SUPPORTING INFORMATION

The supporting information consists of 13 pages, including cover page, containing 4 figures and 6 tables.

Renewable Rubber and Jet Fuel from Biomass: Evaluation of Greenhouse Gas Emissions and Land Use Tradeoffs in Energy and Material Markets

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SUPPORTING FIGURES

Fermentation experimental details: Total MBE yield was 10.02g/L at an efficiency of 65% of the theoretical maximum yield. The temperature of culture was set to 37 °C. Agitation and airflow rates were chosen to simulate the best-case scenario in shake flask testing. The fermenter controller was set to maintain a pH of 7.0 through the addition of 25% ammonium hydroxide as is often optimal for *E. coli* expression systems. Any excess foam was controlled via the addition of 1% antifoam 204. Feeding was achieved through constant addition of hydrolysate at a rate of approximately 1g/L/hr, but was adjusted as necessary to maintain a glucose concentration between 1g/L and 10g/L. Glucose concentration was periodically measured via glucometer during the fermentation and HPLC after the completion of the fermentation. A titer of 10.02g/L of MBE was measured (Figure S1).

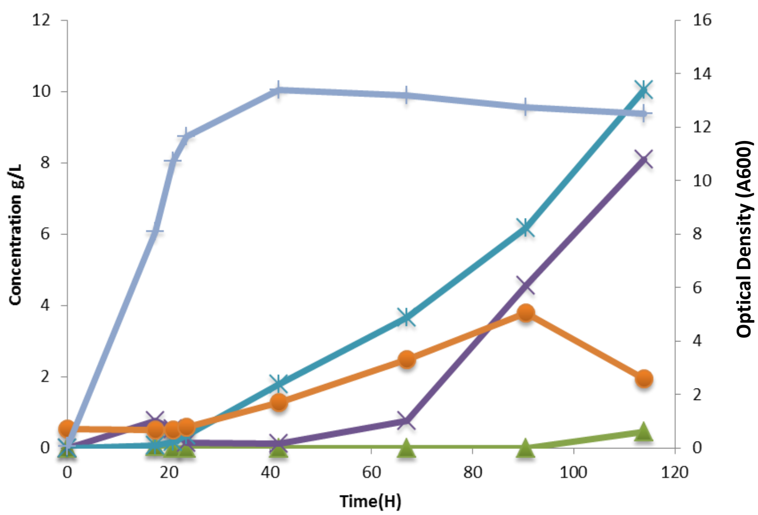

Figure S1. Fermentation in minimal media.

Separation step modeling: The model parameters were subsequently tweaked to achieve a bottoms stream purity of 95% MBE by mass while reducing the reboiler duty and staying within a reasonable number of theoretical stages. The distillation tower was first optimized for operation at atmospheric pressure before being adjusted to reduce reboiler duty at 0.5 bar. The simulation was then modified to incorporate a recycle stream; the distillate from the tower would be recycled to the extractor ("DECANT" in Figure S2), so that benzene could be reused. A design spec constraint was added to the model, specifying that the fresh benzene stream ("BENZENE" stream in Figure S2) would only add enough benzene to the extractor for the feed to the distillation column to contain equimolar amounts of benzene and MBE.

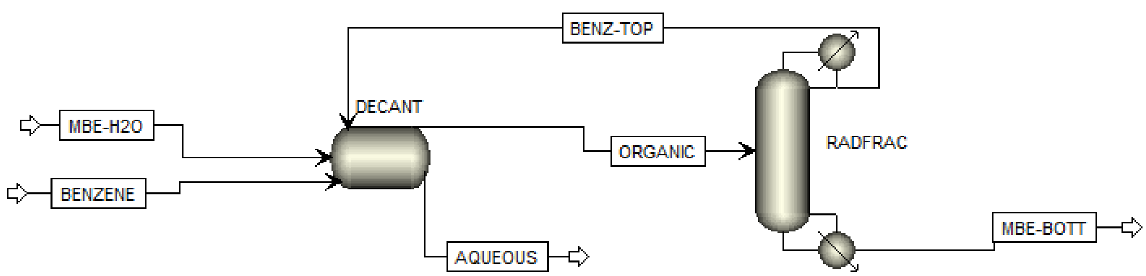

Figure S2. Process flow diagram of separation modeled in Aspen Plus[1].

Methyl butenol dehydration to produce isoprene: A number of experiments were performed with industrial Amberlyst® catalysts. The temperature was varied from 70 °C to 150 °C, LHSV was varied between 6 and 18 per hour. A total of 1 g of catalyst was loaded in a tubular reactor heated by an ATS furnace with PID controller. The experiments were performed for 6 runs each. Figure S3 shows the results of single pass conversion at LHSV of 12 per hour. It can be observed that, conversion is maximum at 110 °C, which is below the boiling point of methyl butenol. Thus, it was concluded that the dehydration reaction is liquid phase. The formed isoprene was simply decanted from unreacted methyl butenol and formed water. The total collected isoprene was measured to estimate total conversion.

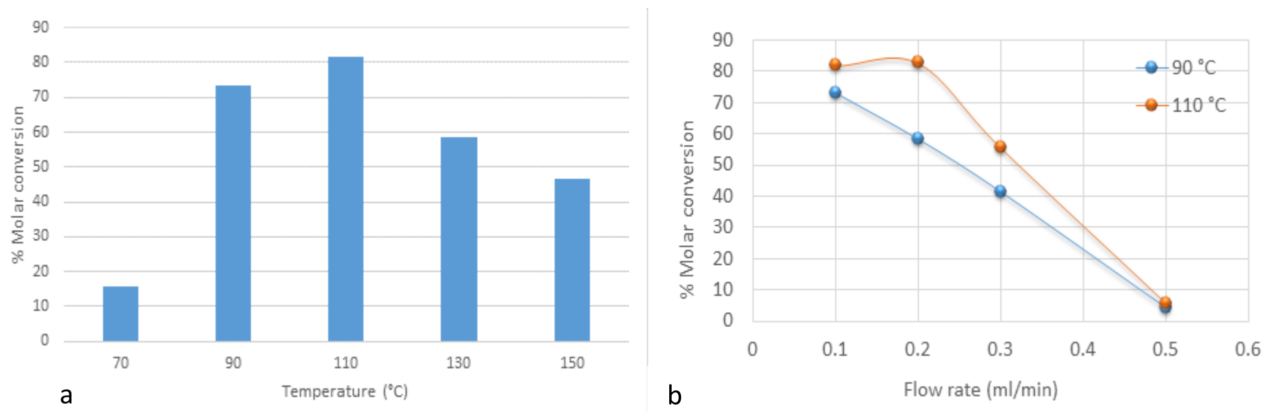

Figure S3. Methyl butenol conversion to isoprene as a function of temperature (a) and flow rates (b).

Sensitivity of select model parameters on life cycle GWP: The sensitivity of select parameters on life cycle GWP for corn stover-based polyisoprene was tested using upper and lower bounds documented in Table 1. Results of this sensitivity analysis are presented in a tornado plot (Figure S4).

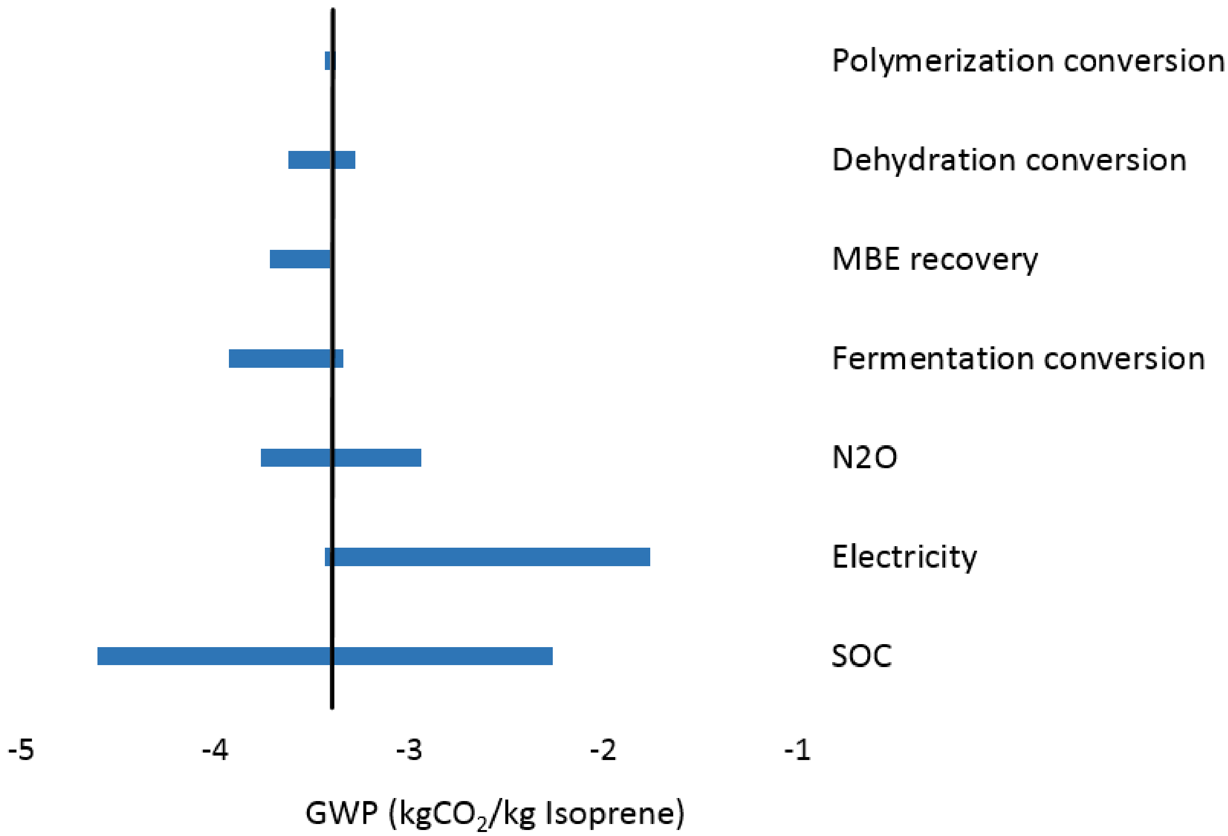

Figure S4. Tornado plot showing the sensitivity of select model parameters on life cycle GWP of corn stover-based polyisoprene.

SUPPORTING TABLES

Three nominally optimized cases are presented in Table S1, showing that the recycle scheme not only allows significant reuse of benzene, it also allows near-complete recovery of the MBE product. The aqueous (wastewater) stream from the extractor consistently contains a negligible amount of MBE and a small amount of benzene (also specified in Table S1).

Table S1. Distillation column simulation cases studied: relevant parameters and results.

Case:	**1 bar**	**0.5 bar**	**0.5 bar with recycle**
Stage (including condenser and reboiler)	14	14	14
Feed stage	5	3	6
Boilup ratio (mol/mol)	4.5	3.8	3.8
Reflux ratio (mol/mol)	2	2	2
Fresh benzene (kg / kg MBE fed)	0.9	0.9	0.04
Bottoms MBE purity (wt/wt)	94.7%	92.1%	96.4%
Bottoms MBE recovery	82%	84%	100%
Condenser duty (kJ / kg MBE recovered)	-1592	-1511	-1533
Reboiler duty (kJ / kg MBE recovered)	1899	1711	1636
Wastewater benzene concentration (ppm)	2.3	2.3	12.2

Table S2. Energy requirements for conversion of fermentable sugars in biomass to polyisoprene

Fermentation heating	711.3	kJ/kg of MBE produced
Separation cooling	-1533.4	kJ/kg of product recovered
Separation heating	1636.4	kJ/kg of product recovered
Dehydration preheating	31.6	kJ/kg of MBE fed
Dehydration reactor duty	1.5	kJ/kg of MBE fed
Polymerization cooling	36	kJ/kg isoprene
Polymerization activation energy	202.7	kJ/kg isoprene
Dimerization energy	246.2	kJ/kg jet fuel

Table S3. Contribution of different life cycle components on total GWP of polyisoprene from corn stover and forest residue

Life cycle components	GWP for polyisoprene from corn stover ($kgCO_2$/kg isoprene)	GWP for polyisoprene from forest residue ($kgCO_2$/kg isoprene)	Model source and assumptions
Harvest/ field operations	0.6	0.2	Using data from Pourhashem et al.[2] and Keedy et al.[3] for corn stover and forest resaidue based scenarios respectively as inputs for our SimaPro[4] model
Nutrient replacement	0.2	-	Based on DayCent model[5] results from Pourhashem et al.[2]
Total soil N_2O emission	0.3	-	Based on DayCent model[5] results from Pourhashem et al.[2]
Change in soil carbon	1.2	-	Based on DayCent model[5] results from Pourhashem et al.[2]
Biogenic carbon	-10.9	-10.9	Calculated based on the carbon content of the feedstock
Feedstock transport	0.1	0.1	Assuming 80.5 km transportation distance including the return trip and using SimaPro[4] software
Boiler	3.8	5.4	Boiler emissions due to onsite power production[1-2]
Pretreatment	0.3	0.2	Data from the literature[2, 6] are used for the LCI model in SimaPro[4] software
Chemicals	0.3	0.3	Using Aspen simulation[1, 7] to find required amount of chemicals and finding GWP of required chemicals using SimaPro[4] software
Direct CO_2 of fermentation	2.3	2.3	Based on stoichiometry of Equation 1
Electricity (credit)	-1.7	-1	Finding required electricity of our modeled bioplant based on Aspen simulation[1, 7] results and using GREET[8] for GWP of extra electricity credit
Net	-3.4	-3.4	

Table S4. Life cycle inventory input data for corn stover based polyisoprene (per 1 kg polyisoprene)

Item	Amount	Unit	Source and assumptions
Upstream			Emissions due to corn stover harvest and replacement of nutrients are allocated to the corn stover and emissions from nutrient inputs for crop production are allocated to the corn crop
Feedstock input	6.6	kg	Calculated based on our model and conversions of different stages
Feedstock yield	9.7	ton/ha/yr	Spatari et al.[9]
Collection	1.7	MJ	Using data from Spatari et al.[9] and Pourhashem et al.[2]
Nutrient replacement	N 33 P 11.9 K 60.7	g	Based on GREET[8] results from Spatari et al.[9] for nutrient replacement due to corn stover removal
N_2O emissions	Direct: 0.3 Indirect: 0.4	g	Based on DayCent model[5] results from Adler et al.[10] and Pourhashem et al.[2] where results are updated to IPCC Fifth Assessment Report (AR5)
Change in soil carbon	1.2	kg CO_2	Based on DayCent model results from Adler et al.[10] and Pourhashem et al.[2]
Diesel for transportation	30.7	ml	Assuming 80.5 km transportation distance including the return trip and using diesel powered truck from the USLCI[11] database in SimaPro[4] software
Biorefinery			Calculated required amount of energy and chemicals using Aspen Plus[1] simulation and using Ecoinvent[12-13] database for life cycle impact assessment
Fermentation energy	898.9	KJ	
Separation cooling energy	-1938.8	KJ	
Separation heating energy	2068.9	KJ	
Dehydrogenation energy	41.9	KJ	
Polymerization cooling energy	36	KJ	
Polymerization activation energy	202.7	KJ	
Surplus electricity	8742	KJ	Difference between the total electricity generated onsite from lignin combustion in the boiler and the electricity required by the bioplant; assumed to replace from the MRO electricity grid
Benzene	0.05	kg	
Chlorobenzene	9.8	kg	
H_2SO_4	0.2	kg	
$Ca(OH)_2$	0.2	kg	
NH_3	0.3	kg	

Table S5. Life cycle inventory input data for forest residue based polyisoprene (per 1 kg polyisoprene)

Item	Amount	Unit	Source and assumptions
Upstream			Calculated required upstream energy using data from Keedy et al.[3] and Ecoinvent[12-13] database for life cycle impact assessment
Feedstock input	5.8	kg	Calculated based on our model and conversions of different stages
Feedstock yield	10	ton/ac	Based on Leinonet[14]
Diesel for feller-buncher	6.7	g	
Diesel for grapple-skidder	11.2	g	
Diesel for chipper	6	g	
Diesel for unloading	0.2	g	
Electricity for mill	0.5	kWh	
Electricity for conveyor	0.1	kWh	
Electricity for baghouse	0.1	kWh	
Electricity for storage	27.7	Wh	
Diesel for transportation	27	ml	Assuming 80.5 km transportation distance including the return trip and using diesel powered truck of USLCI[11] database in SimaPro[4] software
Biorefinery			Calculated required amount of energy and chemicals using Aspen Plus[1] simulation and using Ecoinvent[12-13] database for life cycle impact assessment
Benzene	0.05	kg	
Chlorobenzene	9.8	kg	
H_2SO_4	0.1	kg	
$Ca(OH)_2$	0.2	kg	
NH_3	0.3	kg	
Fermentation energy	898.9	KJ	
Separation cooling energy	-1938.8	KJ	
Separation heating energy	2068.9	KJ	
Dehydrogenation energy	41.9	KJ	
Polymerization cooling energy	36	KJ	
Polymerization activation energy	202.7	KJ	
Surplus electricity	12905	KJ	Difference between the total electricity generated onsite from lignin combustion in the boiler and the electricity required from the bioplant; assumed to replace NPCC electricity grid

Table S3 gives an accounting of carbon balance in terms of CO2 emissions. We also added Table S6 showing biogenic carbon due to carbon content of the feedstock, boiler and fermentation emissions (sending part of biogenic carbon back to the atmosphere), and remained carbon is embedded in the polymer.

Table S6. Carbon balance of the system: partitioning (mass basis) of biogenic carbon in products (polyisoprene), fermentation, and boiler usage

Carbon source	Corn stover (%)	Forest residue (%)	Model source and assumptions
Biogenic carbon	-100	-100	Calculated based on the carbon content of the feedstock
Boiler	34.9	49.5	Boiler emissions due to onsite power production[1-2]
Direct CO_2 of fermentation	21.1	21.1	Based on stoichiometry of Equation 1
Embedded in polyisoprene	44	29.4	Remained biogenic carbon

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