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Polygeneration of Fuels and Chemicals

Thomas A. Adams II, Jaffer H. Ghouse

McMaster University, Department of Chemical Engineering, 1280 Main St West, Hamilton, ON, L8S 4L7, Canada

Corresponding Author: Thomas A. Adams II (tadams@mcmaster.ca)

Abstract

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.

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

30 make economic sense because the syngas generation steps required for the various products can be
31 integrated all into one. Whatever the case, the idea is to gain some advantage by the integration of
32 the different process sections.

33

34 **Terminology and Scope**

35 The word “polygeneration” is very broad since many kinds of processes can produce more than one
36 product simultaneously (e.g. petroleum refining). Although the idea of co-producing multiple
37 products had been understood for some time, the term “polygeneration” first appears in the open
38 engineering literature in 1982 (to the best of the authors’ knowledge) through studies at NASA [1]
39 and General Electric [2]. Although those works and almost all other early works focused on the
40 systems using only coal gasification, researchers now use the term more broadly to apply to systems
41 which use natural gas, biomass, and nuclear energy. Of all academic literature using the term
42 “polygeneration” (that could be identified) published between January 2013 and April 2015 [4-45,51-
43 52], none apply it with respect to crude oil, and in every case in which the term is used except one
44 [26], electricity is a co-product.

45

46 Two seminal works from 1982 represent the genesis of two different meanings of the term
47 developed over the past three decades. The NASA usage [1] helped lead to an understanding of the
48 term in the context of two or more co-products in total where one is a chemical or fuel. The General
49 Electric usage [2] helped lead to an understanding of the term in the context of municipal utilities,
50 where polygeneration is the natural extension of well-understood terms such as “co-generation”
51 (electricity and heat), and “tri-generation” (electricity, heat, and cooling). In the latter context,
52 polygeneration typically means a tri-generation system with more utility products such as drinking
53 water, or secondary forms of heat or cold (e.g. steam, refrigeration, air conditioning, etc.). However,
54 the former definition has won over. All works that the authors can identify in the engineering
55 literature which use the term “polygeneration” since 2013 includes at least one chemical or fuel as a
56 co-product in addition to electricity, except for the works of a few research groups [22, 29, 33, 54]. In
57 addition, all research groups except one [10,21] apply the term to a thermochemical process as
58 opposed to a biochemical one. This represents a shift in the cultural use of “polygeneration” strongly
59 in favour of the former meaning. Therefore, based on the overwhelming consensus of the

60 terminology in the literature, the authors propose the following definitions for use in a chemical
61 engineering context:

62

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

71

72 The term also overlaps with the term “biorefinery”, which can be explained as follows:

73

- 74 ▪ **Biorefinery:** A process for converting biomass into value-added products, including electricity,
75 fuels, chemicals, food, and proteins. This can include thermochemical routes such as gasification,
76 or biochemical routes such as fermentation or digestion. See [3] for a review of the term.
- 77 ▪ **Thermochemical Biorefinery:** A process which is both a polygeneration process and a
78 biorefinery (thus via the thermochemical route).

79

80 As a final note, the scope of this review was limited to processes which self-identify as
81 “polygeneration”. The reader is referred to [48, 49] for recent reviews of biorefineries, which include
82 thermochemical biorefineries and hence, polygeneration.

83

84 **The Syngas Route**

85 In almost all studies examined in this work, polygeneration utilizes the “syngas route,” as
86 summarized in Table 1. The general strategy is to first produce syngas of some variety, usually
87 containing a mix of H₂ and CO (the valuable parts), along with wastes such as CO₂ and H₂O (arising
88 through oxidation of fuels), and impurities such as sulphurous compounds. The syngas has to then
89 be modified to balance the molar ratio of H₂ to CO to some optimum value, based on the

90 stoichiometry of the reaction. Typically, slightly more than twice as much H₂ as CO is optimal for
91 most downstream fuel and chemical conversion processes, such as Fischer-Tropsch synthesis, or
92 methanol synthesis. In some cases, an equimolar ratio is optimal, such as in the case of direct DME
93 conversion. Additionally, the syngas must be cleaned to remove CO₂, H₂O, and impurities that may
94 harm catalysts or cause problematic emissions or inefficiencies. However, the order of these steps
95 varies from process to process. Once the clean, “balanced,” syngas is produced, it can be split and
96 fed to several different synthesis trains in parallel, since they often require very similar syngas
97 compositions. Often, a portion of the unreacted syngas is recycled to the synthesis reactor,
98 depending on the economics of the process. However, nearly always, the remaining off-gas is sent to
99 power generation since syngas has a high heating value, even when it contains a large amount of
100 diluents like H₂O and CO₂. The result is often a large net-excess of power produced arising from this
101 configuration.

102

103 **Syngas Production and Balancing**

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

110

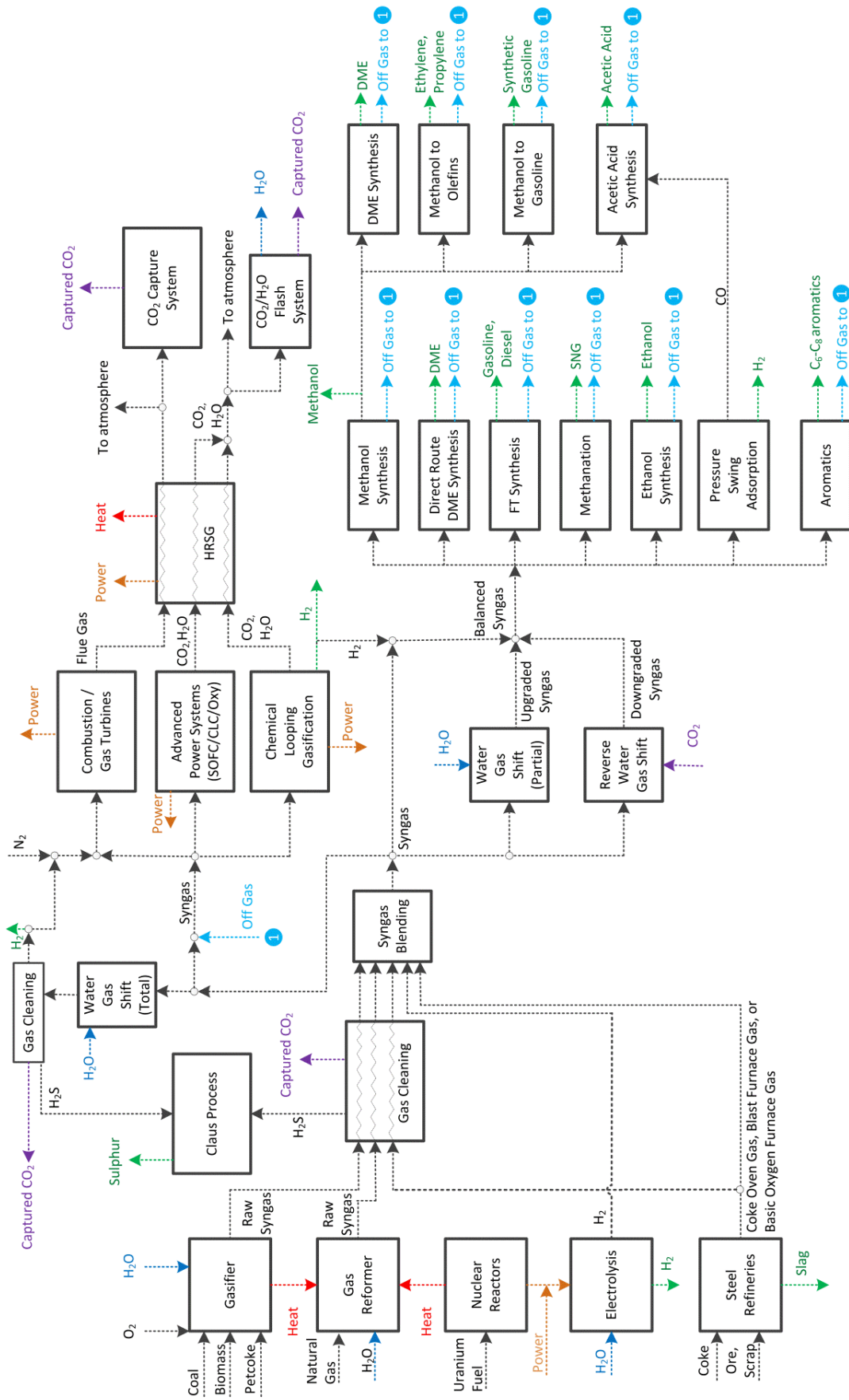
111 Coal and biomass can be converted to syngas through gasification technologies, of which there are
112 many different types. In most cases, this requires the use of high-purity O₂ produced by an air
113 separation process, which is expensive, energy intensive, and a major source of inefficiency. Typically,
114 this produces “H₂-lean” syngas, meaning that the syngas needs to be upgraded to a higher H₂
115 content suitable to the desired downstream molar ratio. Common strategies for this include using a
116 water gas shift reactor, blending in high purity H₂ produced by some other means, or blending in
117 “H₂-rich” syngas which has a high H₂/CO molar ratio, such that the blended mix has the desired
118 balance. Each method has its own special challenges and trade-offs.

119

Table 1: Summary of works in the review period and scope classified as polygeneration by the authors, with feedstock type and product portfolio noted.

Authors	Refs	Feedstocks					Products										Notes
		Coal	Nat. Gas	Biomass	Nuclear	Other	Electricity	FT Fuels	Alcohols	Olefins	DME	H2	SNG	Heat	Other		
																Chemical looping	
Fan & Lin	[4]		X				X				X						
Ghanbari et al.	[5] [43]	X	X	X		steel off gases	X			X							
Guo et al.	[6]					lignite	X										Does not use the syngas route
Guo et al.	[18]	X					X										
Heidenreich & Foscolo	[7]			X			X				X	X	X				
Jana & De	[8] [9]			X			X				X		X	cooling			
Vidal & Martín	[11]			X			X				X						Concentrated solar thermal
Wagner et al.	[12]			X			X					X	X				
Khojastah Salkuyeh & Adams	[13] [51]		X				X			X							
Khojastah Salkuyeh & Adams	[15]	X	X		X		X			X							Chemical looping
Khojastah Salkuyeh & Adams	[37]	X	X		X		X			X							
Carvalho et al.	[16]			X			X					X	X				
Zhang X et al.	[17]	X	X				X										Chemical looping
Li S et al.	[20] [35]	X					X					X					
Illic et al.	[19]		X				X						X				
Cormos	[23]			X			X										
Cormos	[27]	X		X			X					X					Chemical looping
Ruth et al.	[24]	X	X	X	X	wind	X			X							Subsets of these considered
Li Y et al.	[25]	X					X										
Navarez et al.	[42]					syngas	X										
Zhang J et al.	[44]	X					X										
Yi et al.	[52]	X				coke oven gas	X										
Fazlollahi & Maréchal	[28]			X			X				X	X	X				
James et. Al	[30]	X		X			X										
Kaniyal et al.	[31] [32]	X	X	X			X										Solar+co-gasification/reforming
Kyriakarakos et al.	[34]					electricity	X				X	X	X	cooling			Elec. both resource & product
Ng et al.	[36]	X	X	X			X				X	X	X	acetic acid			
Salomón et al.	[38]			X			X						X				
Truong & Gustavsson	[39]			X			X						X	bio-pellets			
He et al.	[53]	X		X			X										Low rank coal

Figure 1. Polygeneration superstructure of works in the review period and scope which use the syngas route. Many blocks, streams, and routes are optional. SOFC=Solid oxide fuel cells, CLC=chemical looping combustion, OXY=oxyfuel



123 Syngas can also be produced by the reforming of natural gas, of which many strategies are possible.
124 Gas reforming strategies differ mostly in the amounts of steam, CO₂, and O₂ which are fed (not all
125 are required), the types of catalyst used, and how heat is supplied since the reforming reactions are
126 quite endothermic. This allows the system designer much control over the H₂/CO ratio produced. For
127 example, it may make sense to either directly produce the appropriate H₂/CO ratio (i.e. of about two)
128 in the reformer, or alternatively produce an H₂-rich syngas that can either be blended with
129 something else, or downgraded using a reverse water gas shift reactor. The heat requirement can be
130 provided by placing the reformer in a furnace, direct oxidation inside the reactor, or by integrating
131 with something highly exothermic such as a coal gasifier or a nuclear reactor (see "Multi-feed
132 processes").

133

134 **Offgas Usage, Power Generation, and CO₂ Emissions**

135 Once balanced syngas is used for chemical or fuel production, there usually remains a substantial
136 amount of off-gases. These off gases exist because of purge requirements necessary to prevent
137 build-up of CO₂ and H₂O. When the expense of removing CO₂ and H₂O to permit recycling is too
138 great, the off gas is typically used for either power generation or burned for heat. There are many
139 power generation options, such as classic combustion with a steam cycle, the more advanced gas
140 combustion turbine with combined cycle, or more futuristic options such as solid oxide fuel cells,
141 oxyfuel combustion, and chemical looping combustion. These power generation options vary in
142 terms of cost, efficiency, and the relative difficulty of capturing CO₂, but all of them can be designed
143 (in theory) to handle off-gas compositions of widely differing amounts, which make them universally
144 attractive as the best and most profitable way to use off-gases. The latter three options in particular
145 are prevalent because they each have the ability to effectively capture up to 100% of the CO₂. This
146 means that some polygeneration systems can be designed such that all of the carbon in the feed
147 ends up in either the products, or, the captured CO₂, leading to systems with effectively zero process
148 CO₂ emissions [13, 14, 15,]. Even if carbon capture is not employed, CO₂ emissions can still be
149 reduced compared to stand-alone alternatives simply due to efficiency improvements as a result of
150 system integration, which was repeatedly demonstrated in the literature surveyed [5, 17, 43, 51, 53].
151 For more on this topic, the reader is referred to [46].

152

153 **Multi-feed processes**

154 Another common approach is to utilize multiple feedstocks together to gain some sort of synergy,
155 which are sometimes referred to as hybrid energy systems (see [47] for a review prior to 2012). Some
156 synergy may be found in the blending of H₂-lean syngas with H₂-rich syngas. This can avoid losses
157 associated with the water gas shift reaction necessary to upgrade coal-derived syngas [17], or avoid
158 losses associated with dry reforming or the reverse water gas shift reaction necessary to downgrade
159 syngas made from natural gas. Or, synergy can be found through heat integration, such as using the
160 high temperatures produced by coal gasification or nuclear reactors to drive natural gas reforming
161 processes, which can simultaneously avoid gas burning for heat or steam production for cooling
162 (which has a lower exergy benefit than reforming natural gas) [17,37].

163
164 Alternatively, it may make sense to blend fuels purely for their superior environmental qualities. For
165 example, a company might try to “green up” a coal-based process by also using large amounts of
166 natural gas or biomass, thus lowering the lifecycle CO₂ emissions as a whole or increasing the use of
167 renewable fuels [5, 53]. Similarly, a polygeneration process can be a means to utilize or dispose of
168 low value feeds like municipal solid waste or petroleum coke by blending it in with coal or
169 integrating with a natural gas reforming route. In some cases, blending in non-trivial amounts of
170 waste might result in only a relatively small negative impact on the system [27], thus providing a very
171 effective and efficient means of disposal by conversion to new products.

172

173 **Optimal Design of Polygeneration Systems**

174 In much of the literature surveyed, the determination of an “optimal” polygeneration system was
175 studied, which often took the form of finding the optimal design parameters (such as recycle
176 amounts of unreacted-gases or off-gases), for a given design concept. Or, the optimization of a
177 polygeneration superstructure was considered, by which the best subset of many candidate routes
178 and products was determined (see [50] for a recent example).

179

180 The optimal results are often highly dependent on market conditions, but also tend to favour two-
181 product systems. For example, if the objective is simply to make the most profitable plant (e.g. the
182 highest net present value) with no attachment to a particular product, it is very often the case that

183 the optimal process co-produces electricity and the choice of only one chemical or fuel. This is
184 because there is very little synergy between the chemical and fuel synthesis trains themselves. For
185 example, it rarely makes sense to make both methanol and dimethyl ether (DME) when DME is
186 produced from methanol dehydration. Either the price of DME is not higher enough than methanol
187 to justify the cost of methanol dehydration and so the dehydration step should not exist, or, the
188 price difference is high enough such that you should build a methanol dehydration reactor and
189 therefore any methanol produced should be used to produce DME. Similarly, it is rarely the case in
190 which the optimal system design is one in which syngas is split between two separate chemical or
191 fuel synthesis trains, such as a Fischer-Tropsch train and a methanol synthesis train; typically syngas
192 should all be routed to just one[†]. In fact, sometimes the most desirable design is simply a single
193 product plant, and not a polygeneration system at all.

194

195 The exceptions to this result tend to be cases in which constraints or objectives outside of pure
196 profitability are considered. For example, if there is a market for it, there can often be a way to sell
197 low-quality heat in the form of low pressure steam or hot water. Or, if there are broader goals such
198 as requiring certain minimum production rates of various products, or a desire to produce a portfolio
199 of products in the same proportion as the global demand. Similarly, some of the works in the survey
200 noted that polygeneration may lower the overall production costs of producing some required
201 "chemical X" by capturing value associated with the co-products of polygeneration. However, in
202 some cases this is because it simply is more profitable to make the co-products than the primary
203 product of interest, and the lower production costs of chemical X are mostly the result of accounting
204 style rather than of any meaningful synergies arising from the integration of the co-processes. In
205 those cases, polygeneration is not likely to be much of a help, unless the production of chemical X is
206 required regardless of cost.

207

208 However, it is often the opposite when considering multiple types of feeds. Because of the synergies
209 that are inherent in the use of multiple feeds (see previous section), there are many cases in those
210 surveyed in which it was optimal to use multiple types of feeds from a purely profit driven
211 perspective. For example, under certain carbon taxes, blending a certain percentage of biomass into

[†] Of course, an individual train may by necessity co-produce a basket of related products, such as Fischer-Tropsch diesel and naphtha, but the point still holds.

212 coal for gasification may be the best overall strategy; using no biomass (all coal) would require heavy
213 CO₂ tax or capture expense penalties, but using too much would have too many negative impacts on
214 the system such that the overall efficiency and profitability drops too far. Or, the avoidance of syngas
215 upgrading or downgrading by blending coal-derived syngas with syngas made from natural gas may
216 have enough efficiency improvements to have a net positive impact on profitability compared to any
217 single-feed system.

218

219 **Conclusions and Future Directions**

220 Polygeneration systems research is growing rapidly because the core concepts of synergistic process
221 integration can be applied to a wide variety of systems and applications, including some newer
222 examples in the steel and mining industries. The key benefits can include higher profitability, better
223 efficiency, and lower environmental impact, although the choice of the “best” design is highly
224 dependent on particular business, regulatory, or market circumstances. Because market conditions
225 (which can be highly variable) greatly affect the optimal process topologies, it makes sense to pay
226 closer attention to flexible polygeneration systems which change the relative amounts of each
227 product produced or feedstock used periodically (yearly, seasonally, weekly, or even daily) in order
228 to respond to these changes and make more profit than a static, unchanging plant would. This may
229 be the most promising use for polygeneration since the general system structure is favourable,
230 provided that it is designed for excess capacity and enough turndown capability is possible.

231

232 **Acknowledgements**

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234 Council Discovery Grant.

235

236 **References and recommended reading**

237 Papers of particular interest, published within the period of review, have been highlighted as:

238 * of special interest

239 ** of outstanding interest

240

241 **1. Burns RK, Staiger PJ, Donovan RM. **Integrated gasifier combined cycle polygeneration**
242 **system to produce liquid hydrogen.** *NASA Technical Memorandum*, Report No NASA TM-82921,
243 July 1982

244 This is the first engineering article to use the term polygeneration, and it demonstrated to excellent
245 detail that one coal-based polygeneration system requires lower energy consumption than a
246 collection of standalone facilities (11-13% in this case), along with potential economic benefits as
247 well.

248

249 2. Alger J, Ahner DJ. **Cool water demonstration project and its industrial applications.** *Proc.,*
250 *Interso. Energy Convers Eng Conf* 1982, 1:17

251

252 3. Berntsson T, Sandén B, Olsson L, Åsblad A. **What is a biorefinery?** In: *Systems Perspectives on*
253 *Biorefineries.* Sandén B, Pettersson, K, eds. 2014. Chalmers University of Technology.

254

255 4. Fan J, Lin Z. **Performance analysis of a feasible technology for power and high-purity**
256 **hydrogen production driven by methane fuel.** *App Thermal Eng* 2015 75:103-114.

257

258 **5. Ghanbari H, Pettersson F, Saxén H. **Sustainable development of primary steelmaking under**
259 **novel blast furnace operation and injection of different reducing agents.** *Chem Eng Sci* 2015,
260 129:208-22.

261 This is interesting in that it specifically links polygeneration with steel manufacturing to co-produce
262 steel products with methanol and/or DME. A large polygeneration superstructure and many possible
263 fuel sources are considered by making syngas from coke plant, blast furnace and basic oxygen
264 furnace residual gases. A follow-up article from [43].

265

266 6. Guo Z, Wang Q, Fang M, Luo Z, Cen K. **Simulation of a lignite-based polygeneration system**
267 **coproducing electricity and tar with carbon capture.** *Chem Eng Technol* 2015, 38:463-472.

268

269 *7. Heidenreich S, Foscolo PU. **New concepts in biomass gasification.** *Prog Energy Combust Sci*
270 2015, 46:72-95.

271 Contains a review of different ways of producing syngas for polygeneration from biomass, including
272 some interesting unconventional designs which incorporate gasification, cleaning, and conditioning
273 in one reactor.

274

275 8. Jana K, De S. **Polygeneration using agricultural waste: Thermodynamic and economic**
276 **feasibility study.** *Renew Energy* 2015,74:648-660.

277

278 9. Jana K, De S. **Techno-economic evaluation of a polygeneration using agricultural residue – A**
279 **case study for an Indian district.** *Bioresource Technol* 2015, 181:163-173.

280

281 *10. Lythcke-Jørgensen C, Haglind F. Design optimization of a polygeneration plant producing
282 power, **heat, and lignocellulosic ethanol.** *Energy Convers Manage* 2015,91:353-366.

283 Based on retrofitting an existing co-generation plant, this high quality work is notable for
284 considering flexible production on an hour by hour basis. It uses simultaneous saccharification and
285 fermentation to produce ethanol and is not classified as polygeneration under the definition put
286 forward in this work.

287

288 *11. Vidal M, Martín M. **Optimal coupling of a biomass based polygeneration system with a**
289 **concentrated solar power facility for the constant production of electricity over a year.** *Comp*
290 *Chem Eng* 2015,72:273-283.

291 This work is notable for the integration of flexible polygeneration with concentrated solar thermal
292 energy with molten salt energy storage. The molten salts handle daily energy storage issues while
293 hydrogen is produced at different amounts each month based on seasonal variations in average
294 sunlight.

295

296 *12. Wagner H, Wulf C, Kaltschmitt M. **Polygeneration of SNG, heat and power based on biomass**
297 **gasification and water electrolysis—concepts and their assessment.** *Biomass Conv Bioref*
298 2015,5:103-114.

299 This process either produces or consumes power depending on prices; when power is low,
300 electrolysis is purchased to produce hydrogen for energy storage purposes.

301

302 13. Khojestah Salkuyeh Y, Adams TA II. **Co-production of olefins, fuels, and electricity from**
303 **conventional pipeline gas and shale gas with near-zero CO₂ emissions. Part II: Economic**
304 **performance.** *Energies* 2015, 8:3762-3774.

305 The optimization results of this paper show that unless market prices for chemicals and fuels are in a
306 very particular and narrow range, the most profitable polygeneration plants are those that co-
307 produce electricity with only one of the possible products considered (dimethyl ether, olefins, or
308 methanol). It rarely makes sense to co-produce two kinds of chemicals due to the lack of synergies
309 between their process trains.

310

311 14. Khojestah Salkuyeh Y, Adams TA II. **A novel polygeneration process to co-produce ethylene**
312 **and electricity from shale gas with zero CO₂ emissions via methane oxidative coupling.** *Energy*
313 *Convers Manage* 2015, 92:406-420.

314

315 *15. Khojestah Salkuyeh Y, Adams TA II. **A new power, methanol, and DME polygeneration**
316 **process using integrated chemical looping systems.** *Energy Convers Manage* 2014, 88:411-425.

317 This work considers coal-only and coal/natural gas co-feeds in different proportions, and under
318 current market conditions, using both coal and natural gas are the most profitable. Also, heat from a
319 nuclear reactor can be used to power natural gas reforming to reduce fossil fuel consumption
320 associated with heat production and improve the efficiency.

321

322 **16. Carvalho M, Romero A, Shields G, Millar DL. **Optimal synthesis of energy supply systems for**
323 **remote open pit mines.** *App Thermal Eng* 2014,64:315-330.

324 This excellent work solves MILP polygeneration superstructure optimization problems to find the
325 best solutions for a remote mining operation, noting monthly and hourly variability in demands for
326 heat, diesel, and power. It is particularly interesting because in this case there are limits to the
327 capacity of power grid that can be reached and the optimal energy storage (such as syngas storage)
328 and power management systems change drastically with the distance to the connection point.

329

330 *17. Zhang X, Li S, Jin H. **A polygeneration system based on multi-input chemical looping**
331 **combustion.** *Energies* 2014, 7:7166-7177.
332 Combines coal and natural gas to co-produce methanol and electricity. This shows that using natural
333 gas to upgrade H₂-lean coal-derived syngas instead of the water gas shift reaction is more efficient
334 and has lower exergy destruction.
335

336 18. Guo Z, Wang Q, Fang M, Luo Z, Cen K. **Thermodynamic and economic analysis of a**
337 **polygeneration systems integrating atmospheric pressure coal pyrolysis technology with**
338 **circulating fluidized bed power plant.** *App Energy* 2014, 113:1301-1314.
339

340 19. Ilic DD, Dotzauer E, Trygg L, Broman G. **Introduction of large-scale biofuel production in a**
341 **district heating system-an opportunity for reduction of global greenhouse gas emissions.** *J*
342 *Cleaner Prod* 2014, 64:552-561.
343

344 20. Li S, Jin H, Gao L, Zhang X. **Exergy analysis and the energy saving mechanism for coal to**
345 **synthetic/substitute natural gas and power cogeneration system without and with CO₂**
346 **capture.** *App Energy* 2014, 130:552-561.
347

348 21. Lythcke-Jørgensen C, Haglind F. **Design optimization of a polygeneration plant producing**
349 **power, heat, and lignocellulosic ethanol.** *Energy Convers Manage* 2014, 91:353-366.
350

351 22. Kasivisvanathan H, Ubando AT, Ng DKS, Tan RR. **Robust optimization for process synthesis**
352 **and design of multifunctional energy systems with uncertainties.** *Ind Eng Chem Res* 2014
353 53:3196-3209.
354

355 23. Cormos CC. **Biomass direct chemical looping for hydrogen and power co-production:**
356 **Process configuration, simulation, thermal integration and techno-economic assessment.** *Fuel*
357 *Process Technol* 2015, 137:16-23.
358

359 *24. Ruth MF, Zinaman OR, Antkowiak M, Boardman RD, Cherry RS, Bazilian MD. **Nuclear-renewable**
360 **hybrid energy systems: Opportunities, interconnections, and needs.** *Energy Convers Manage*
361 2014 78:684-694.

362 This work provides an overview into the various ways in which nuclear energy can be integrated into
363 polygeneration systems, such as providing the heat for natural gas reforming needs.

364

365 25. Li Y, Zhang G, Yang Y, Zhai D, Zhang K, Xu G. **Thermodynamic analysis of a coal-based**
366 **polygeneration system with partial gasification.** *Energy* 2014, 72:201-214.

367

368 26. Brau J-F, Morandin M, Berntsson T. **Hydrogen for oil refining via biomass indirect steam**
369 **gasification: energy and environmental targets.** *Clean Techn Environ Policy* 2013, 15:501-512.

370

371 *27. Cormos C-C. **Assessment of flexible energy vectors polygeneration based on coal and**
372 **biomass/solid wastes co-gasification with carbon capture.** *Int J Hydrogen Energy* 2013, 38:7855-
373 7866.

374 This work proposes blending low value feedstocks (such as municipal solid waste) with coal for
375 gasification such the net negative effects on the system (compared to coal-only) are small.

376

377 28. Fazlollahi S, Maréchal F. **Multi-objective, multi-period optimization of biomass conversion**
378 **technologies using evolutionary algorithms and mixed integer linear programming (MILP).**
379 *App Thermal Eng* 2013, 50: 1504-1513.

380

381 29. Hossain AK, Thorpe R, Vasudevan P, Sen PK, Citroph RE, Davies PA. **Omnigen: Providing**
382 **electricity, food preparation, cold storage and pure water using a variety of local fuels.**
383 *Renewable Energy* 2013, 49:197-202.

384

385 30. James OO, Chowdhury B, Auroux A, Maity S. **Low CO₂ selective iron based Fischer–Tropsch**
386 **catalysts for coal based polygeneration.** *Applied Energy* 2013, 107:377-383.

387

388 31. Kaniyal AA, van Eyk PJ, Nathan G, Ashman PJ, Pincus JJ. **Polygeneration of Liquid Fuels and**
389 **Electricity by the Atmospheric Pressure Hybrid Solar Gasification of Coal.** *Energy Fuels* 2013,
390 27:3538-3555.

391

392 *32. Kaniyal AA, van Eyk PJ, Nathan GJ. **Dynamic Modeling of the Coproduction of Liquid Fuels**
393 **and Electricity from a Hybrid Solar Gasifier with Various Fuel Blends.** *Energy Fuels* 2013,
394 27:3556-3569.

395 This and the above works are notable for the use of a gasifier which incorporates concentrated solar
396 energy to provide some of the heat requirement.

397

398 33. Kasivisvanathan H, Bariela IDU, Ng DKS, Tan RR. **Optimal operational adjustment in multi-**
399 **functional energy systems in response to process inoperability.** *Applied Energy* 2013, 102: 492-
400 500.

401

402 *34. Kyriakarakos G, Piromalis DD, Dounis AI, Arvanitis KG, Papadakis G. **Intelligent demand side**
403 **energy management system for autonomous polygeneration microgrids.** *Applied Energy* 2013,
404 103:39-51.

405 This work provides a framework for optimal design and operation of autonomous, small
406 polygeneration systems for microgrids, considering flexible operation and load-following aspects.

407

408 35. Li S, Jin H, Gao L. **Cogeneration of substitute natural gas and power from coal by moderate**
409 **recycle of the chemical unconverted gas.** *Energy* 2013, 55: 658-667.

410

411 *36. Ng KS, Zhang N, Sadhukhan J. **Techno-economic analysis of polygeneration systems with**
412 **carbon capture and storage and CO₂ reuse.** *Chem Eng J* 2013, 219:96-108.

413 This work looks at a number of interesting configurations using a variety of fuels and products,
414 including a unique way of using combining gas-derived and coal-derived syngas.

415

- 416 37. Khojestah Salkuyeh Y, Adams TA II. **Combining coal gasification, natural gas reforming, and**
417 **external carbonless heat for efficient production of gasoline and diesel with CO₂ capture and**
418 **sequestration.** *Energy Convers Manage* 2013, 74:492-504.
- 419
- 420 38. Salomón M, Gomez MF, Martin A. **Technical polygeneration potential in palm oil mills in**
421 **Columbia: A case study.** *Sustain Energy Technol Assess* 2013, 3:40-52.
- 422
- 423 39. Truong NL, Gustavsson L. **Integrated biomass-based production of district heat, electricity,**
424 **motor fuels and pellets of different scales.** *Applied Energy* 2013, 104:623-632.
- 425
- 426 40. Xin S, Yang H, Chen Y, Wang X, Chen H. **Assessment of pyrolysis polygeneration of biomass**
427 **based on major components: Product characterization and elucidation of degradation**
428 **pathways.** *Fuel* 2013, 113:266-273.
- 429
- 430 41. Yang S, Yang Q, Qian Y. **A composite efficiency metrics for evaluation of resource and**
431 **energy utilization.** *Energy* 61, 455-462.
- 432
- 433 42. Narvaez A, Chadwick D, Kershenbaum L. **Small-medium scale polygeneration systems:**
434 **Methanol and power production.** *Applied Energy* 2014, 113:1109-1117.
- 435
- 436 43. Ghanbari H, Saxen H, Grossmann I. **Optimal design and operation of a steel plant integrated**
437 **with a polygeneration system.** *AIChE J* 2013, 59,3659-3670.
- 438
- 439 44. Zhang J, Ma L, Li Z, Ni W. **The impact of system configuration on material utilization in the**
440 **coal-based polygeneration of methanol and electricity.** *Energy* 2014, 75:136-145.
- 441
- 442 45. Wang B, Gebreslassie BH, You F. **Sustainable design and synthesis of hydrocarbon biorefinery**
443 **via gasification pathway: Integrated life cycle assessment and techno-economic analysis with**
444 **multiobjective superstructure optimization.** *Comp Chem Eng* 2013, 52:55-76.
- 445

446 46. Adams TA II. **Future Opportunities and Challenges in the Design of New Energy Conversion**
447 **Systems.** *Comp Chem Eng* 2015, in press.

448

449 *47. Floudas CA, Elia JA, Baliban RC. **Hybrid and single feedstock energy processes for liquid**
450 **transportation fuels: A critical review.** *Comp Chem Eng* 2012, 41:24-51.

451 This is a rather detailed review of processes (mostly polygeneration processes) which involve
452 transportation fuels as a co-product, but prior to 2012.

453

454 48. Haro P, Ollero P, Perales ÁLV, Vidal-Barrero F. **Potential routes for thermochemical**
455 **biorefineries.** *Biofuels Bioprod Bioref* 2013, 7:551-572.

456

457 49. Maity SK. **Opportunities, recent trends and challenges of integrated biorefinery: Part II.**
458 *Renew Sustain Energy Rev* 2015, 43:1446-1443.

459

460 *50. Niziolek AM, Onel OO, Elia JA, Baliban RC, Floudas CA. **Coproduction of liquid transportation**
461 **fuels and C₆-C₈ aromatics from biomass and natural gas.** *AIChE J* 2015, 61:831-856.

462 This is just one of several good examples of studies which look at the process synthesis using global
463 optimization techniques on a large polygeneration superstructure to determine the best topologies.

464

465 51. Khojestah Salkuyeh Y, Adams TA II. **Co-production of olefins, fuels, and electricity from**
466 **conventional pipeline gas and shale gas with near-zero CO₂ emissions. Part I: Process**
467 **development and technical performance.** *Energies* 2015, 8:3739-3761.

468

469 *52. Yi Q, Feng J, Wu Y, Li W. **3E (energy, environmental, and economy) evaluation and**
470 **assessment to an innovative dual-gas polygeneration system.** *Energy* 2014, 66:285-294.

471 This work has an interesting approach to use coal coking off gases which are rich in hydrogen and
472 methane to upgrade coal-derived syngas.

473

474 53. He C, You F, Feng X. **A novel hybrid feedstock to liquids and electricity process: Process**
475 **modeling and exergoeconomic life cycle optimization.** *AIChE J* 2014, 60:3739-3753.

- 476 54. He C, You F. **Shale gas processing integrated with ethylene production: Novel process**
477 **designs, exergy analysis, and techno-economic analysis.** *Ind Eng Chem Res* 2014, 53:11442-11459.