Ethanol, Plastics and Butadiene from Forestry Biomass via Optimum Production System

Raphael O. Idewele1* and Othuke D. Iduh2

1Research Support Services Department, Rubber Research Institute of Nigeria, P.M.B. 1049, Benin City, Edo State, Nigeria
2Chemical Engineering Department, Federal Uni. of Petroleum Resources, P.M.B. 1221, Effurun, Delta State, Nigeria
*Telephone: +234(0)8025633532
*E-Mail: ideweleraphael@gmail.com

Abstract

Presently, the desire to reduce import and raise balance of trade, and the need to mitigate problems of petroleum consumption like CO₂ emission and global warming, is driving nations into seeking renewable and sustainable alternatives. In this work, optimized production system from robust comparison is used to estimate the potential of forestry waste woody biomass for bioproducts worldwide and in Europe. Bioproducts considered are bioethanol for fuel, plastics (polyethylene, polypropylene, polyvinylchloride, polystyrene, polyethylene-terephthalate) for material, and butadiene for chemical. Chemical synthesis, syngas fermentation, direct fermentation and carboxylate routes to products were investigated. Smart utilization increased production over a number of conversion routes. Optimum utilization patterns compared to when whole biomass is used directly through (i) thermochemical route gave 16.7% increase in production (ii) biochemical route provides 33.3% increase in production which represent significant savings for the biorefinery. It was found that while 52.7% and 71.9% of feedstock is required to satisfy demand for plastics worldwide and Europe respectively and, 2.7% and 4.5% of biomass worldwide and in Europe respectively is the feedstock level required to replace petroleum based butadiene production, meeting 40% and 48.4% of gasoline energy demand worldwide and in Europe respectively completely deplete this biomass resource.

Keywords: Biomass Utilization, Biorefinery, Bioproduct, Conversion Route, Theoretical Yield

1. Introduction

In the past, the discovery of crude oil stalled the growth of biobased fuels, chemicals and materials (collectively referred to as bioproducts) because petroleum possessed the cost advantage and was found to be available in enormous quantity. Today, the desire for renewable and eco-friendly products is bringing them back into the competition with crude oil. Renewable energy target by concerned nations aims to reduce fossil consumption. Also, outside the problem that accompanies petroleum consumption, there remains this standing realization that continuous exploitation of it will also lead to its complete exhaustion in a few decades away from now, a view that makes any measures put in place now to cut down on petroleum consumption a good saving for the future (Sheehan et al, 1998; Caledria et al, 2003; Demain et al, 2005; Zhang, 2008 and Raphael & Yang, 2013).

Presently, bioproducts are thriving due to subsidies and tax waivers which, though good in enabling them make successful entry into a fossil saturated market, are not sustainable in the long run. Integrated biorefinery, which would resemble petroleum refinery that can churn out a wide range of bioproducts, is thought of as a technological complex that could optimize the utilization of biomass. A number of investigations are ongoing in that direction e.g. Jong et al (2012), Cherubini & Jungmeier (2010). But the presence of multiple product lines in this biorefinery further widens the strain in the ability of available biomass supply to sati-
sify and sustains demand for these competing uses. Thus, there remains the need to select better technological routes to ensure effective utilization of the available biomass for biomass economy to thrive.

Virtually every nation of the world has its forest replete with waste wood that can contribute significantly to renewable energy target. Enormous benefit accrues when biomass is used for products since it can mitigate the environmental and climate problems associated with the consumption of petroleum based ones. Generally, when petroleum is used as fuel its emissions raise the CO₂ level in the atmosphere appreciably. When biofuel is used instead, there is reduction in emissions to the atmosphere. Farther afield, when it is biobased products it culminates in even far higher reduction in emissions to the atmosphere. When biofuel is used instead, there is reduction in emissions to the atmosphere. Farther afield, when it is biobased products it culminates in even far higher CO₂ savings (Patel et al, 2006; Hermann et al, 2007; Albercht et al, 2010; Cherubini & Jungmeier, 2010 and Jong et al, 2012). A consideration of these benefits has encouraged the argument that using biomass for more stable, strong and durable product guarantees greater CO₂ saving over a long time. The same holds true for products that are recyclable (Jong et al, 2012). Thus, the best should be used for the first-materials before biofuel or bioenergy. In line with this argument, it would seem appealing that biomass be cornered to materials and chemicals while the leftover should be used for fuels, heat and power as the case may be since these may be obtained from other renewable sources such as solar and hydro power systems.

This paper considers three important bioproducts i.e. bioethanol, plastics and butadiene. Bioethanol is taken as a representation of fuels, plastics for materials, and butadiene as chemical. Bioethanol is considered because it has generated great market interest as a renewable and neat alternative to petroleum gasoline over the years and because it can be used as whole fuel or blend (Balata et al, 2008) using existing infrastructure. On the material side, polymer plastics are investigated as in Raphael & Yang (2013) for environmental benefits (Pervaz & Sain, 2006; Patel & Crank, 2007 and Hottle et al, 2013) and universality of their usage in packaging, automobile etc. Butadiene is largely consumed for synthetic rubber (Bhatnagar, 2004) where it could offer renewable and environmentally friendly "green" benefit in complementing natural rubber when it displaces synthetic rubber from crude oil that has an established market niche like in the case of plastics (Shen et al, 2010 and Raphael & Yang, 2013). Meanwhile, bio-based materials with identical building block as petroleum based ones have been found to give similar performance as in plastics (Shen et al, 2010). The two top global end use of butadiene in decreasing other are styrene butadiene Rubber (the highest synthetic rubber by volume production) and polybutadiene rubber (Brentin & Sarnacke, 2011). Some other synthetic rubbers from butadiene are butyl rubber, nitril butyl rubber and polychloroprene (Brentin & Sarnacke, 2011).

Meanwhile Brazil and USA, in decreasing order of production, are the two leading producers of bioethanol (Kim & Dale, 2004 and Justine et al, 2009). They owe this credit to the contribution of first generation biomass; the former makes from sugar cane and the latter makes from starch. The cost of feedstock is a typical challenge for these biorefineries. Although it is compensated for by the ease and efficiency of processing using existing technologies that are better developed, ethical concerns for competition with food and feed persist in the use of these first generation feedstocks (Drapcho et al, 2008 and Justine et al, 2009). Therefore, second generation or lignocellulosic feedstock (LCF) such as agriculture and forest residues that can be obtained, in most cases, at no extra material procurement cost penalty and available in abundance (Zhang, 2008), and third generation feedstock of aquaculture like algae that can be cultivated with just nutrients and offers no competition for land (Goh & Lee, 2010) inter alia, however difficult and stubborn they are to processing, are believed to be the way out if true progress is to be made in the drive towards a green world of bioproducts.

In this work, attempt is made based on “sensible biorefining” to quantitatively determine, from variant of production systems, the optimum production configuration in terms of route combinations and utilization patterns. This optimum is used to evaluate the potential of LCF of forestry origin to bioproducts as well as the substitution they can provide as functional substitutes for transport gasoline and direct substitutes with respect to material and chemical.

Several investigations have been carried out on biomass to bioethanol on the fuel perspective, e.g. Kim & Dale (2004), Najafi et al (2009) and Limayema & Ricke (2012). It has been shown in Holtzapple & Granda (2009), Justine et al (2009) and Jong et al (2012) that C₃ products (e.g. ethanol) can readily be converted to chemicals and liquid fuels as Fischer-Tropsch (FT) Diesel, Naphtha etc. via well-known chemistry. Werpy et al (2004) of the National Renewable Energy Laboratory (NREL) had previously profiled, from biomass basic construct to final products, promising chemicals that can be gotten from sugar and syngas. Raphael & Yang (2013) considered the actual potential for whole biomass based on the individual production routes of direct fermentation, syngas fermentation and chemical synthesis to produce plastics that can substitute those of petroleum origin. Lignocellulosic feedstock of agricultural and forestry waste was used to establish the feedstock requirements for making polyethylene (PE, including both low-density and high-density types), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS, including both solid and expandable types) and polyethylene-terephthalate (PET) plastics. They were ascertained to be sufficient for making these plastics that accounted for 85% and 75% of all plastics in the world and Europe respectively (Plastics Europe, 2012 and Schorr, 2012) (Table 1).
Naturally, biomass is fed whole into the reactor after undergoing any one or more pre-processing steps of dewatering, size reduction, densification, torrefaction, pelletisation, etc. in popular usage. This seems convenient in many cases and is predominantly followed in the tradition style in developing nations where burning forestry biomass for heat and power is the leading use, while modelling biomass to product analysis for conditions within the biorefinery may end up the same way unnoticed. A pattern which may not be best for the given situation as it may not guarantee effective utilization of this already limited biomass resource.

Table 1. Global and European Plastic Consumption in 2011 (in 1000 tonnes)

<table>
<thead>
<tr>
<th>Plastic Type</th>
<th>PE</th>
<th>PP</th>
<th>PVC</th>
<th>PS</th>
<th>PET</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>World</td>
<td>76890</td>
<td>51726</td>
<td>36115</td>
<td>16310</td>
<td>16310</td>
<td>197351</td>
</tr>
<tr>
<td>Europe</td>
<td>13630</td>
<td>8930</td>
<td>5170</td>
<td>3525</td>
<td>3055</td>
<td>34310</td>
</tr>
</tbody>
</table>

Lignin has sturdy nature that presence of random crosslink structure foists on it (Hatakeyama & Hatakeyama, 2005). By implication, when whole biomass is fed directly into any of the biological routes, this component will be left out unutilized. This is because lignin is recalcitrant to enzymatic activities, only thermochemical conversion works on it (Hatakeyama & Hatakeyama, 2005; Zhang, 2008 and Holtzapple & Granda, 2009). So, any route combination and comparison performed in this way, along biological conversion step, will carry this flaw with it and not optimize yield in comparison with actual production from any unit of biomass. This is why in this paper it is deemed necessary to examine utilization patterns over conversion routes that can take advantage of this constituent to develop a utilization template for biomass to bioproducts and use it to answer questions of relevance within the biorefinery. This helps to give a realistic optimum production system of routes and patterns depending on biorefining objective.

This article starts off with technological routes comparison of direct fermentation, syngas fermentation, chemical synthesis, and carbohydrate routes for converting biomass to products over identified utilization patterns. Detailed attention is paid to the impact of lignin consumption across routes and cases reviewed. Meanwhile, Holladay et al (2007) at the Pacific North National Laboratory (PNNL) had done screening for chemicals from lignin and gave syngas and fuel as some of the short term opportunities available in lignin. This component represents about 30% of biomass weight (Hatakeyama & Hatakeyama, 2005 and Holladay et al, 2007) and provides around 40% of its energy (Hatakeyama & Hatakeyama, 2005).

This work will establish the yield from the conversion reactions for production routes, present utilization schemes for biomass consumption that is meant to establish utilization template to aid in decision making, and in estimation of yield of products based on the optimum from comparison of technological routes over utilization patterns. This is then used in evaluating the substitution of the fossil based alternative that is realizable from this forestry LCF by way of estimation of achievable substitution of gasoline and feedstock requirements for plastics and butadiene within two geographical climes -World and EU. To disambiguate, ethanol is quoted as the intermediate product of this biorefining, and bioethanol as final fuel in the context of this paper.

2. Petroleum Products and Biomass Volume

The respective volumes of products and biomass for the world and Europe used for estimation in this work like in Raphael & Yang (2013) are based on the reference year 2011 for the consistency in the availability of the various data. The volume of gasoline consumed for 2011 is assumed to be same as that for 2010 for incompleteness of reported data for the base year from International Energy Agency (IEA).

On the product side, 8,055,185,000 barrels and 848,807,500 barrels of motor gasoline were consumed worldwide and in EU respectively as sourced from IEA database (EIA, 2014). For plastics, global consumption volume is gotten from Schorr (2012) and European volume was obtained from Plastics Europe (2012). Butadiene annual world production attained 10,000,000 tonnes (Dow, 2013) and that in Europe 2,087,000 tonnes from Petrochemicals Europe (PE, 2014) in the base year. The total biomass residues volume of 1,056,426,000 and 134,726,000 dry tonnes in world and EU respectively from forestry residues was estimated to be the quantity of forestry woody biomass available for product (Raphael & Yang, 2013).

3. Biomass Conversion, Utilization and Production Reaction

This section examines situation in biomass to ethanol conversion within the biorefinery.

3.1. Biomass Modelling

In making ethanol from gasification of biomass, achieving the right biomass capable of sufficient energy for product is a major challenge and to circumvent this limitation, the biomass first needs to be adjusted. Thus biomass used in modelling this project is taken to be the already built in ratio of polysaccharide to lignin from Holtzapple & Granda (2009) which satisfies this criteria. This ideal biomass formula on ash free basis contains 68.3% polysaccharide and 31.7% lignin composition typical of hard wood. With cellulose and other non-lignin components of biomass represented jointly as polysaccharide with the formula \( C_{6}H_{10}O_{5} \) and lignin as \( CH_{12}O_{3} \), the lignin/ polysaccharide...
Ccharide molar ratio is 3.93:1. This arrangement helps to maintain uniformity in estimation across routes and cases presented. Normally, where there is excess of polysaccharide or lignin, there is no need aiming full conversion. Here, it is assumed that excess of either component is burnt to heat and power to meet energy requirement within the biorefinery. Hemimcellulose (C_5 fraction) of biomass is aggregated together with the Cellulose (C_6) as polysaccharides to maintain polysaccharide-lignin binary reactions in Holtzapple & Granda (2009) in a manner that its weight will not be missing from estimation.

3.2. Conversion Routes

Four routes to product as shown in Figure 1 below are considered in this work namely:

1. **Direct Fermentation Route.** Where the polysaccharides are hydrolysed to simple sugars and then fermented to ethanol. Cellulose is converted to hexose sugar which yeast can efficiently ferment while the hemicel luloses to pentose sugar that enzymes, like zymomonas mobilis, ferment it to ethanol (Balata et al, 2008; Drapcho et al, 2008; Holtzapple & Granda, 2009 and Raphael & Yang, 2013).

![Figure 1. Biorefinery Showing Conversion Routes to Products Investigated](image)

2. **Carboxylate Route.** This is used to describe here the path based on the carboxylate platform that use mixed culture of microorganism to ferment non-lignin constituents of biomass to carboxylate salt that are subsequently converted to chemicals and liquid fuels (e.g. alcohols and alkanes). This work is pattern after MixAlco process (Holtzapple & Granda, 2009 and Pham et al, 2010) which is an example of this conversion route that uses mix acid culture of microbes under anaerobic condition. This route is gaining research attention because with it there is no need for addition of enzyme or sterile condition for enzyme fermentation as required in direct fermentation.

3. **Syngas Fermentation Route.** Gasification of biomass to syngas is the first performed, followed by fermentation of the syngas by bacteria to ethanol (Munasinge & Khanal, 2010; Maddipati et al, 2011 and Raphael & Yang, 2013).

4. **Chemical Synthesis Route.** Biomass undergoes gasification to syngas, and by a catalyst, the CO is shifted to H_2 via water gas shift reaction. Subsequently this mixture of gases is used to synthesise alcohols (Holtzapple & Granda, 2009 and Raphael & Yang, 2013).

The first two routes are biochemical and the last two are thermochemical. This work intends to bring these routes together to pull a broad comparison over utilization cases examined in succeeding section. Naturally, in chemical synthesis, methanol possesses higher conversion efficiency compared to ethanol (Holtzapple & Granda, 2009). On the contrary, ideally in forming hydrocarbons as alkane from these alcohols there is lesser loss of energy and mass from dehydration in ethanol than in methanol (Pham et al, 2010). Thus, ethanol path is followed in this work, and doing so allow for uniform comparison at any point in the biorefinery (i.e. intermediate or product end).

3.3. Utilization Pattern Review

The various ways of spending biomass are presented as cases for the various conversion routes in this portion of the paper as material balance.

3.3.1. Case A: Conversion without Lignin

This is the base case without lignin. In this particular case you have the lignin utilized for heat and power or like it was considered in Raphael & Yang (2013), it could be used to source some aromatic chemicals (e.g. Benzene) which otherwise would be obtained from fossil based feedstock. It was estimated that 10-20% of available lignin is needed to meet the demand for petroleum based aromatic chemicals for plastics (Raphael & Yang, 2013). In renewable terms, it would be a better option in further shoving dependence on petroleum through displacing these chemicals. Outside for power and heat generation, this option will be grossly ineffective in situation where bioethanol and butadiene production is the goal since at every point the prudent use of the limited biomass resources is sine qua non to success of this industry. The main objective is an option that allows for optimal consumption of the biomass components with minimal wastage.

3.3.2. Case A*: Conversion of Whole Biomass Using Single Route

This represents the traditional approach where you feed whole biomass into the refinery. This is performed through transforming biomass to product by any individual of the conversion routes represented in Figure 1. Most papers on biomass conversion do estimation based on this pattern e.g. Raphael and Yang (2013).
3.3.3. Case B: Conversion with Lignin using Catalyst

3.3.4. Case C: Conversion with Lignin using Enzymes

Lignin can via the thermochemical route of gasification be converted to valuable syngas that is capable of further improving the ethanol yield overall from the conversion of this biomass when pitched against Case A. Two things could happen to this syngas produced. It can by catalyst be converted or by enzyme fermented to ethanol. The conversion by catalyst, in a reaction known as catalysis, is presented here as Case B in manner similar to that in Holtzapple & Granda (2009). While enzyme fermentation of syngas to ethanol known as syngas fermentation is taken as Case C. These are used for all the routes considered in this work to observe how in the overall they will impact on ethanol production in comparison with the base case.

3.3.5. Case D: Using External Hydrogen over Cases & Routes

Particular attention is paid to the significance of using hydrogen to maximize the production of ethanol across core cases. Holtzapple & Granda (2009) have demonstrated the possibility of using hydrogen for Case B, and also have shown the energy efficiency of CO and CO\textsubscript{2} individual conversion to alcohol using hydrogen with respect to carbon numbers. It was shown that the efficiency is the same for either of them and decreases with increasing carbon number of alcohol produced. The respective catalytic reactions for conversion of CO and CO\textsubscript{2} to alcohol as contained in (Holtzapple & Granda, 2009) apply here.

3.4. Production Reactions

The reaction for these conversion routes and utilization schemes are presented in this section. The approach adopted is similar to that used in some literatures e.g. (Holtzapple & Granda, 2009).

Lignin Gasification and Catalysis:

\[ 3.93CH_{12}O_{0.377} + 3.80H_2O + 1.290 \rightarrow 3.93CO_2 + 6H_2 \]

Lignin Gasification and Fermentation:

\[ 3.93CH_{12}O_{0.377} + 1.290 + 0.80H_2O \rightarrow C_2H_5OH + 1.93CO_2 \]

3.4.1. Case A: Conversion without Lignin

**Chemical Synthesis**

\[ C_6H_{10}O_5 + 1.5O_2 \rightarrow 1.5C_2H_5OH + 0.5H_2O + 3CO_2 \]

**Syngas Fermentation**

\[ C_6H_{10}O_5 + 1.5O_2 \rightarrow 1.5C_2H_5OH + 0.5H_2O + 3CO_2 \]

**Direct Fermentation**

\[ C_6H_{10}O_5 + 1.5O_2 \rightarrow 2C_2H_5OH + 2CO_2 \]

**Carboxylate**

\[ C_6H_{10}O_5 \rightarrow 3CH_2COOH + 2H_2O \]

3.4.2. Case B: Conversion with Lignin Using Catalyst

**Chemical synthesis**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 2.790 \rightarrow 14.79H_2 \rightarrow 4.97C_2H_5OH + 7.09H_2O \]

**Syngas Fermentation**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 1.5O_2 \rightarrow 2.5C_2H_5OH + 4.93CO_2 + 0.2H_2O \]

**Direct Fermentation**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 1.80H_2O + 1.290 \rightarrow 3C_2H_5OH + 3.93CO_2 \]

**Carboxylate**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 1.290 \rightarrow 3C_2H_5OH + 3.93CO_2 \]

3.4.3. Case C: Conversion with Lignin using by Enzymes

**Chemical Synthesis**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 2.790 \rightarrow 2.5C_2H_5OH + 4.93CO_2 + 0.70H_2O \]

**Syngas Fermentation**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 2.790 \rightarrow 2.5C_2H_5OH + 4.93CO_2 + 1.50H_2O \]

**Direct Fermentation**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 0.80H_2O + 1.290 \rightarrow 3C_2H_5OH + 3.93CO_2 \]

**Carboxylate**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 1.290 + 0.80H_2O \rightarrow C_2H_5OH + 3CH_2COOH + 1.93CO_2 \]

3.4.4. Case D: Using External Hydrogen over Cases and Routes

**Over Case A**

**Chemical Synthesis**

\[ C_6H_{10}O_5 + 1.5O_2 + 9H_2 \rightarrow 3C_2H_5OH + 5H_2O \]

**Syngas Fermentation**

\[ C_6H_{10}O_5 + 1.5O_2 + 9H_2 \rightarrow 3C_2H_5OH + 5H_2O \]

**Direct Fermentation**

\[ C_6H_{10}O_5 + 6H_2 \rightarrow 3C_2H_5OH + 2H_2O \]

**Carboxylate**

\[ C_6H_{10}O_5 + 6H_2 \rightarrow 3C_2H_5OH + 2H_2O \]

**Over Case B**

**Chemical Synthesis**

\[ C_6H_{10}O_5 + 3.93CH_{12}O_{0.377} + 2.790 + 14.79H_2 \rightarrow 4.97C_2H_5OH + 7.09H_2O \]
Syngas Fermentation
\[ C_2H_4O_3 + 3.93CH_4, O_{0.177} + 2.79O_2 + 14.79H_2 → 4.97C_2H_6OH + 7.59H_2O \]

Direct Fermentation
\[ C_2H_4O_3 + 3.93CH_4, O_{0.177} + 1.29O_2 + 11.79H_1 → 4.97C_2H_6OH + 4.10H_2O \]

Carboxylate
\[ C_2H_4O_3 + 3.93CH_4, O_{0.177} + 1.29O_2 + 11.79H_1 → 4.97C_2H_6OH + 4.10H_2O \]

Over Case C:

Chemical Synthesis
\[ C_2H_4O_3 + 3.93CH_4, O_{0.177} + 2.79O_2 + 14.79H_2 → 4.97C_2H_6OH + 8.10H_2O \]

Syngas Fermentation
\[ C_2H_4O_3 + 3.93CH_4, O_{0.177} + 2.79O_2 + 14.79H_2 → 4.97C_2H_6OH + 8.10H_2O \]

Direct fermentation
\[ C_2H_4O_3 + 3.93CH_4, O_{0.177} + 1.29O_2 + 11.79H_1 → 4.97C_2H_6OH + 5.10H_2O \]

Carboxylate
\[ C_2H_4O_3 + 3.93CH_4, O_{0.177} + 1.29O_2 + 11.79H_1 → 4.97C_2H_6OH + 5.10H_2O \]

In Case D: hydrogen can be obtained from renewable and non-renewable sources. The case for sourcing hydrogen from solar has been made and it was shown to be a viable option that offers a number of merits and electrolysis is argued to be the least effective option (Holtzapple & Granda, 2009). The non-renewable source of natural gas is a worthy possibility for its abundance and richness in hydrogen.

3.5. Estimation of Product Yield

This portion reports the production based on the core utilization pattern (A-C) and reasoning on the individual downstream processing steps for plastics as given by Raphael & Yang (2013). The actual yields significantly near the theoretical for these downstream processes as they use established chemistry and technologies unlike that for the core conversion routes (Table 2), that are still developing. Only the yield for self-sufficient system producing ethanol with no need for external hydrogen is used in establishing evaluation criteria to final products.

The results from estimation to product yield are presented in Table 3.

4. Results and Discussion

The following submissions can be drawn from Tables 2-3.

- Case A is a proven ineffective utilization pattern for the biorefinery if the goal is the optimized production of ethanol.

- In Case A and A*, the carboxylate route will only be able to give acetic acid which, without hydrogen from gasification of biomass or any of its components or from external sources, will be impossible to convert to ethanol. Thus it will be an unwise choice in this light.

- For Case A*, between thermo-chemical routes and direct fermentation route, the former give higher production than direct fermentation, not just because of loss of carbon to CO\(_2\) as reported in Raphael & Yang (2013) but mainly because of the ability of these routes to convert lignin which enzymes cannot ferment in biochemical routes. This can be seen in Case A where the production gives reverse order of yield in comparison.

- For core cases B, production is in decreasing order of biological to thermo-chemical route.
Table 3. Theoretical Yield (kg/kg) to Products from Optimum Production

<table>
<thead>
<tr>
<th>Routes</th>
<th>Chemical Synthesis</th>
<th>Syngas F’tation</th>
<th>Direct F’tation</th>
<th>Carboxylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioethanol</td>
<td>0.485</td>
<td>0.485</td>
<td>0.582</td>
<td>0.194</td>
</tr>
<tr>
<td>Plastics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE</td>
<td>0.295</td>
<td>0.295</td>
<td>0.354</td>
<td>0.118</td>
</tr>
<tr>
<td>PP</td>
<td>0.295</td>
<td>0.295</td>
<td>0.354</td>
<td>0.118</td>
</tr>
<tr>
<td>PVC</td>
<td>0.659</td>
<td>0.659</td>
<td>0.791</td>
<td>0.264</td>
</tr>
<tr>
<td>PS</td>
<td>1.097</td>
<td>1.097</td>
<td>1.317</td>
<td>0.439</td>
</tr>
<tr>
<td>PET</td>
<td>2.025</td>
<td>2.025</td>
<td>2.430</td>
<td>0.810</td>
</tr>
<tr>
<td>Chemical</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butadiene</td>
<td>0.285</td>
<td>0.285</td>
<td>0.342</td>
<td>0.114</td>
</tr>
</tbody>
</table>

F’tation: Fermentation; PE: Polyethylene; PP: Polypropylene; PVC: Polyvinylchloride; PS: Polystyrene; PET: Polyethylene-terephthalate

- In case C, production is in decreasing order of direct fermentation, thermochemical and carboxylate as carboxylic acid have no hydrogen for conversion to ethanol.
- The Carboxylate Route in the absence of external H\textsubscript{2} can only be effective in chemical synthesis where the CO from lignin is easily shifted to H\textsubscript{2}. Direct fermentation requires that the syngas from lignin be converted directly to alcohol which is a difficult catalytic reaction.
- When external hydrogen is used per case you get maximum yield to products and this yield is same for every routes. But, these come with significant hydrogen penalty required to perpetuate the process.
- Case A though it represents the least effective when pitched in line with the objective of getting best utilization to give optimal ethanol production, when juxtaposed against the need for some chemicals as allayed in Raphael & Yang (2013) where aromatic chemicals which otherwise are sourced from petroleum is substituted, it may end up the better consumption pattern to follow.
- Direct fermentation and Carboxylate Routes are best in case B while direct fermentation alone is for Case C, in which carboxylate is the least productive because of the absence of H\textsubscript{2} in self-sufficient system. But with cost benefit in mind Chemical synthesis through B (equivalent to chemical synthesis in A*) may be the true route to take where one factors in the point that additional compartment or separate catalyst for the conversion of lignin is not necessary. While syngas fermentation may be the viable path to follow in C (tantamount to syngas fermentation in A*) as you will not need separate enzyme compartment to ferment the syngas from lignin.
- In using lignin, while the thermochemical routes maintain equal yield increase of 66.7% with respect to base case only and 50% raise for direct fermentation in any of Case A or A*, it jumpstart the carboxylate route yield to 0.194 and 0.582 Kg/Kg in case C and B respectively in from either Case A or A*.
- Using external hydrogen the thermochemical routes require higher volume of hydrogen than the biochemical ones. The hydrogen demand is the same for all thermochemical routes and equal for all biochemical routes.
- All cases, outside A, where there is a demand for aromatic compound they can be obtained from petroleum or coal (Bhatnagar, 2004).

4.1. Production Analysis and Substitution

Evaluation is made to assess bioethanol production and biobased plastics and butadiene feedstock requirement. The substitution realizable from bioethanol in replacing motor gasoline is shown in Table 4.

Table 4. Feedstock Capacity for Fuel

<table>
<thead>
<tr>
<th>Bioethanol Capacity by Region</th>
<th>Bioethanol LHV Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>World absolute (in 1000 GJ)</td>
<td>16416226.2</td>
</tr>
<tr>
<td>*World percentage (%)</td>
<td>40</td>
</tr>
<tr>
<td>Europe absolute (in 1000 GJ)</td>
<td>2093561.2</td>
</tr>
<tr>
<td>*Europe percentage (%)</td>
<td>48.4</td>
</tr>
</tbody>
</table>

*Percentage substitution is with respect to gasoline energy.

When biobased butadiene and plastics chemical is produced one might have the feedstock demand presented in Tables 5 and 6 respectively. The Lower Heating Value (LHV) data from Oak Ridge National Laboratory, ORNL (ORNL, 2006) as followed in other related works e.g. (Kaparaju et al, 2009) is used for estimation at the fuel end.

Table 5. Feedstock Demand for Chemical

<table>
<thead>
<tr>
<th>Butadiene Demand by Region</th>
<th>Butadiene</th>
</tr>
</thead>
<tbody>
<tr>
<td>World absolute (in 1000 tones)</td>
<td>29,271</td>
</tr>
<tr>
<td>World percentage (%)</td>
<td>2.7</td>
</tr>
<tr>
<td>Europe absolute (in 1000 tones)</td>
<td>6,108.9</td>
</tr>
<tr>
<td>Europe percentage (%)</td>
<td>4.5</td>
</tr>
</tbody>
</table>
6. Conclusion

Biomass as useful source of fuel, material and chemical through using bioethanol, plastics and butadiene, its capability in making bioproducts has been acknowledged. Utilization template which can serve as a decision support tool depending on objective for biomass consumption was established based on ideal biomass.

The best utilization pattern for biomass to bioproducts was found to be the one that took cognizance of lignin consumption through using it to upgrade the production from fermentable constituents of biomass. Maximum production was found to be attainable when external hydrogen is integrated into the system, but this for its cost penalty is jettisoned from being the optimum. Any of direct fermentation of polysaccharides upgraded with chemical synthesis or syngas fermentation of lignin, or that of polysaccharides via carboxylate route upgraded with hydrogen from shifted lignin CO represents the best utilization pattern to product. This optimum utilization compared when whole biomass is used directly through (i) thermochemical route gave 16.7% increase in production (ii) biochemical route provides 33.3% increase in production, which represents significant savings for the biorefinery. These savings resulted from better utilization of lignin in these schemes. The difficulty in finding corresponding literature yields for these optimum utilization schemes are because they are relatively new.

For biofuel focused application, meeting 40% and 48.4% of gasoline energy demand worldwide and in Europe respectively completely deplete this forestry woody biomass, leaving none for other uses. For material, 52.7 and 71.9% of feedstock is required to satisfy demand for plastics worldwide and Europe respectively. For chemical, 2.7 and 4.5% of biomass worldwide and in Europe respectively is the feedstock level required to replace petroleum based butadiene production. Looking at this trend, forestry biomass capacity for fuel that can substitute petroleum gasoline is very limited. There will be even a further reduction in biomass ability to meet the demand for these bioproducts when realistic production hinged on the actual capacity of technologies presently is set in perspective.

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