HARDWOOD BIOMASS TO OLEFINS AND AROMATICS: PROCESS SYNTHESIS AND DETERMINISTIC GLOBAL OPTIMIZATION

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In honor of Professor Christodoulos A. Floudas

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Abstract

The thermochemical conversion of biomass into valuable hydrocarbons represents an opportunity toward the creation of a more environmentally sustainable energy landscape. A crucial challenge to meet this goal is the development of economically competitive biomass-based processes. In this work, we introduce a deterministic global optimization-based process synthesis framework with simultaneous heat, power, and water integration to determine the most profitable processes for the production of aromatics and olefins from hardwood biomass via methanol. Aromatics and olefins represent the two most important classes of high-value chemicals and are intermediates used for the production of everyday products, such as plastics, polyester fibers, resins, and dyes. A process superstructure with several novel, commercial, and/or competing technologies is modeled and described. The resulting mixed-integer, nonlinear, non-convex optimization model is solved using a branch-and-bound global optimization algorithm and is demonstrated on three case studies that investigate the effect of refinery capacity on the overall profit. The results indicate that at the largest scale investigated (2000 metric tons of product per day), the biorefinery is profitable with a net present value of $892 MM and a required investment cost of $2163 MM.

Keywords

Deterministic global optimization, aromatics, olefins, biomass, simultaneous heat and power integration

Introduction

A recent perspective article by Floudas et al. (2016) has outlined how biomass-based processes have benefited from multi-scale systems engineering analysis, which includes modeling, design, synthesis, simulation, and optimization. As such, greater incorporation of renewable resources into the energy landscape has received significant attention over the past decades owing to the potential for more sustainable energy processes. The state of the art approaches and future challenges in integrated biomass and fossil fuel systems has also been discussed in a recent perspective (Onel et al.,

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2015). Studies in the literature have focused on the conversion of biomass into liquid transportation fuels (Baliban et al., 2013), electricity, and more recently, into aromatic hydrocarbons (Niziolek et al., 2016a; Lin et al., 2013). In this work, we present the first-ever standalone process synthesis superstructure that converts hardwood biomass into predominantly C6-C8 aromatics and C2-C4 olefins, two of the most important classes of chemicals.

Olefins and aromatics are used in a wide variety of applications. Ethylene, for example, is used to produce polyethylene, ethylene dichloride, and ethylene oxide (Onel et al., 2016). Para-xylene, the most important xylene isomer, is used in the production of polyethylene terephthalate (PET) fibers, resins, and films (Meyers, 2004). The global consumption of ethylene, propylene, and butadiene was 114.6, 73.5, and 10.1 million tons per year in 2007, while the global consumption of benzene, toluene, and xylenes in the same year was 40.6, 20.9, and 40.7 million tons (de Klerk, 2011).

In order to determine the economic and technical feasibility of a standalone biomass to olefins and aromatics (BTOA) refinery, a combined process synthesis and deterministic global optimization approach is used that simultaneously compares millions of process designs to determine the optimal process topology. A superstructure of process alternatives containing several novel, commercial, and competing alternatives is modeled as a large-scale mixed-integer nonlinear optimization (MINLP) model. The MINLP model is then solved to global optimality using a branch-and-bound global optimization algorithm. Simultaneous heat, power, and water integration is included in all refinery designs investigated (Elia et al., 2010). The branch-and-bound global optimization algorithm mathematically guarantees the profit of these BTOA refineries is within a few $/GJ of the best possible value (Baliban et al., 2012).

Biomass to Olefins and Aromatics, BTOA, Process Superstructure

The following subsections will describe the key sections of a biomass to olefins and aromatics (BTOA) process refinery in detail. For a more detailed description of the process synthesis superstructure, please see Niziolek et al. (2016a, 2016b) and Onel et al. (2016).

Biomass Gasification and Synthesis Gas Cleaning

The hardwood biomass is delivered to the refinery as wood chips with a moisture content of 45 wt %. The hardwood is passed through a biomass drier to reduce its moisture content down to 20 wt % before being lockhopped using compressed CO_2 (10 wt %). The hardwood is then transferred to the gasifier, which operates at a pressure of 30 bar and a temperature of either 900 °C, 1000 °C, or 1100 °C. The optimal operating temperature is determined using the deterministic global optimization branch-and-bound algorithm.

The effluent of the biomass gasifier is determined using the stoichiometric model proposed by Baliban et al. (2010). The biomass synthesis gas (syngas) exiting the gasifier is passed through two ash cyclones before being directed to a catalytic tar cracker operating at 825 °C. The raw syngas exiting the tar cracker is then directed to the syngas cleaning section.

A portion of the biomass syngas can be split to a dedicated sour water-gas-shift (WGS) reactor operating at a pressure of 26 bar and a temperature of either 300 °C, 400 °C, 500 °C, or 600 °C (Niziolek et al., 2016a). The unit can be used as either a forward (fWGS) or reverse (rWGS) water-gas-shift reactor. The fWGS reactor will increase the H_2/CO ratio of the syngas at the expense of producing CO_2. The rWGS reactor provides a means of consuming any CO_2 generated within the refinery, but will require H_2 to facilitate the reaction. The syngas effluent exiting the WGS reactor, as well as any biomass syngas that bypasses the WGS reactor, is cooled down to 185 °C before being sent to the scrubbing section.

A Rectisol unit exists within the BTOA refinery to remove acid gases from the synthesis gas, thereby preventing contamination of the downstream hydrocarbon production and upgrading processes. A Claus recovery system hydrogenates H_2S and SO_2 into solid sulfur. The captured CO_2 from the acid gas recovery units can either be compressed to 31 bar and recycled within the refinery, compressed to 150 bar for sequestration, or vented to the atmosphere; a decision that is determined by the global optimization algorithm. The treated syngas is directed to the hydrocarbon production section.

Hydrocarbon Production and Upgrading

The clean syngas is input into a methanol synthesis reactor that operates at 250 °C and 45 bar. The methanol synthesis reaction, Eq. (1), and the water-gas-shift reaction, Eq. (2), are assumed to be in equilibrium in the reactor effluent.

$$\mathrm{CO} + 2\mathrm{H_2} \leftrightarrow \mathrm{CH_3OH} \quad (1)$$

$$\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \quad (2)$$

The raw methanol effluent is flashed, heated to form a vapor and expanded in a turbine to generate electricity, and passed through a degasser distillation column that removes the entrained gases from the methanol and water mixture. The methanol/water mixture is then split among the methanol-to-aromatics (MTA) reactor, the GTC GT-TolAlk toluene methylation reactor, the methanol-to-propylene (MTP) reactor, and the methanol-to-olefins (MTO) reactor (Niziolek et al., 2016a, 2016b; Onel et al., 2016). The optimal split fraction to each process will be determined via the deterministic global optimization algorithm.

The MTA reactor operates at a temperature of 425 °C and utilizes a Ag/ZSM-5 catalyst to convert the methanol into hydrocarbons and water (Inoue et al., 1995). The hydrocarbon effluent consists of aromatics, hydrogen, light gases, and C5+ aliphatics. The MTO reactor utilizes a SAPO-34 catalyst and operates at a temperature of 375 °C to produce an olefin-rich effluent along with water (Mokrani and Scurrell, 2009). The MTP reactor converts the methanol into a propylene-rich hydrocarbon product with water. The MTP reactor utilizes a ZSM-5 based proprietary catalyst, operates at 425 °C, and the resulting hydrocarbon effluent contains more than 70% propylene (Koempel and Liebner, 2007). The toluene methylation reactor uses a proprietary ZSM-5 based catalyst to convert a 4 to 1.80 wt % ratio of toluene to methanol into xylenes, fuel gas, C9 aromatics, and water (GTC, 2014). The toluene methylation reactor operates at 500 °C (GTC, 2014).

The olefins from the MTO and MTP reactor are sent to the olefins purification section. The MTA product is upgraded in the liquefied petroleum gas-aromatics separation section before the higher hydrocarbon product is directed to the aromatics complex. The aromatics from the toluene methylation reactor are directly sent to the aromatics complex. Ultimately, a portion of the higher non-aromatic hydrocarbons from the methanol conversion units are sent to the gasoline pool. Any light gases generated from the processes are recycled back to the refinery. The wastewater produced from the methanol conversion units is treated at the wastewater treatment network.

Aromatics Complex

Aromatics produced in the BTOA refinery are upgraded and separated in the aromatics complex (Niziolek et al., 2016a, 2016b). Aromatic-rich streams are first directed to the UOP Sulfolane process (Meyers, 2004), which recovers aromatic hydrocarbons from paraffinic hydrocarbons. Paraffins are directed to the gasoline pool, while the aromatic effluent is mixed with any other aromatic streams in the BTOA refinery before being sent to the benzene distillation column. The distillate of the benzene distillation column recovers high-purity benzene, while the bottom product is directed to the toluene distillation column. High-purity toluene product is recovered in the distillate, while the bottom product predominantly contains heavier (C8+) aromatics. The toluene distillate can either be: (1) output as product, (2) directed to the UOP Tatoray reactor, (3) directed to the UOP TAC9 reactor, (4) directed to the UOP PXPLUS reactor, or (5) directed to the toluene methylation reactor (Niziolek et al., 2016a, 2016b).

The bottom product from the toluene distillation column is sent to either one of two xylene distillation columns. The first xylene distillation column allows for the separation and production of ortho-xylene, the second does not. The distillate from both xylene distillation columns are allowed to be split to either the UOP Parex process or the UOP MX Sorbex process (Meyers, 2004), which are two adsorptive separation systems that selectively separate high purity para- and meta-xylene, respectively. The effluents from the two adsorptive separation systems are directed to the UOP Isomar process to re-establish an equilibrium mixture of xylene isomers and convert ethylbenzene to mixed xylenes with 30% wt per pass conversion (Meyers, 2004). The UOP Isomar effluent is passed through a deheptanizer column that purges the C7 light ends, and the C8-rich aromatic mixture is recycled back to either one of the two xylene distillation columns.

The bottom product from the ortho-xylene distillation column and the second xylene distillation column are sent to the C9 distillation column. The C9 distillation column recovers 99% of the incoming C9 aromatics in the distillate, along with a small portion of the C10 aromatics. The high-purity C9 distillate can be mixed with toluene and split to either the UOP Tatoray process or the UOP TAC9 process. The UOP Tatoray process creates mixed xylenes and benzene from the disproportionation of toluene and the transalkylation of toluene with C9 aromatics. The UOP TAC9 process produces mixed xylenes via the transalkylation of toluene with C9 aromatics.

Toluene directed to the UOP PXPLUS process undergoes selective toluene disproportionation to produce mainly para-xylene rich mixed xylenes and benzene. The effluent is sent to a single-stage crystallization system to recover para-xylene.

LPG Processing

Liquefied petroleum gases, LPG, produced within the refinery can either be output as byproduct, split to upgrading units that produce olefins or aromatics, or recycled back within the refinery. The Cyclar process utilizes a Ga/H-ZSM-5 catalyst to convert the LPG into aromatics, hydrogen, and light gases (Gregor et al., 1989). Alternatively, the LPG can be split to a debutanizer distillation column that separates the C3 hydrocarbons from the C4 hydrocarbons (Onel et al., 2016). The C3 distillate can be split to one of two propane dehydrogenation processes, either the C3 CB&I Catofin process or the C3 UOP Oleflex process, to produce propylene which is output as product. The C4 bottom is first directed to the UOP Butamer process to isomerize n-butane into isobutene, which is then split to either the C4 Oleflex process or the C4 CB&I Catofin process to produce isobutylene which is output as product.

Olefins Purification

Raw olefins from the MTO process and the propylene-rich olefin stream from the MTP process are fed into the olefins purification section (Onel et al., 2016). The olefins from the MTO process and the olefins produced from the olefin cracking process are directed to a deethanizer distillation column that separates C2 hydrocarbons in the distillate from C3-C4 hydrocarbons in the bottom. The distillate can be split to a selective hydrogenation unit that converts acetylene into ethylene, or it can bypass this unit and be directly sent to a C2 distillation column that recovers ethylene as a final product in the distillate. The bottom product from the C2 distillation column contains mostly ethane and is recycled back to the refinery.

The bottom product from the deethanizer distillation column is mixed with the C3 olefins from the MTP process and sent to a depropanizer distillation column. The distillate of the depropanizer distillation column contains C3 hydrocarbons, which are subsequently directed to a C3 distillation column that separates propylene from propane. The propylene is output as product, whereas the propane is recycled back to the refinery. The bottom product of the depropanizer column contains C4 hydrocarbons.

The C4 hydrocarbons are directed to a dimethylformamide (DMF)-based extractive distillation process that separates mixed butenes from butanes. The butenes can either be: (1) sold as a crude mixture, (2) separated to 1- and 2-butene, (3) dehydrogenated to butadiene via an oxo-dehydrogenation (Oxo-D) process, or (4) cracked to produced more ethylene or propylene (Onel et al., 2016). The Oxo-D process dehydrogenates the mixed butenes into 1,3-butadiene in the presence of oxygen. The olefin cracking process converts the C4 olefins to ethylene and propylene at a temperature of 500 °C and utilizes a zeolite-based catalyst (Chen et al., 2005).

Utilities

The process synthesis superstructure includes alternatives for the production of oxygen (air separation or electrolysis of water) and hydrogen (pressure-swing adsorption or electrolysis of water). A comprehensive wastewater treatment network consisting of a biological digestor, sour stripper, and reverse osmosis process is included to to recycle, reuse, and output wastewater within the refinery. Simultaneous heat and power integration utilizes a series of postulated heat engines to convert excess waste heat into electricity or steam. This integration is performed using a three-stage decomposition method, as previously described (Elia et al., 2010).

Deterministic Global Optimization

Objective Function

The process synthesis superstructure describing the biomass to olefins and aromatics process is modeled mathematically as a large-scale, non-convex, mixed-integer, nonlinear optimization (MINLP model) with 19,566 continuous variables, 32 binary variables, 23,998 constraints, and 779 non-convex terms. The objective function represents the total negative profit of the refinery and is minimized, as illustrated in Eq. (3):

$$MIN\ \sum_{f\in Feed} Cost^{f} + Cost^{El} + Cost^{Seq} + \sum_{u\in U_{Inv}} Cost_{u}^{U} - \sum_{p\in Products} Cost^{p} \qquad (3)$$

The feedstock costs ($Cost^f$), the electricity costs/revenues ($Cost^{El}$), the CO_2 sequestration cost ($Cost^{Seq}$), the investment cost of units ($Cost_u^U$), and the revenue from the products ($Cost^p$) are all included in the Eq. (3). The feedstock costs ($Cost^f$) include contributions from the hardwood biomass and freshwater. All terms in the objective function are normalized with respect to the total energy of products produced.

Branch-and-Bound Algorithm

At each node within the branch-and-bound tree, a mixed-integer linear optimization (MILP) model is solved using CPLEX to determine the lower bound of the original MINLP model by underestimating any nonlinearity with linear relaxations. Bilinear terms are underestimated using piecewise McCormick underestimators where the number of pieces used depends logarithmically on the number of binary variables. Concave cost functions are underestimated using piecewise linear relaxations where each piece is represented using a binary variable. Each node is branched to form two children nodes and branching is performed on continuous variables that participate in nonlinear expressions. The solution of the MILP provides several starting points for the upper bound problem. Binary variables are fixed at the upper bound and the resulting nonlinear optimization (NLP) model is solved using CONOPT (Drud, 1985). An optimality-based bounds tightening (OBBT) routine and feasibility-based bounds tightening (FBBT) routine is implemented to tighten variable bounds within the model. A more detailed explanation of deterministic global optimization theory and algorithms is given in the textbooks by Floudas (1995, 2000).

Discounted Cash Flow Analysis

After the solution of the optimal process topology determined from the deterministic global optimization algorithm, a second profitability measure, the net present value (NPV), is calculated. The BTOA plant is assumed to operate for 330 days per year for 30 years. The discount rate is assumed to be 10% and the 10 year MACRS depreciation scheme is used. The net present value is calculated using Eq. (4):

$$\sum_{i=-2}^{30}(Inv_i + W_i + NAE_i + D_i)(1 + Disc.Rate)^{0-i} \qquad (4)$$

where Inv_i is the investment in year i, W_i is the working capital in year i, NAE_i is the net annual earnings in year i, D_i is the depreciation credit gained in year i, and *Disc. Rate* represents the discount rate. The following references provide a more detailed description of the NPV calculation (Niziolek et al., 2016a; Onel et al.; 2016).

Computational Studies

The process synthesis model is used to examine three case studies that investigate the effect of refinery scale on the production of olefins and aromatics from hardwood biomass. The total output from the refinery is constrained to be either 500, 1000, or 2000 metric tons (MT) per day of ethylene equivalent (based on its lower heating value) chemical. At least 75% of the products output are constrained to be olefins and aromatics to enforce the stand-alone chemicals concept. The BTOA refineries additionally constrain the olefins to aromatics ratio to be 2:1, commensurate with the global demand ratio for these valuable chemicals. The types are chemicals within each class (i.e., olefins, aromatics) are left unrestricted. The refineries are denoted as U-500, U-1000, and U-2000. Cost parameters used in the model are shown in Table 1.

Table 1. Cost parameters used in the BTOA process

Item	Cost	Item	Cost
Hardwood	$70/dry metric ton	Freshwater	$0.50/metric ton
Electricity	$0.07/kWh	Butadiene	$1.874/kg
Gasoline	$2.86/gal	LPG	$0.99/gal
Ethylene	$1.382/kg	Propylene	$1.340/kg
1-Butene	$2.050/kg	2-Butene	$1.940/kg
CO_2 TS&M[1]	$5/metric ton	Mixed butenes	$0.353/kg
Isobutylene	$1.587/kg	Benzene	$1.431/kg
Toluene	$1.294/kg	P-xylene	$1.602/kg
O-xylene	$1.367/kg	M-xylene	$1.405/kg

Table 2. Overall Profit Breakdown

$/GJ of products	U-500	U-1000	U-2000
Hardwood	5.07	6.59	6.59
Water	0.02	0.02	0.03
Investment	14.32	12.45	10.63
CO2 TS&M	0.00	0.00	0.00
O&M	3.50	3.06	2.65
Electricity	0.62	-2.06	-1.69
Gasoline	-2.32	-2.32	-2.32
LPG	-0.11	-0.11	-0.11
Benzene	-0.95	-0.95	-0.96
Toluene	0.00	0.00	0.00
P-xylene	-4.82	-4.82	-9.43
O-xylene	-3.94	-3.94	0.00
M-xylene	0.00	0.00	0.00
Ethylene	-6.21	-6.21	-6.21
Propylene	-8.78	-8.78	-8.79
Isobutylene	0.00	0.00	0.00
1-Butene	-3.67	-3.67	-3.67
2-Butene	-0.55	-0.55	-0.55
Mixed-Butenes	0.00	0.00	0.00
Butadiene	0.00	0.00	0.00
Total	-7.83	-11.31	-13.82
NPV ($MM)	-133	142	892
Investment ($MM)	728	1266	2163

The breakdown of the profits for the three BTOA case studies investigated are shown in Table 2. The required investment cost and the NPVs are also shown. The overall profit increases as the refinery scale increases, due to economies of scale. Although the U-500 refinery has a negative NPV, the U-1000 and U-2000 refineries have NPVs of $142 and $892 MM, respectively. The largest contributor to the cost for the refineries is the investment cost. The U-500 BTOA refinery has a total capital investment of $728 MM, while the U-1000 and U-2000 refineries have investment costs of $1266 MM and $2163 MM, respectively. All case studies produce byproduct gasoline. The U-1000 and U-2000 refineries produce electricity, the U-500 refinery inputs electricity. The types of aromatics and olefins produced and their respective revenues are shown in Table 2.

The optimal process topologies are illustrated in Table 3. The decisions are denoted as yes (Y) or no (-). The biomass gasifier can input a solid feed (S) or solid/vapor feed (S/V) using recycle light gases. The U-500 refinery inputs a solid/vapor feed, while at larger scales the refinery only inputs solid biomass. The U-500 gasifier operates at 850 °C, while the U-1000 and U-2000 gasifiers operate at 800 °C. Methanol conversion proceeds through MTO and MTA technologies. In all cases, a portion of the LPG is sent to the Cyclar process and the remaining is output from the refinery; none of the LPG is converted into additional olefins. In the U-500 and U-1000 case studies, the refinery includes production of ortho-xylene; in the U-2000 case study, para-xylene is the only C8 aromatic produced. All case studies convert toluene and heavy aromatics into additional mixed xylenes and benzene with the UOP Tatoray and UOP TAC9 processes. The UOP PXPLUS process was never selected.

Table 3. Optimal Process Topologies

	U-500	U-1000	U-2000
BGS Conv.	S/V	S	S
BGS Temp.	850	800	800
WGS Temp.	300	300	300
MTO	Y	Y	Y
MTP	-	-	-
OXOD	-	-	-
Butene Dist.	Y	Y	Y
OCP	-	-	-
C3 Oleflex	-	-	-
C3 Catofin	-	-	-
C4 Oleflex	-	-	-
C4 Catofin	-	-	-
MTA	Y	Y	Y
GTC TolAlk	-	-	-
Ortho-Dist.	Y	Y	-
UOP Tatoray	Y	Y	Y
UOP TAC9	Y	Y	Y
UOP Cyclar	Y	Y	Y
CO2 Seq.	-	-	-

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[1] TS&M – transportation, storage, and monitoring

Conclusions

This paper introduced novel processes for the production of olefins and aromatics from hardwood biomass via methanol. A process synthesis superstructure consisting of several novel, competing, and commercial processes is modeled and solved to global optimality using a tailored deterministic global optimization branch-and-bound algorithm. The stand-alone biorefineries are capable of producing at least 75% by mass of olefins and aromatics. Three case studies that produce 500, 1000, and 2000 metric tons per day of product are investigated to determine optimal topologies. Economic analysis is illustrated for all case studies presented.

The most profitable hardwood biomass to olefins and aromatics refinery produced benzene, p-xylene, ethylene, propylene, 1-butene, and 2-butene along with byproduct LPG, gasoline, and electricity. The net present value of a biorefinery that produces 2000 MT/day of product is $892 MM and requires an investment cost of of $2163 MM. The proposed biorefinery designs are environmentally superior to current petroleum-based processes.

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