Integrated Biomass and Fossil Fuel Systems Towards the Production of Fuels and Chemicals: State of the Art Approaches and Future Challenges

Onur Onel^{1,2,3}, Alexander M. Niziolek^{1,2,3}, and

Christodoulos A. Floudas^{2,3*}

1. Department of Chemical and Biological Engineering

Princeton University

Princeton, NJ 08544, USA

2. Texas A&M Energy Institute

302D Williams Administration Building

3372 Texas A&M University

College Station, TX 77843, USA

3. Artie McFerrin Department of Chemical Engineering

Texas A&M University

College Station, TX 77843, USA

May 19, 2015

*Corresponding author; Tel: (979) 458-0253; Fax: (979) 845-0593; E-mail: floudas@tamu.edu.

Abstract

Volatility of crude oil prices and dependence of the United States on petroleum imports make the development of alternative refineries inevitable. Recent work has focused on developing and simulating such alternative processes from integrated biomass/natural gas and biomass/coal feedstocks to produce fuels and chemicals. These process simulations provide invaluable information on the performance and capability of the specific process alternative considered. However, the development of many alternative technologies, along with multiple feedstock and product possibilities, made the superstructure based optimization methods the natural approaches to be pursued. These process superstructures can be efficiently optimized to provide insights into topological, economic, and environmental trade-offs by simultaneously weighing the strengths and weaknesses of each alternative. Despite the development of these powerful tools, several outstanding challenges need to be systematically addressed. These challenges include the implementation of different conversion technologies and feedstock types, investigating the production of a superset of fuels and chemicals, systematically addressing price uncertainties for robust refinery designs, and synthesizing a supply network optimization to potentially displace the petroleum demand. This perspective article reviews the current work on integrated biomass/natural gas and biomass/coal refineries, highlights the major advances in these fields, and discusses future directions.

1 Introduction

The United States demands about 19.03 million barrels of petroleum products per day²², of which 38.6% (7.34 million) are supplied via imports²². As Figure 1 illustrates, recent market trends make crude oil prices extremely volatile. Additionally, petroleum industries in the United States accounted for 2254 million metric tons of CO₂ emissions in 2012¹⁶. This motivates the development of processes that utilize domestically available coal, biomass, and natural gas for fuels production to reduce dependence on crude oil imports and mitigate greenhouse gas (GHG) emissions.

Figure 1: Spot Price of Crude Oil in Recent Years¹⁸

Biomass is an attractive feedstock that is abundantly available in the United States¹³ and can reduce lifecycle GHG emissions. Coal is an abundantly available feedstock with low delivered cost (\$2.0-\$2.5/MM Btu)²¹, but has a high carbon content that can trigger higher conversion to CO₂^{15,28,39,45}. Natural gas is an attractive feedstock with a high hydrogen to carbon ratio and a low price (7.97 \$/TSCF in 2008 to 2.66\$/TSCF in 2012¹⁷). Therefore, integrating biomass with coal or natural gas can provide reduced GHG emissions and attractive process economics. A recent review highlighted key developments for the processes that utilize these feedstocks towards the production of fuels²³. Figure 2 presents a flow diagram that spans all the process alternatives

that are considered in the literature. In this article, we present the existing alternatives, state-of-the-art approaches, new directions, and outstanding challenges towards the integrated biomass and fossil fuel systems for the production of fuels and chemicals.

Figure 2: Block Flow Diagram of Integrated Biomass and Fossil Fuel Systems: Although the major sections of all the considered refinery designs are consistent, there are numerous process alternatives that need to be evaluated simultaneously.

2 Integration of Biomass and Natural Gas

The combination of biomass and natural gas within an integrated refinery provides a synergistic advantage compared to single feedstock systems. Borgwardt considered biomass and natural gas to be the feedstock of such hybrid refineries in 1997⁸. Despite utilizing a fixed topology and producing a single product (methanol), the techno-economic analysis revealed a savings of \$4.28 per gigajoule of gasoline displaced⁸. Borgwardt's environmental analysis also showed that the net CO₂ emissions avoided were superior than the equivalent single feedstock counterparts⁸. Dong and Steinberg¹⁴ studied a process design where the gasification effluent is directed into the steam reformer along with natural gas that has high hydrogen content¹⁴. The economic and the environmental analysis suggested that this process can be economically competitive and can reduce CO₂ emissions¹⁴.

In 2009, Agrawal and Singh² proposed conversion of biomass through fast-hydropyrolysis and hydrodeoxygenation and integrated this process with a steam methane reformer. The resulting process increased the combined fuel yield 60% compared to the equivalent single feedstock counterparts². In 2010, Li et al., suggested that mixing the reformed gases from natural gas and biomass gasification can provide the optimal H/C ratio while avoiding extra water-gas-shift units³². Liu et al., proposed co-producing liquid fuels and electricity through gasification and autothermal reforming³⁴ to reduce GHG emissions significantly. Chakravarti and coworkers presented results on a natural gas enhanced biomass to liquids process⁹. The process is simulated and optimized for a fixed topology, and some topological alternatives were considered for which the selection was made qualitatively⁹. These process simulations provided valuable information regarding the economics and environmental benefits of the process alternatives investigated, however they cannot simultaneously compare competing technologies. As other process alternatives or technologies are developed, the number of possible process designs grow exponentially, and simulating each design alternative individually becomes impossible.

In this regard, superstructure based optimization approaches are becoming more popular because they simultaneously compare technologies and weigh the strengths and weaknesses of each process alternative. Gencer et al.²⁴ synthesized and optimized a superstructure with two different alternatives for biomass conversion (gasification and fast-hydropyrolysis). A more comprehensive superstructure was presented by Baliban et al.⁴ that considered multiple natural gas conversion pathways, multiple hydrocarbon production alternatives, and several upgrading technologies to produce liquid fuels at the lowest possible cost⁴. Recent efforts by Onel et al.,⁴³ and Niziolek et al.,⁴¹ have expanded this superstructure by allowing co-production of fuels and chemicals (olefins⁴³ and aromatics⁴¹) while maximizing the profit.

3 Hybrid Energy Systems Utilizing Coal and Biomass

In an attempt to develop alternative processes that can address the problems associated with the use of petroleum, the research community has also investigated hybrid energy systems that utilize coal and biomass. Many studies within the literature include the simulation and economic evaluation of fixed process topologies.^{29,33,50} Several of these approaches have focused solely on the conversion

of synthesis gas into hydrocarbons using the Fischer-Tropsch process.^{29,33,50} Chmielniak and Sciazko investigated the co-gasification of biomass and coal in the context of methanol production.¹² Warren and El-Halwagi determined the economic feasibility of a coal and municipal solid waste plant utilizing liquefaction.⁴⁹ Recent papers utilizing fixed topologies have incorporated synthesis gas conversion into methanol and subsequently methanol-to-gasoline technologies.^{35–37}

Motivated by the same reasons outlined above, several researchers have investigated these systems via an optimization based superstructure approach. Chen et al., proposed a nonlinear programming model that coproduced power and liquid fuels, and maximized the net present value of such polygeneration systems.^{10,11} Recently Niziolek et al., have investigated the conversion of coal and biomass to liquid transportation fuels using an optimization-based process synthesis framework.⁴² Several alternative pathways for synthesis gas (syngas) conversion and hydrocarbon upgrading were compared simultaneously to determine the optimal process topology that can produce liquid fuels at the lowest cost.⁴²

4 Process Details

The systems considered in this context provide numerous process alternatives (Figure 2). It is vital to identify all the alternatives to evaluate within a single framework. In the following subsections, we identify all possible alternatives of these systems.

4.1 Feedstock Conversion

The potential feedstock conversion alternatives for biomass, coal, and natural gas are shown in Figure 3. Although biomass conversion in energy applications can be thermochemical^{5–7,19,23}, catalytic^{3,23}, or biological^{1,23,44} the integrated systems only considered methods of thermochemical conversion, mainly gasification. The gasification process produces a syngas intermediate, which creates an opportunity for biomass to be integrated with fossil feedstocks. Meanwhile, catalytic and biological conversion routes were never considered in an integrated refinery. The syngas produced from gasification is usually treated, but Dong et al.¹⁴ considered sending gasifier effluent into the steam reformer along with the natural gas feed. Chmielniak and Sciazko¹² investigated the co-gasification of biomass and coal within the same gasifier instead of separate trains. Several

studies considered variable operating conditions for the gasifier^{4-7,41-43}, which is an important strength of superstructure based optimization since the optimal operating conditions are functions of the plant scale, production constraints, and GHG limitations^{4-7,41-43}. Aside from gasification, several studies also considered fast-hydropyrolysis^{2,24}.

The conversion of coal mainly proceeds through gasification, which is an established route for coal conversion in energy applications. Natural gas can be converted via different types of reforming to produce syngas or direct conversion processes such as partial oxidation and oxidative coupling. Steam reforming and autothermal reforming processes are commercially available processes, but it is not possible to know *a priori* the optimal conversion technology, the optimal operating condition, and the optimal steam to natural gas ratio. A superstructure based optimization approach can evaluate all of these process alternatives at different operating conditions^{4,24,41-43}.

Figure 3: Various feedstock conversion alternatives are shown. Blue color represents the processes going through the synthesis gas intermediate. Green color represents the direct conversion processes.

4.2 Hydrocarbon Production/Upgrading

The type of hydrocarbon produced in these integrated processes can vary. The desired hydrocarbon product can either be methanol or drop-in fuels such as gasoline, diesel, and kerosene. Methanol can be produced through a methanol synthesis process indirectly via synthesis gas, or directly from natural gas⁴. On the other hand, the drop-in fuels can be produced by variations of Fischer-Tropsch processes (different temperatures, different catalysts) or methanol conversion processes (methanol to gasoline, methanol to olefins, olefins to gasoline/distillate). Several competing upgrading schemes also exist that vary the yields of the fuel products. Liu et al.³⁵ compares the Fischer-Tropsch and methanol-to-gasoline processes in this context through the use of fixed topologies. However, the syngas conversion alternatives for hydrocarbon, heat, electricity, and hydrogen production (Figure 4) produces semi-infinitely many process designs due to existence of various alternatives and split decisions. A more rigorous and systematic set of studies considered most of these possible production and upgrading schemes using a global optimization branch-and-bound framework^{4,41–43}. These studies^{4,41–43} have shown that important trade-offs can be identified among the production and upgrading alternatives depending on the plant scale and production constraints.

Figure 4: Syngas conversion alternatives to hydrocarbons, heat, hydrogen, and electricity are shown. Each line represents a decision, whereas the blue boxes represent more decisions are to be made. Red boxes represent that the terminal decision is made for the branch. It should be noted that some decisions (catalyst or temperature selection) are binary, whereas other decisions can be a split creating semi-infinitely many combinations.

4.3 Chemicals Production

An emerging area towards the synthesis of alternative refineries is the consideration of high value chemicals production. Some work in the literature focused on the co-production of fuels and chemicals from a single feedstock. Vlysidis et al.⁴⁷ performed a techno-economic analysis of a refinery that co-produces biodiesel and succinic acid. Kelloway and Daoutidis³⁰ introduced a superstructure that allows for the co-production of Fischer-Tropsch fuels and various chemicals (lactic acid, succinic acid, acetic acid, levulinic acid, and xylitol) from biomass. Wang et al.⁴⁸ simulated an integrated biomass refinery that considers the co-production of gasoline, diesel, olefins, and aromat-

ics. Gong and You²⁵ introduced and optimized a superstructure capable of co-producing biodiesel, propylene glycol, glycerol-tert-butyl-ether, and poly-3-hydroxybutyrate from microalgae. However, none of these refineries attempted to integrate fossil fuels along with their biomass based feedstock.

In 2014, He and You²⁶ studied an integrated shale gas recovery and ethylene production plant. In a subsequent study²⁷, they proposed an integrated system that utilizes shale gas and bioethanol to produce olefins and natural gasoline. Onel et al.⁴³ proposed a superstructure that co-produces liquid transportation fuels and olefins from biomass and natural gas. Niziolek et al.⁴¹ proposed a superstructure that considers the co-production of liquid transportation fuels and aromatics from biomass and natural gas. It is shown that olefins and aromatics can significantly improve the plant profitability (see Table 1 and Figure 5^{41,43}). Even though there are efforts towards the co-production of liquid fuels and chemicals, there are many types of chemicals and production routes that can be considered. Identification of a complete superset of chemicals and synthesis of a complete chemicals production superstructure is needed to account for all the processes and all the products.

Figure 5: Effect of Olefins and Aromatics Production: It was observed that the olefins and aromatics production increase the plant profitability in a significant manner^{41,43}

Table 1: Effect of Chemicals Co-Production on a 10 thousand barrels per day fuels plant from biomass and natural gas

Chemicals Production (MT/day)	0	50	100	150	200
Fuels + Olefins Profit (\$/GJ) ⁴³	8.38	8.75	9.17	9.57	9.94
Fuels + Aromatics Profit (\$/GJ) ⁴¹	8.38	8.60	8.91	9.23	9.53

4.4 Superstructure Based Optimization

The combinatorial nature of the problem shown in Figures 3 and 4 creates semi-infinitely many alternatives that need to be evaluated simultaneously. The evolution of superstructure based optimization stemmed from this intrinsic challenge of the problem. Recent increases in the available computing power and development of many efficient algorithms provided the ability to optimize these large-scale superstructures^{4-7,11,24,27,41-43} within a reasonable time-scale (≤ 100 hours).

Meanwhile, it is practically impossible to compare all the alternatives as a separate flowsheet optimization problem, therefore superstructure based optimization is necessary for a fair comparison of alternatives for performance and synergistic effects.

5 Economic Viability and Environmental Benefits

The successful commercialization of these technologies is economically driven. Utilization of biomass is also environmentally driven to reduce GHG emissions. Table 2 shows the major economical and environmental findings of refineries that utilize biomass and natural or coal and biomass over the years.

The processes that utilize *biomass and natural gas* as a feedstock are presented in the first part of Table 2. These processes are performed over a large range of years, production scales, and products, therefore the investment costs range between 150-1760 MM\$. The economic indicators are generally positive, but they are very sensitive to current energy prices. As an illustration, the break-even oil price reported by Baliban et al.⁴, \$80.36/bbl, can be economically viable or not depending on the possible large range of crude oil prices outlined in Figure 1. It is also reported that the GHG emissions can be reduced by at least 41% and this can be higher depending on the ratio of biomass to natural gas input.

The processes that utilize *coal and biomass* as a feedstock are presented in the second part of Table 2. Although these studies are performed over a smaller range of years (2007-2012), the production scales are similar, and the main products are mostly the conventional liquid transportation fuels, the investment costs still range between 958-1600 MM\$. The break-even oil prices mostly exceed \$100/bbl, which makes these processes more likely to be not viable. However, the superstructure based approach resulted in a break-even oil price of \$68.65/bbl, which makes it more likely to be economically viable. Through the use of these processes, the greenhouse gas emissions can be reduced by at least 50% and the net emissions can be negative depending on the amount of CO₂ sequestration and the ratio of biomass to natural gas input.

The processes investigated can be economically and environmentally viable while a superstructure based approach provides the "best" possible alternative. However, sensitivity to the volatile feedstock and product prices needs to be addressed. Some studies address the feedstock and prod-

uct price uncertainty in the processes using a Monte Carlo simulation method^{26,27}. Liu et al. developed a decomposition based two stage stochastic programming approach for polygeneration systems of this type for design under uncertainty³⁸. Lee et al., optimized a gas-to-liquids plant under different price scenarios³¹. Morales-Rodrigues et al., developed a stochastic programming based framework that can be applied to process design problems for evaluating the impact of technical, market, and political uncertainties⁴⁰. Tay et al. considered robust optimization of a biorefinery considering the uncertainties in the biomass supply and product demand amounts⁴⁶. Therefore, it is of primary importance to systematically identify the types of uncertainties and address them within the superstructure based framework^{4-7,41-43}.

6 Summary and Future Outlook

This article presents the advances and the state of the art approaches for integrated biomass and fossil fuel refineries. Since many process alternatives exist, a superstructure based optimization approach is a strong tool to evaluate all the alternatives within the same platform. The emerging computational resources make it possible to solve these optimization problems to global optimality within a reasonable time scale. Recent work also suggests that co-production of chemicals along with fuels can provide economically more attractive refineries. However, there are still many outstanding challenges to be addressed.

As noted before, biomass conversion can occur via biological or catalytic routes. Existing studies do not attempt to integrate biological or catalytic conversion processes with fossil fuel systems. Implementation of these routes are important in evaluating trade-offs between alternatives. A relevant challenge is the lack of consideration of different types of feedstocks. Biomass, coal, and natural gas can have different compositions depending on the specific type (biomass: lignocellulosic, algal, municipal solid waste etc.; coal and natural gas: different composition depending on geography, well, mine etc.) being considered. Most of the previous contributions do not consider variability in these feedstocks. Consideration of multiple types and combinations can provide information about topological trade-offs. Moreover, the fossil feedstocks considered in the literature are only coal and natural gas. Although the United States is import dependent on petroleum, the domestic production is still high. Displacing the petroleum demand emerges as an opportunity

Table 2: Economic and Environmental Performance of Processes that use Biomass and Natural Gas or Coal and Biomass as feedstocks

Biomass and Natural Gas										
Source	Economic Year	Platform	Product	Scale	Economic Indicator	Value	Economic Indicator 2	Value	Investment Cost (MM\$)	GHG Reduction
Borgwardt ⁸	1991	Aspen Plus	M ^a	6 mil gallons/day of M ^a	Production Cost	\$0.479/gal	BEGP ^b	\$1.16/gal	1760	71%
Dong and Steinberg ¹⁴	1993	N/A	M ^a	0.3 mil gallons/day of M ^a	Production Cost	\$0.43/gal	BEGP ^b	\$0.66/gal	150.8	41%
Liu et al. ³⁴	2007	Aspen Plus	GDK ^c	8.4 kBD ^d of fuels	Levelized Electricity Cost	\$0.102/kwh	N/A	N/A	1149	90%
Baliban et al. ⁴	2011	GAMS	GDK ^c	10 kBD ^d of fuels	Cost of Production	\$16.34/GJ	BEOP ^e	\$80.36/bbl	879	50%
Onel et al. ⁴³	2014	GAMS	GDK ^c + O ^f	10 kBD ^d of GDK ^c + 500 MT/day ^g of O ^f	Profit	\$11.81/GJ	NPV ^h	859 MM\$	981	50%
Niziolek et al. ⁴¹	2014	GAMS	GDK ^c + A ⁱ	10 kBD ^d of GDK ^c + 500 MT/day ^j of A ⁱ	Profit	\$10.55/GJ	NPV ^h	597 MM\$	1090	50%
Coal and Biomass										
Source	Economic Year	Platform	Product	Scale	Economic Indicator	Value	Economic Indicator 2	Value	Investment Cost (MM\$)	GHG Reduction
Liu et al. ³³	2007	Aspen Plus	GDK ^c	8.036 kBD ^d of fuels	Production Cost	\$22.2/GJ	BEOP ^e	\$110/bbl	1427	91%
Liu et al. ³⁷	2012	Aspen Plus	G ^j	9.871 kBD ^d of fuels	Production Cost	\$28.5/GJ	BEOP ^e	\$129/bbl	1600	100%
Liu and Larson ³⁵	2012	Aspen Plus	G ^j	9.871 kBD ^d of fuels	BEOP ^e	\$126/bbl	N/A	N/A	1549	100%
Niziolek et al. ⁴²	2012	GAMS	GDK ^c	10 kBD ^d of fuels	Cost of Production	\$14.79/GJ	BEOP ^e	\$68.65/bbl	958	50%
a. M = Methanol; b. BEGP = break-even gasoline price; c. GDK = gasoline, diesel, kerosene; d. kBD = thousand barrels per day; e. BEOP = break-even oil price f. O = olefins g. MT/day = metric tons per day; h. NPV = net present value; i. A = aromatics; j. G = gasoline										

a. M = Methanol; b. BEGP = break-even gasoline price; c. GDK = gasoline, diesel, kerosene; d. kBD = thousand barrels per day; e. BEOp = break-even oil price

f. O = olefins g. MT/day = metric tons per day; h. NPV = net present value; i. A = aromatics j. G = gasoline

to integrate petroleum with biomass based systems to evaluate synergistic gains, economic viability, and environmental performance. Recent prices of petroleum suggests that an oversupply of petroleum can provide inexpensive sources to the market.

The existing efforts in the literature mainly focused on liquid fuels production. Co-production of fuels and chemicals was only considered for two classes of chemicals such as olefins^{27,43,48} and aromatics^{41,48}. However, the spectrum of possible chemicals can be much wider. Allowing for the co-production of such chemicals can provide valuable insights on which chemicals to co-produce. Along the same lines, the existing work never considered the demands of certain type of chemicals. Unlike the large market for liquid transportation fuels, excessive production of certain chemicals can oversupply the market quickly. An integrated refinery and a chemicals complex with a wide product spectrum should also consider the relative demands of each candidate product and necessary upper bounds should be placed.

Due to the volatility in the market, the feedstock and product prices are subject to change frequently. These uncertainties may result in non-profitable refinery topologies for undesired price scenarios. It is important to address these uncertainties in a systematic fashion (e.g., robust optimization, stochastic programming) within the superstructure based framework. These will lead to robust plant topologies that can remain profitable under different price scenarios.

Lastly, the existing work in the literature usually considers a single plant capable of producing these fuels and chemicals. A single plant provides valuable information about economic viability and environmental performances, but it does not provide sufficient information about the possibility of displacing the current petroleum demand. Hence, a rigorous supply network optimization is needed to investigate if it is possible to displace a fraction of the current petroleum demand. This would also incorporate the demand locations of the potentially co-produced chemicals. Elia et al. presented an extensive review of energy supply chains and pointed out the future opportunities for consideration of multiple feedstocks, downstream operations, and nationwide supply chains²⁰. A strategic planning optimization is further required to propose a feasible planning horizon towards building these refineries.

Acknowledgments

The authors acknowledge partial financial support from the National Science Foundation (NSF EFRI-0937706 and NSF CBET-1158849).

References

- [1] M. T. Agler, B. A. Wrenn, S. H. Zinder, and L. T. Angenent, “Waste to bioproduct conversion with undefined mixed cultures: the carboxylate platform,” *Trends in biotechnology*, vol. 29, no. 2, pp. 70–78, 2011.
- [2] R. Agrawal and N. R. Singh, “Synergistic routes to liquid fuel for a petroleum-deprived future,” *AIChE journal*, vol. 55, no. 7, pp. 1898–1905, 2009.
- [3] D. M. Alonso, J. Q. Bond, and J. A. Dumesic, “Catalytic conversion of biomass to biofuels,” *Green Chemistry*, vol. 12, no. 9, pp. 1493–1513, 2010.
- [4] R. C. Baliban, J. A. Elia, and C. A. Floudas, “Biomass and Natural Gas to Liquid Transportation Fuels: Process Synthesis, Global Optimization, and Topology Analysis,” *Ind. Eng. Chem. Res.*, vol. 52, pp. 3381–3406, 2013.

Special Interest: This paper is the first example of a superstructure of BGTL systems
- [5] ———, “Biomass to Liquid Transportation Fuels (BTL) Systems: Process Synthesis and Global Optimization Framework,” *Energy Environ. Sci.*, vol. 6, pp. 267–287, 2013.
- [6] R. C. Baliban, J. A. Elia, C. A. Floudas, B. Gurau, M. B. Weingarten, and S. D. Klotz, “Hardwood Biomass to Gasoline, Diesel, and Jet Fuel: 1. Process Synthesis and Global Optimization of a Thermochemical Refinery,” *Energy & Fuels*, vol. 27, pp. 4302–4324, 2013.
- [7] R. C. Baliban, J. A. Elia, C. A. Floudas, X. Xiao, Z. Zhang, J. Li, H. Cao, J. Ma, Y. Qiao, and X. Hu, “Thermochemical Conversion of Duckweed Biomass to Gasoline, Diesel, and Jet Fuel: Process Synthesis and Global Optimization,” *Ind. Eng. Chem. Res.*, pp. 11 436–11 450, 2013.
- [8] R. H. Borgwardt, “Biomass and natural gas as co-feedstocks for production of fuel for fuel-cell vehicles,” *Biomass and Bioenergy*, vol. 12, no. 5, pp. 333–345, 1997.
- [9] S. Chakravarti, D. P. Bonaquist, R. F. Drnevich, and M. M. Shah, “Natural gas enhanced

biomass to liquids: Project development and modeling,” *Computers & Chemical Engineering*, vol. 47, pp. 67–75, 2012.

Special Interest: This paper considers multiple process alternatives and identifies the need for a single platform to evaluate them all.

[10] Y. Chen, T. A. Adams, II, and P. I. Barton, “Optimal design and operation of flexible energy polygeneration systems,” *Ind. Eng. Chem. Res.*, vol. 50, no. 8, pp. 4553–4566, 2011.

[11] —, “Optimal design and operation of static energy polygeneration systems,” *Ind. Eng. Chem. Res.*, vol. 50, no. 9, pp. 5099–5113, 2011.

Special Interest: This paper is one of the earliest examples of a superstructure that produces fuels from coal and biomass.

[12] T. Chmielniak and M. Sciazko, “Co-gasification of biomass and coal for methanol synthesis,” *Applied energy*, vol. 74, no. 3, pp. 393–403, 2003.

[13] Department of Energy, “Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply. Document Number: DOE/GO-102005-2135,” <http://www1.eere.energy.gov/biomass/publications.html>, 2005.

[14] Y. Dong and M. Steinberg, “Hynol—an economical process for methanol production from biomass and natural gas with reduced CO_2 emission,” *Int. J. Hydrogen Energy*, vol. 22, no. 10-11, pp. 971–977, 1997.

[15] J. J. Dooley, R. T. Dahowski, and C. L. Davidson, “The potential for increased atmospheric CO_2 emissions and accelerated consumption of deep geologic CO_2 storage resources resulting from the large-scale deployment of a ccs-enabled unconventional fossil fuels industry in the u.s.” *Int. J. Green. Gas Cont.*, vol. 3, pp. 720–730, 2009.

[16] EIA, “Monthly Energy Review – April 2013,” <http://www.eia.gov/tools/faqs/faq.cfm>, 2013.

[17] —, “U.S. Energy Information Administration Database,” <http://www.eia.gov/todayinenergy/detail.cfm?id=15071>, 2014.

- [18] —, “U.S. Energy Information Administration Petroleum Database,” <http://www.eia.gov/petroleum/>, 2015.
- [19] J. A. Elia, R. C. Baliban, C. A. Floudas, B. Gurau, M. B. Weingarten, and S. D. Klotz, “Hardwood Biomass to Gasoline, Diesel, and Jet Fuel: 2. Supply Chain Optimization Framework for a Network of Thermochemical Refineries,” *Energy & Fuels*, vol. 27, pp. 4325–4352, 2013.
- [20] J. A. Elia and C. A. Floudas, “Energy supply chain optimization of hybrid feedstock processes: A review,” *Annual review of chemical and biomolecular engineering*, vol. 5, pp. 147–179, 2014.
- [21] Energy Information Administration, “Annual Energy Outlook 2013 with Projections to 2035. Document Number: DOE/EIA-0383(2012),” <http://www.eta.doe.gov/oiaf/aeo/>, 2012.
- [22] —, “Short-Term Energy Outlook – March 2015,” http://www.eia.gov/forecasts/steo/report/us_oil.cfm, 2014.
- [23] C. A. Floudas, J. A. Elia, and R. C. Baliban, “Hybrid and Single Feedstock Energy Processes for Liquid Transportation Fuels: A Critical Review,” *Comp. Chem. Eng.*, vol. 41, pp. 24–51, 2012.

Outstanding Interest: This paper is a very extensive review of single and hybrid energy systems that considers all the feedstock alternatives.

- [24] E. Gencer, D. Mallapragada, M. Tawarmalani, and R. Agrawal, “Synergistic biomass and natural gas conversion to liquid fuel with reduced CO₂ emissions,” *FOCAPD 2014*, pp. 525–530, 2014.

Special Interest: This paper presents synergistic gains for a BGTL superstructure for different biomass to natural gas ratios and a novel biomass conversion method.

- [25] J. Gong and F. You, “Value-added chemicals from microalgae: Greener, more economical, or both?” *ACS Sustainable Chemistry & Engineering*, 2015.

- [26] C. He and F. You, “Shale gas processing integrated with ethylene production: novel process designs, exergy analysis, and techno-economic analysis,” *Industrial & Engineering Chemistry Research*, vol. 53, no. 28, pp. 11 442–11 459, 2014.
- [27] ———, “Toward more cost-effective and greener chemicals production from shale gas by integrating with bioethanol dehydration: Novel process design and simulation-based optimization,” *AIChE Journal*, 2014.
- Special Interest: This paper presents a process that co-produces olefins and natural gasoline from shale gas and bioethanol while considering uncertainty.
- [28] P. Jaramillo, W. M. Griffin, and H. S. Matthews, “Comparative analysis of the production costs and life-cycle ghg emissions of ft liquid fuels from coal and natural gas,” *Env. Sci. Technol.*, vol. 42, no. 20, pp. 7559–7565, 2008.
- [29] Y. Jiang and D. Bhattacharyya, “Plant-wide modeling of an indirect coal–biomass to liquids (cbtl) plant with co₂ capture and storage (ccs),” *International Journal of Greenhouse Gas Control*, vol. 31, pp. 1–15, 2014.
- [30] A. Kelloway and P. Daoutidis, “Process synthesis of biorefineries: optimization of biomass conversion to fuels and chemicals,” *Industrial & Engineering Chemistry Research*, vol. 53, no. 13, pp. 5261–5273, 2013.
- [31] C.-J. Lee, Y. Lim, H. S. Kim, and C. Han, “Optimal gas-to-liquid product selection from natural gas under uncertain price scenarios,” *Industrial & Engineering Chemistry Research*, vol. 48, no. 2, pp. 794–800, 2008.
- [32] H. Li, H. Hong, H. Jin, and R. Cai, “Analysis of a feasible polygeneration system for power and methanol production taking natural gas and biomass as materials,” *Appl. Energy*, vol. 87, pp. 2846–2853, 2010.
- [33] G. Liu, E. D. Larson, R. H. Williams, T. G. Kreutz, and X. Guo, “Making fischer-tropsch fuels and electricity from coal and biomass: Performance and cost analysis,” *Energy Fuels*, vol. 25, pp. 415–437, 2011.

- [34] G. Liu, R. H. Williams, E. D. Larson, and T. G. Kreutz, "Design/economics of low-carbon power generation from natural gas and biomass with synthetic fuels co-production," *Energy Procedia*, vol. 4, pp. 1989–1996, 2011.
- [35] G. Liu and E. D. Larson, "Comparison of coal/biomass co-processing systems with ccs for production of low-carbon synthetic fuels: Methanol-to-gasoline and fischer-tropsch," *Energy Procedia*, vol. 63, pp. 7315–7329, 2014.
- [36] G. Liu, E. D. Larson, R. H. Williams, and X. Guo, "Gasoline from coal and/or biomass with co2 capture and storage, part a: Process designs and performance analysis," *Energy & Fuels*.
- [37] —, "Gasoline from coal and/or biomass with co2 capture and storage, part b: Economic analysis and strategic context," *Energy & Fuels*, 2015.
- [38] P. Liu, E. N. Pistikopoulos, and Z. Li, "Decomposition based stochastic programming approach for polygeneration energy systems design under uncertainty," *Industrial & Engineering Chemistry Research*, vol. 49, no. 7, pp. 3295–3305, 2010.

Outstanding Interest: This paper presents a stochastic programming framework for the optimization of polygeneration systems under uncertainty.

- [39] H. C. Mantripragada and E. S. Rubin, "Techno-economic evaluation of coal-to-liquids (ctl) plants with carbon capture and sequestration," *Energy Policy*, vol. 39, no. 5, pp. 2808–2816, 2011.
- [40] R. Morales-Rodriguez, A. S. Meyer, K. V. Gernaey, and G. Sin, "A framework for model-based optimization of bioprocesses under uncertainty: Lignocellulosic ethanol production case," *Computers & Chemical Engineering*, vol. 42, pp. 115–129, 2012.
- [41] A. M. Niziolek, O. Onel, J. A. Elia, R. C. Baliban, and C. A. Floudas, "Coproduct of liquid transportation fuels and c6_c8 aromatics from biomass and natural gas," *AIChE Journal*, vol. 61, no. 3, pp. 831–856, 2015.

Outstanding Interest: This paper presents the first superstructure that considers fuels and aromatics co-production

- [42] A. M. Niziolek, O. Onel, J. A. Elia, R. C. Baliban, X. Xiao, and C. A. Floudas, “Coal and biomass to liquid transportation fuels: Process synthesis and global optimization strategies,” *Industrial & Engineering Chemistry Research*, vol. 53, no. 44, pp. 17 002–17 025, 2014.

Special Interest: This paper presents a comprehensive superstructure for CBTL systems.

- [43] O. Onel, A. M. Niziolek, J. A. Elia, R. C. Baliban, and C. A. Floudas, “Biomass and natural gas to liquid transportation fuels and olefins (bgtl+c2_c4): Process synthesis and global optimization,” *Industrial & Engineering Chemistry Research*, vol. 54, no. 1, pp. 359–385, 2015.

Outstanding Interest: This paper presents the first superstructure that considers fuels and olefins co-production

- [44] V. Pham, M. Holtzapple, and M. El-Halwagi, “Techno-economic analysis of biomass to fuel conversion via the mixalco process,” *Journal of industrial microbiology & biotechnology*, vol. 37, no. 11, pp. 1157–1168, 2010.
- [45] B. K. Sovacool, C. Cooper, and P. Parenteau, “From a hard place to a rock: Questioning the energy security of a coal-based economy,” *Energy Policy*, vol. 39, pp. 4664–4670, 2011.
- [46] D. H. Tay, D. K. Ng, and R. R. Tan, “Robust optimization approach for synthesis of integrated biorefineries with supply and demand uncertainties,” *Environmental Progress & Sustainable Energy*, vol. 32, no. 2, pp. 384–389, 2013.
- [47] A. Vlysidis, M. Binns, C. Webb, and C. Theodoropoulos, “A techno-economic analysis of biodiesel biorefineries: Assessment of integrated designs for the co-production of fuels and chemicals,” *Energy*, vol. 36, no. 8, pp. 4671–4683, 2011.
- [48] K. Wang, L. Ou, T. Brown, and R. C. Brown, “Beyond ethanol: a techno-economic analysis of an integrated corn biorefinery for the production of hydrocarbon fuels and chemicals,” *Biofuels, Bioproducts and Biorefining*, 2014.

Special Interest: This paper is the first example that considers the co-production of liquid fuels, olefins, and aromatics from biomass.

- [49] A. Warren and M. El-Halwagi, “An economic study for the co-generation of liquid fuel and hydrogen from coal and municipal solid waste,” *Fuel Proc. Technol.*, vol. 49, pp. 157–166, 1996.
- [50] R. H. Williams, G. Liu, T. G. Kreutz, and E. D. Larson, “Coal and biomass to fuels and power,” *Annual review of chemical and biomolecular engineering*, vol. 2, pp. 529–553, 2011.