BIOBASED CHEMICALS: TECHNOLOGY, ECONOMICS AND MARKETS

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Abstract
A recent study estimates that, by 2025, over 15% of the three trillion dollar global chemical sales will be derived from bio-derived sources. Yet another study highlights that over 90 % of the annual global plastic production of 270,000 ktons is technically feasible for substitution by bioplastics. Many of these bioproducts would be manufactured in bio-refineries by the deployment of rapidly emerging industrial biotechnology. It is expected that bioderived chemicals will come from three sources: direct production using conventional thermochemical and catalytic process, biorefining, and expression in plants. Direct production is already a reality, as evidenced by the production of propane diol and polylactic acid from corn-derived glucose and others. There has been recent commercialization of bio-derived plasticizers for polyvinyl chloride, polyester resins for coatings and inks, biopolyols for urethane foams, high performance polymaides and others based on vegetable oil and carbohydrate renewable sources. Chemical biorefineries, on the other hand, based on various platforms such as carbohydrate/ cellulose, oil, and glycerin, a co-product of biodiesel production, and algae are in the pilot stage. Chemicals expressed in genetically enhanced plants to accentuate target functionalities such as primary hydroxyls, oxirane and others are in the discovery phase and furthest from commercialization. The white paper highlights some of the recent developments and trends in each of the three waves for bioderived chemicals. Further, it also covers some of the opportunities and challenges, both from a technical and commercial perspective, facing bioproducts industry to realize its potential.

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Introduction

A recent report (C&News, 2009) estimates over $100 billion of the current global chemicals market, about 3%, are derived from either bio-based feedstock or fermentation or enzymatic conversion or combination of them. This report projected that the share of bio-derived chemicals would grow to about 15% of global chemical sales by 2025. A June 2009 study from the University of Utrecht, as shown in Figure 1, suggests that over 90 % of the global annual production of plastics is technically feasible for substitution by bioplastics. However, it will not be possible to exploit this technical substitution potential in the short to medium term. The main reasons are economic barriers (especially production costs and capital availability), technical challenges in scale-up, the short-term availability of bio-based feedstocks and the need for the plastics conversion sector to adapt to the new plastics. Nevertheless, the Utrecht study shows that, from a technical point of view, there are very large opportunities for the replacement of petrochemical by bio-based plastics.

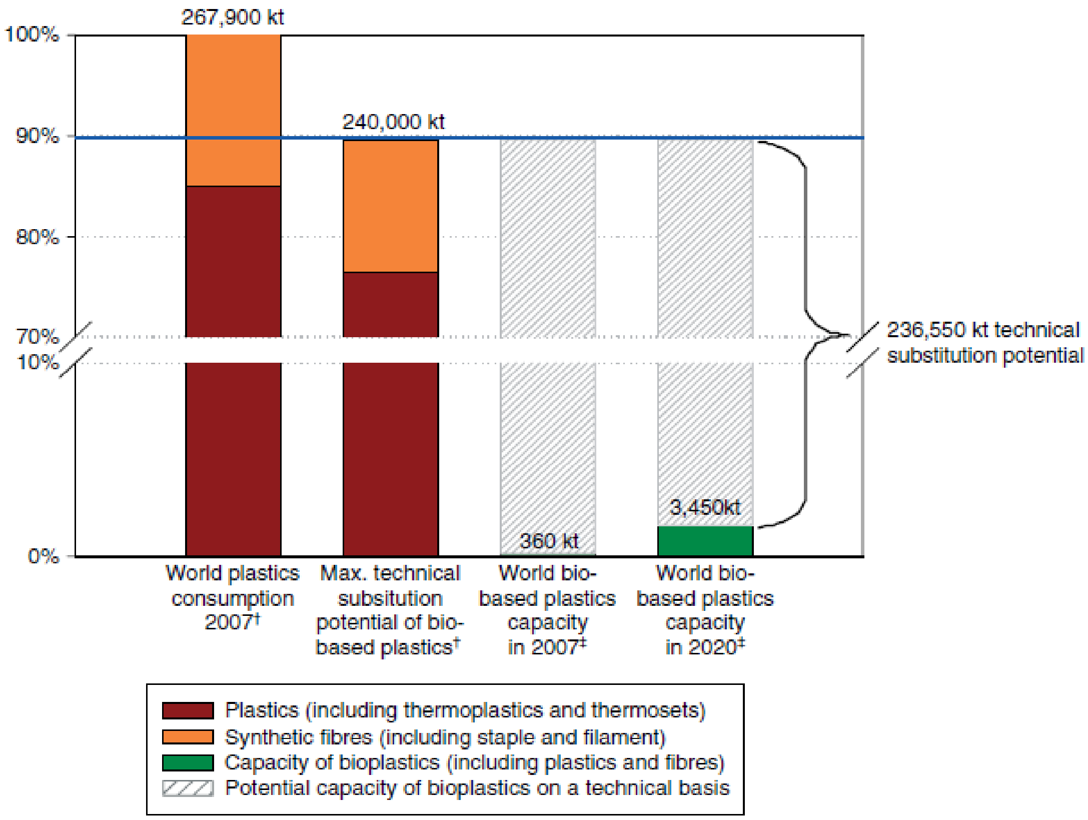

Figure 1: Comparing the projections for 2020, based on company announcements with market potential, based on maximum technical substitution

There are several drivers for the interest and growth of bio products in the marketplace. A few that are worth mentioning include increasing availability of cost effective technologies and improved processes, concerns about long term sustainability and price volatility of fossil-based feedstock, a more benign footprint on the environment, and consumer interest in green products and public policy. Many large and established chemical and biotechnology companies as well as numerous smaller startup and venture companies are actively involved in the development and commercialization of bioproducts from a variety of renewable biomass sources. These companies are trying to follow a bio-refinery model, similar to current petrochemical refineries, which co-produce large volume commodity fuels and high value chemicals.

This paper covers the following topics related to these emerging technologies:

- Various bio refinery models
- Conversion technologies
    - First wave of bioproducts by thermo chemical/catalytic conversion of bio-derived feedstock
    - Bio feedstock platforms
    - Second wave of bioproducts by biochemical conversion technologies
    - Third wave of bioproducts from genetically engineered plants with designed functionality of bio-monomers/building blocks
- Some opportunities and challenges for bio products

VARIOUS BIO REFINERY MODELS

There are various bio refinery models under development, most of which differ based on the biomass source. A palm plantation-based bio refinery is shown in Figure 2.

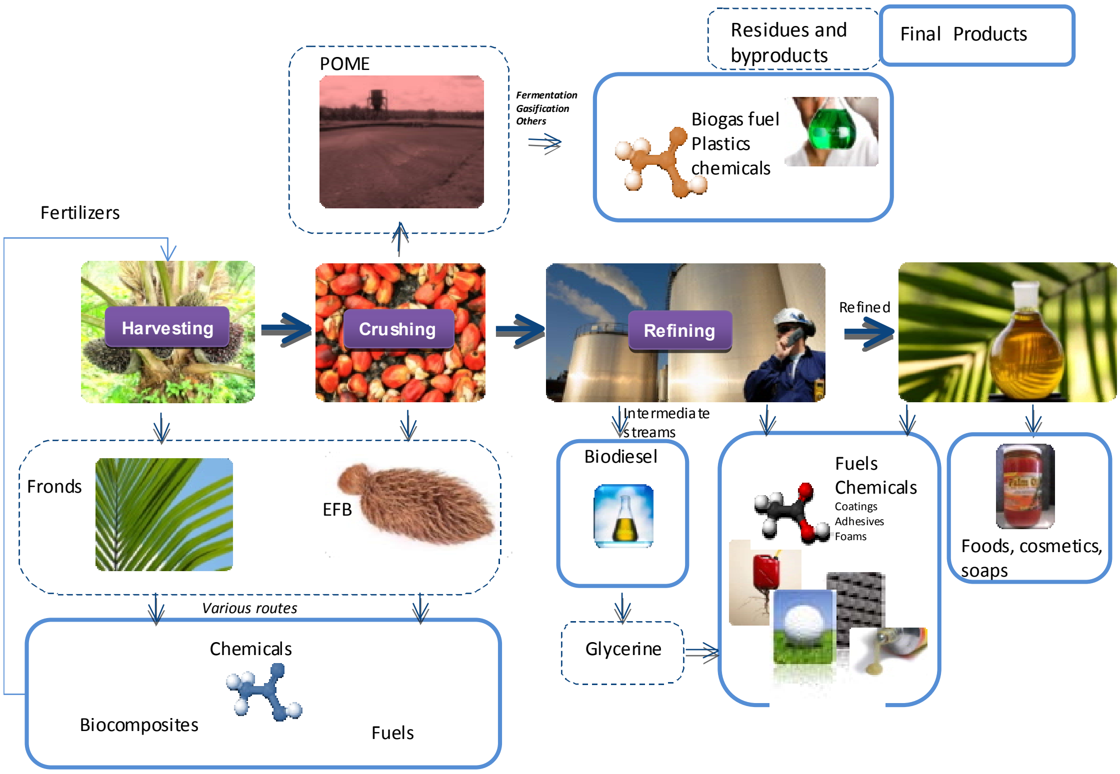

Figure 2: Emerging Palm biorefinery concept

The concept of palm-based bio refinery (and others such as corn wet mill, sugar cane, and soybean) is quite simple and similar to the current petroleum refineries. Biomass is converted to fuels (biodiesel from palm oil and bioethanol from lignocellulosic contained in the feedstock, in this case empty fruit bunches, fronds, etc. that are residues from palm oil processing) and value added chemicals. In a typical palm plantation, besides the oil and lignocellulosic biomass sources, there is some activity to convert palm oil mill effluent (POME) to high value chemicals and biogas. In the case of corn wet mill and sugar cane plantations, biomass is converted to fuel (mostly bio ethanol) and chemicals such as polyols, acids, and others. One major difference between a bio refinery and petroleum refinery is that one of the main products from a bio refinery—at least for the first generation ones based on palm, corn, and sugar cane—is food for humans and animals. This is an important consideration and challenge and has created a serious debate as to the sustainability of first generation bio fuels in particular, and to a lesser extent for smaller volume bio products. Technologies are being developed to use co-products from the first generation bio refineries that are not targeted for food and feed. To address this problem more directly, the trend is to develop non-food energy crops such as jatropha, switch grass, and others as the biomass source for future bio refineries. The general consensus is that the bio refineries that are still in the nascent stage will initially focus on large volume fuels followed by high value chemicals similar to the evolution of petrochemical refineries.

FIRST WAVE BIOPRODUCTS

Many first wave bioproducts are already in the marketplace and are finding applications in myriad end uses. These bioproducts are derived from thermochemical conversion of new bio monomers or building blocks. Products often fall in two categories, namely, the ones that are chemical replacement for petroleum-derived chemicals such as ethylene or lactic acid or functional equivalent of existing chemicals. The main driver for successful first wave bio products is the competitive cost of bio-derived feedstock compared to the current petroleum counterpart that is being replaced. This is very true for bio products such as bio ethylene derived from sugar cane or bio 1, 3 propane diol that are targeted to replace corresponding petroleum derived products.

A few of the first wave bio product initiatives are captured in Figure 3.

Some Recent Large Projects

	DuPont Bio-PDO (Serona®)	NatureWorks™ PLA	Braskem Bio Ethylene
Plant Scale	45 kTA	140 kTA	200 kTA
Fermented Product	1,3-Propanediol	Lactic Acid	Ethanol
Key Processes	Fermentation, Condensation Polymerization	Fermentation, Oligomerization, Ring-Closing, & Ring-Opening Polymerization	Fermentation, Dehydration, Polymerization
Initial Product	PDO/TPA Copolymer	Polylactic acid	Ethylene, Polyethylene, Copolymers
Flexibility	Moderate	Low	High

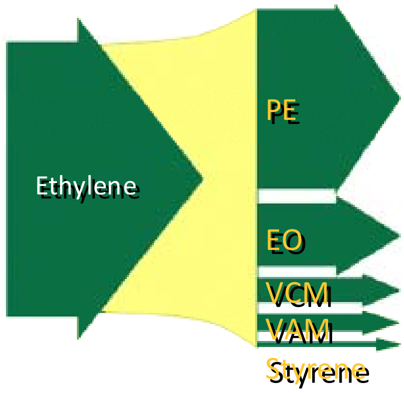

Figure 3: Bio-Derived Plastics – First Wave

It is worth noting that there are other projects such as the propylene glycol plant to be commissioned by Archer Daniel Midland (ADM) shortly, high performance polyamides by Arkema and the polyvinyl chloride (PVC) by Solvay Indupa in Brazil from bio based feedstock (Martinz, et al., 2007).

BIO FEEDSTOCK PLATFORMS

The bio feedstock platform for the production of bio products is mainly focused on the following chemical functionalities.

Vegetable oil/fatty acid esters of glycerol. Vegetable oils and fats provide useful chemical functionalities such as unsaturation and ester groups for further modifications using conventional schemes such as hydrogenation, selective oxidation, epoxidation, meta thesis reaction and others to introduce functionality of value in diverse applications such as plasticizers, coatings, adhesives, polymers, composites, etc. Several bio products such as bioplasticizers for PVC (Vijayendran, . 2005), bio toners (Vijayendran, 2008), biopolyols (Benecke, et al., 2008) based on this approach have been commercialized recently.

Sugar-based platform. Platforms based on sugars (Werpy, et al., 2004) have been deployed to create acids such as succinic acid and convert the acid to high value chemicals such as 2- pyrrolidone, 1, 4 butane diol, tetra hydrofuran and others.

More recently cellulosic feedstock (Zhang, et al.,) has been converted to 5-hydroxymethyl furfural (HMF) using some novel catalysts and ionic liquids as platform chemical to make a variety a high value chemicals derived from petroleum sources, as shown in Figure 4.

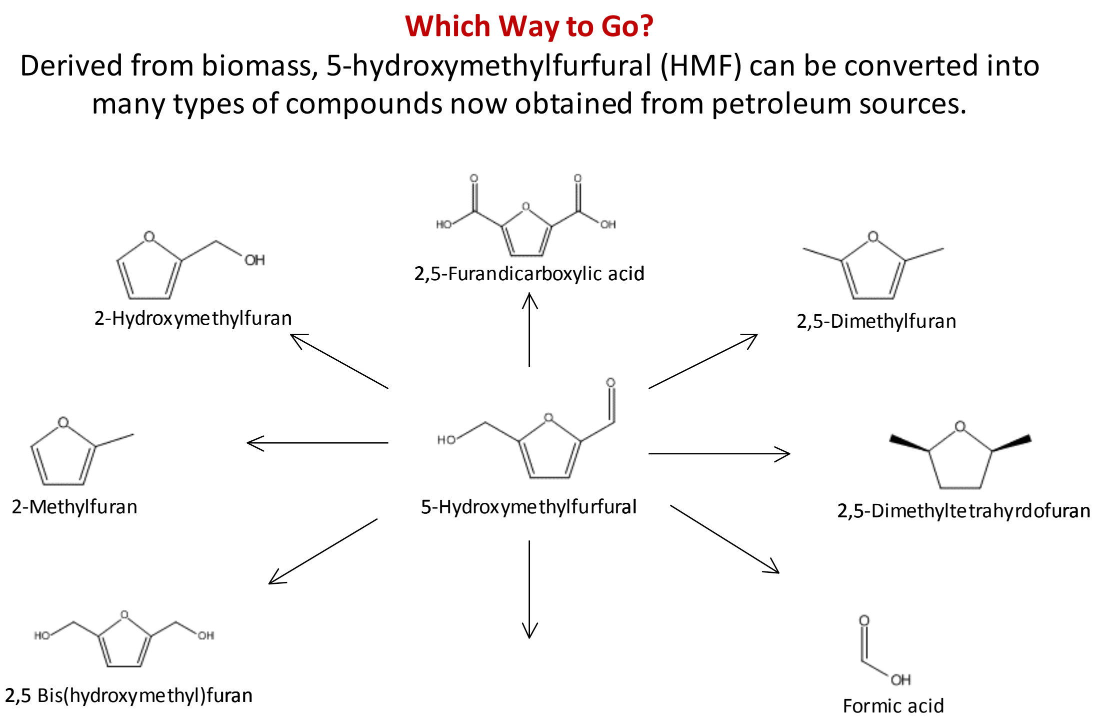

Figure 4: Cellulosic Platform

Various building block molecules such as 5-hydroxymethylfurfural (HMF), derived from cellulosic biomass, can be converted into many types of value added chemicals now obtained from petroleum sources.

Startup companies such as Segetis are developing novel chemicals based on levulinic acid for use as replacement solvents and plasticizers. Roquette has been actively pursuing commercial scale production of isosorbide from sugar feedstock useful in the development of bioplasticizers and bisphenol free polycarobonate resins.

Glycerine Platform. Figure 5 shows bio products derived from crude glycerine, a co-product of biodiesel production.

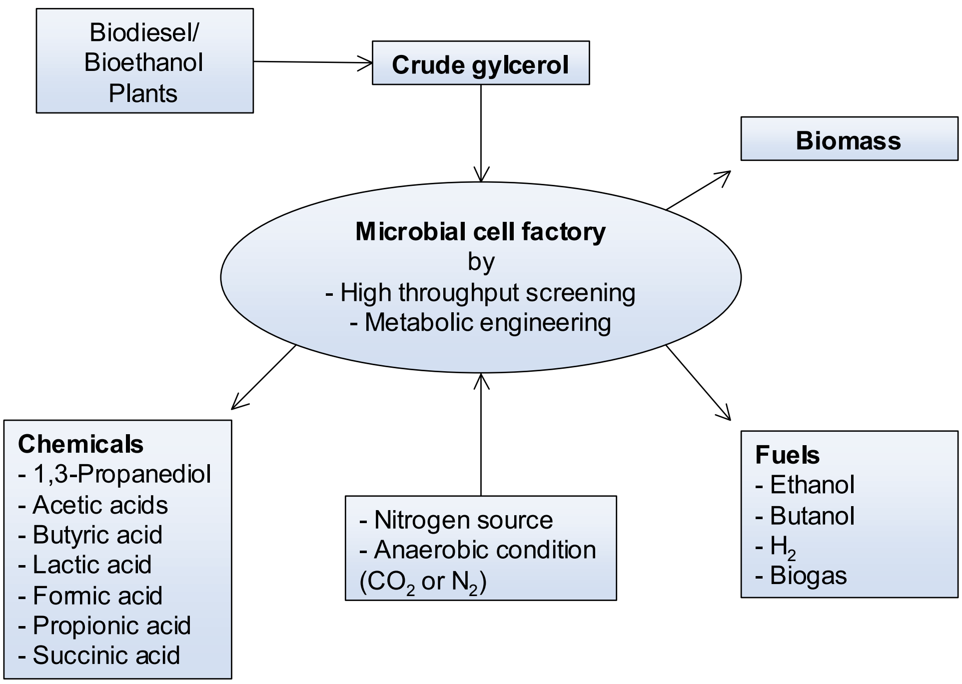

Figure 5: Glycerine Platform

There have been recent activities to convert abundant and low cost lignin to value added chemicals and fibers (Baker,2009).

Recent commercialization efforts of first wave bioproducts have clearly shown that it is important that the technology is proven at the pilot scale and the economics are competitive with the petroleum products. In many cases, such as in bio plasticizers for PVC and biotoners for office copiers and printers, the bio product replacements have functional attributes that are of value and not available from current petroleum products. In the case of bio plasticizers, it is shown that one of the new bio plasticizers, reFlexTM 100 has significantly better thermal stability, lower plasticizer migration, and improved plasticization efficiency compared to industry standard (butyl benzyl phthalate [BBP]) and a petroleum-based phthalate replacement (DINCH from BASF), as shown in Figure 5.

Figure 6. Improved thermal stability of reFlex™ 100, a bio-derived green plasticizer, compared to butyl benzyl Phthalate (BBP) plasticizer, and diisononylcyclohexane-1, 2 dicarboxylate (DINCH), a petroleum-based non-phthalate plasticizer. Test conducted on heat stability in a metastat oven set to 375 degrees for 5-to-60 minutes

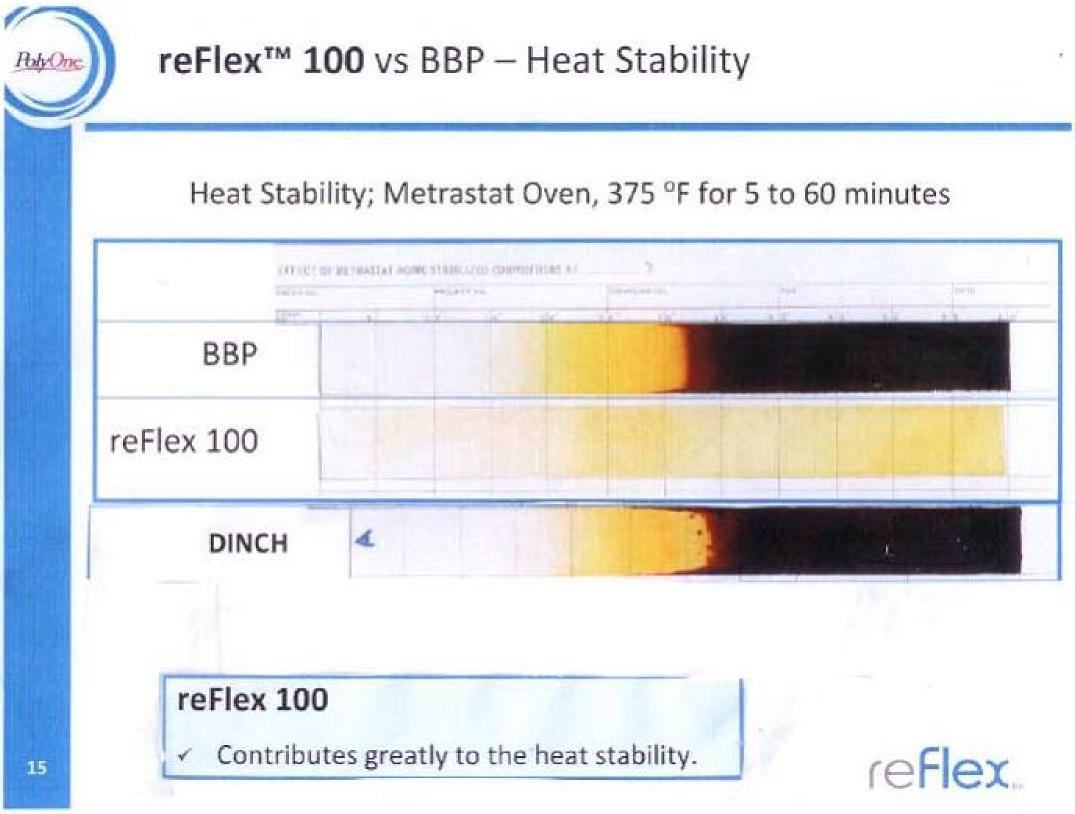

Figure 6. Heat Stability

Plasticization efficiency and thus lower use level with no known health concerns compared to the petroleum based phthalate plasticizers, besides being "green" and environmentally friendly. See Table 1 for some comparative data of reFlex™ 100 bioplasticizer from PolyOne and the industry control, butyl benzyl phthalate (BBP).

Feature	Benefit
Bio-derived	✓ Allows the incorporation of high levels of renewable content
Improved air release	✓ Reduced evacuation time ✓ Improved productivity ✓ Reduced defect rate
Greater efficiency	✓ Reduced usage level
Fast gelation and fusion	✓ Fast processing ✓ Low fusion temperatures possible
Lower paste viscosity	✓ Easier material handling
Imparts excellent thermal stability	✓ Reduction of heat stabilizers ✓ More robust performance

Table 1. reFlex™ 100 vs BPP - Summary.

In the case of bio toners, the bioproduct replacement has lower fusion temperature and easier recycling of office waste paper (Vijayendran, 2008). The message that is becoming clear is that any new bio products that are targeted to replace existing pertroleum-derived products should be able compete on cost and performance. Just being "green" and bio-derived from a sustainable source are not enough to be accepted in the marketplace.

SECOND WAVE BIO PRODUCTS

The second wave bio products involving the conversion of bioderived sugars, cellulosics and oils by biochemical routes are in the advanced R&D and early pilot scale phases. Biochemical processing using advances in metabolic engineering and separation technologies to produce high value chemicals have made great strides in the last few years.

Bioprocessing tends to have the following attributes compared to conventional thermo chemical conversion technologies:

- Lower yields
- Fairly dilute solutions with lower concentrations of actives
- Most reactions are done at ambient temperature and pressure thus offering processes with potential lower capital and operating investments
- Microorganisms have several pathways to make the same products and rapid screening tools have helped to design metabolic pathways to achieve high yields of target molecules
- Most of the initiatives in the second wave bio products are in the advanced R&D or pilot scale. Major milestone is to demonstrate commercial viability of many of the technologies that have shown R&D feasibility in the laboratory scale.

A few of the players that are active in the second wave bio product development and commercialization are shown in Table 2.

• Butanol	• Succinic Acid
• Isobutanol	• 1,4 Butanediol
• Acrylic Acid	• MEK
• Propylene Glycol	• Isoprene
• Glycolic Acid	• Adipic Acid
• Acetic Acid	• SAP (Substitute)
• Caprolactam	• Algae based chemicals
• Hydroxy Alkanoates	

Table 2. Examples of Second Wave Chemicals/Polymers.

It will be interesting to watch over the next several years how successful the second wave products from these companies are going to be in the marketplace.

It is worth mentioning here that there are several algae based initiatives to make biofuels and high value chemicals such as acids, alcohols, esters etc (Solix Biofuels.com). It should also be mentioned that there is a joint venture between ADM and Metabolix to produce poly hydroxyl alkanoates, a polyester biopolymer with some interesting properties (Chen, 2010).

THIRD WAVE BIO PRODUCTS

Third wave bio products derived from plant expression through genetic engineering to produce chemicals with designed functionality are still in the early discovery stage and furthest from commercialization. The work on high oleic acid oils is perhaps furthest along in terms of commercialization.

There are several patents describing the use of such high oleic acid oils in several industrial applications such as inks, lubricants, etc. (Knowlton,1999) . Some early work has shown the feasibility of introducing primary hydroxyl functionality in vegetable oils such as canola. About 12% riconelic acid has been expressed in conventional canola seed (Grushcow, 2007).

Primary hydroxyl functionality from such modified oils has several useful functionalities and attributes of interest in lubricant, coating and polymer applications. Recent work at CSIRO, Australia (Green et al., 2009) has shown the feasibility of expressing high levels of epoxy functionality in some native oil seeds.

A crop producing epoxy oil would be an interesting replacement for epoxidized oils produced by the convention per acid route. The same group has also expressed acetylinic functionality in plant oils with the potential provide useful reactivity and functionality of value in several high value chemical applications.

OPPORTUNITIES AND CHALLENGES

Opportunities for bioproducts over the next decade are plentiful. Future products in the chemical industry will rely more and more on feedstock, building blocks and products from bio-derived source. Over the last 100 years or so the chemical industry has relied on petroleum-based sources and seems to have reached a plateau in terms of new and innovative products and the future growth is expected from bioproducts, as shown in Figure 7 based on some recent study by DSM, a major chemical company.

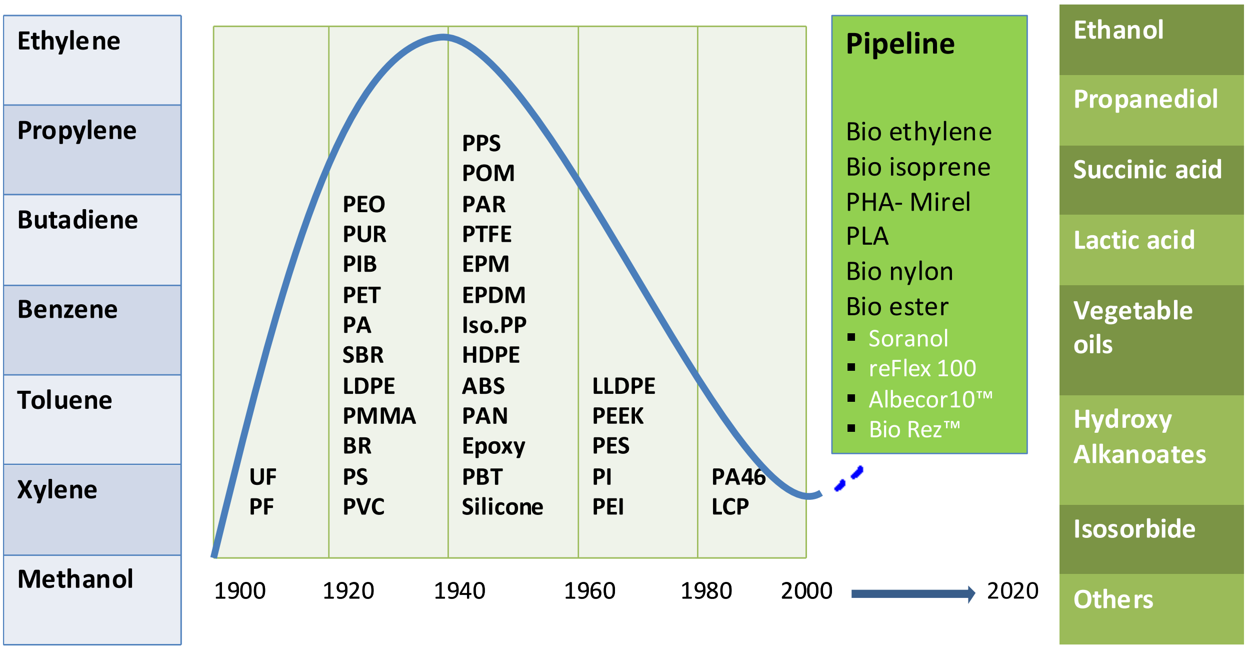

Figure 7: Innovation Potential of Bio-Based Materials.

The challenges facing the emerging bioproduct industry to realize its full potential are real and cover a myriad of areas such as establishing a clear value proposition for bioproducts, offering high value differentiated solutions that are cost effective. This would require sustained R&D investment coupled with establishment of reliable supply chain options that are compatible with existing infrastructure and investments.

SUMMARY

Use of bio products is growing with the first wave products derived from thermochemical conversion of bio-derived building block taking the lead in commercialization. Second wave bio products produced by metabolic engineering and bioprocessing technologies are in the pilot scale. Third wave bio products based on plant expression are in the discovery phase.

Bio refineries based on a variety of biomass feedstock are still in the nascent stage and will require some time to fully develop. Continued R&D investment to improve the technologies to provide cost effective solutions is very much needed. Also, establishment of supply chain of feedstock as well as compatibility with existing infrastructure of the well established petrochemical industry is expected to facilitate commercialization of bioproducts.

It is expected that bio products from bio refiners will continue to grow and compliment the petrochemical refineries to serve the global chemicals markets.

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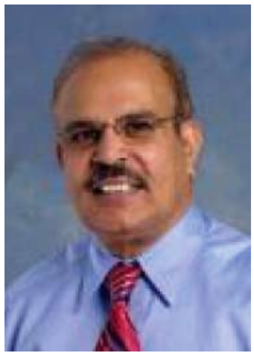
About the author



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Dr. Bhima Vijayendran served as the Chief Research officer for the Renewable Energy Laboratory (REL), Kuala Lumpur, Malaysia until September 2010. Dr Bhima has more than 40 years of experience in industrial R&D and product commercialization.

1995 – 2008: Battelle-Columbus USA

Dr. Bhima Vijayendran joined Battelle in February 1995 and is one of the leading recognized authorities on specialty chemical and polymer systems for a wide range of applications. Dr. Vijayendran has several inventions and new products/ processes to his credit in the fields of colloid, polymer, and surface chemistry, adhesives and adhesion, interfacial phenomenon, specialty coatings, composites, water-based emulsions, synthetic and natural water soluble polymers, rheology, plastic processing and additives, paper chemicals, and recycling of plastics and paper.

More recently he has been taken a leadership role in identifying opportunities and relevant technologies in the areas of Renewable Resources, Fuel cells, Nanotechnology and Photonics. He has been recognized for his contributions in the field with ***six R&D 100 Awards in 2001, 2002, 2003, 2004, 2006, 2008 and 2009***. The ***Ohio Soybean Council in 2001 and the United Soybean Board in 2003*** recognized Dr. Vijayendran for his contributions to soybean research with the ***Outstanding Achievement Award***. In 2004, he won the prestigious ***Battelle Inventor of the Year Award*** for his many contributions in the field of advanced materials.

Dr. Vijayendran received the TopCAT inventor of the year Award in January 2005. He was awarded the outstanding achievement award from American Oil Chemists Society in 2005. He was a Finalist at the First Global BioPack Award, Frankfurt (2006). He received the "Design for Stainability" award for 2007 by the SPE Plastics Environmental Division, March 2007. Council of Scientific Industrial Research (CSIR, India) ALFA Award for Life Time contributions in April 2007 received the ***2008 Presidential Green Chemistry Challenge Award for "Development and Commercialization of Biobased Toners***."

In 2009, ***Dr. Vijayendran was inducted to Battelle's Hall of Inventors. He also was awarded the coveted Life Time Achievement Award from United Soybean Board and American Soybean Association for his contributions to the soybean industry***. He has over 75 patents and 50 technical papers to his credit. Dr. Vijayendran is keenly interested in linking technologies to business opportunities through project management, decision-risk analysis, and quality processes leading to rapid commercialization of new and emerging technologies.

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1970-1976- Research Staff- Pitney Bowes Inc., Stamford, CT
1969-1970- Post Doctoral Fellow- R.J. Reynolds Tobacco Company, Winston Salem, NC

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- Innovations in Conversion Technologies and Application Development in Personal/Home Care, Packaging, Automotive, Coatings, Solvent, Pulp & Paper
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