranium/. Accessed Feburary 28, 2014.

World Nuclear Association (2014). Thorium (September 2014 update). http://www.world-nuclear.org/info/Current-and-Future-Generation/Thorium/. Accessed April 10, 2015.

Zapp, P., Schreiber, A., Marx, J., Haines, M., Hake, J.-F., & Gale, J. (2012), Overall environmental impacts of CCS technologies—A life cycle approach. *International Journal of Greenhouse Gas Control, 8,* 12-21.

Zeman, N. (2014) FutureGen begins construction, but project faces some hurdles. *Engineering News Record, 273*(11).

Zhang, Y.; Dubé, M. A.; McLean, D. D.; & Kates, M. (2003). Biodiesel production form waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology*, 89, 1-16.