Production of precursors for specialty polyamides from bio-sourced lipids

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Importance of renewable materials

Synthesis of commodity chemicals and fuels from renewable sources is gaining an increasing attraction due to concerns over depletion of fossil resources as well as the effects on the climate change. According to a recent theoretical model on the oil production, the peak of oil production lies somewhere between 2010 and 2025 and in the ideal case, the oil production peak was to be in 2013. Both, the extraction of existing oil resources and the demand for oil, is rapidly increasing with the current population growth. Fuels, polymers, surfactants, and lubricants are few essential commodities in today's life, which are derived from petroleum sources. To cater the growing demand with the depleting nature of petroleum resources, world is searching for alternative sources for the existing petroleum based materials. Bio-based materials such as bio-fuels, biopolymers, bio-surfactants, and bio-lubricants are hopeful alternatives that have been discussed frequently in scientific literature to overcome hurdles incurred by limitation of petroleum sources. Use of bio-based materials has extra advantages over petroleum-based materials when the environmental impact is considered. Environmental pollution is linked with all the steps of oil processing and can be affected to water, air, soil and all the living being of the planet. Bio-based materials are easily biodegradable, renewable, and account less for the carbon footprint of the planet.

Bio-sourced lipids as a feedstock

Among the obtainable constituents (carbohydrates, lipids, proteins) from biomass, lipids are especially suitable as a feedstock for commodity and specialty chemicals because of their less oxygenated nature. Thus, the majority of the processes for production of biofuels, biosurfactants, bio-based coatings, and biopolymers were developed using lipids as a feedstock. For example, in the field of polymer industry, synthesis of polyesters, polyamides, polyurethanes, polyepoxides, and polycarbonates from fatty acids have been reported. The rapid advancement of the technologies however has not yet impacted chemical industries to replace the traditional feedstock, in part due to lack of economic advantage. Therefore, new technologies for production of renewable commodity/specialty chemicals, that is not only clean and efficient but also economically competitive, is still actively being sought and researched.

Polymers

Polymers are macromolecules made from large number of monomers. They can be natural (such as polysaccharides, proteins, silk, DNA, and natural rubber) or synthetic (such as polyolefins, polyamides, polyesters, and polyurethanes). Synthetic polymers have become essential materials in modern world: nearly replacing the use of metals, woods and natural fiber based cloths in many industries. Their precursors are mainly synthesized from petrochemicals although alternative feedstocks such as natural lipids are also studied.

Specialty polyamides

Polyamide is a polymer with the general molecular formula $-[(CH_2)_n\text{-CONH}]-$ or $-[(CH_2)_n\text{-CONH-}(CH_2)_m\text{-CONH}]-$ invented by Wallace Carothers and has become one of the most widely using polymers today. Polyamides such as polyamide 11 and 12 are described as specialty polymers as they are produced for special purposes. Polyamide 11 and 12 are two high value specialty polyamides that find applications in many fields including medical, automobile, electrical, mechanical and sports industries due to their excellent physical and chemical properties. Polyamide 13 is also reported to have similar properties to nylon 11 and 12 (Figure 01).

Figure 01: Examples of three specialty polyamides

At present, synthesis of polyamide 12 precursor is done by using petrochemical 1,3-butadiene as the substrate while precursor for polyamide 11 is synthesized from castor oil extracted from seeds of castor beans. Polyamide 13 is still not produced in industrial scale. Polyamides 11 and 12 have become essential materials in automobile industry today. This was clearly proven by a shortage of polyamide 12 to the automobile industry due to an explosion occurred in a leading polyamide 12 manufacturing plant in Germany in the year 2012. After this incident, an article appeared in Chemical & Engineering News reported it, as "without Nylon 12, production of vehicles would grind to a halt, one model at a time, in only a few weeks".

Many alternative syntheses for precursors of these specialty polyamides are found in literature. Most of these studies are focused on the use of renewable feedstocks and to device safer synthetic routes. Fatty acids available in fats and oils have become the major starting material in many of these studies. Examples for several fatty acids that can be used to produce polyamide 11, 12, and 13 precursors are shown in the figure 2.

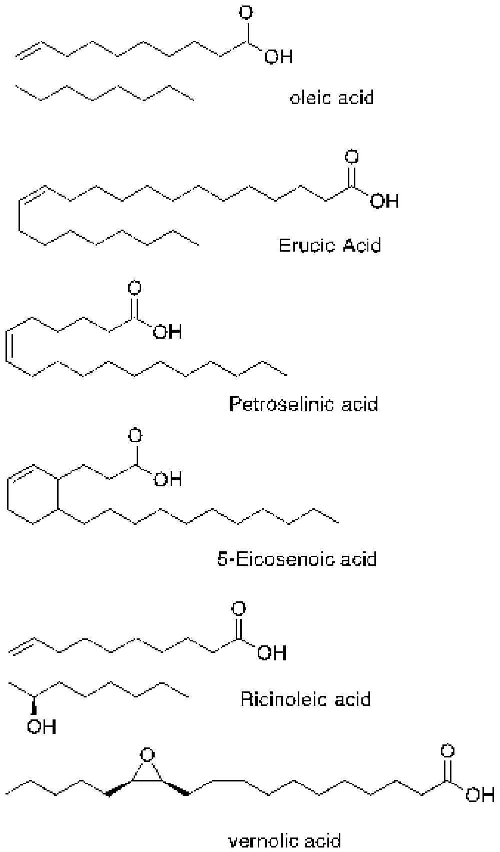
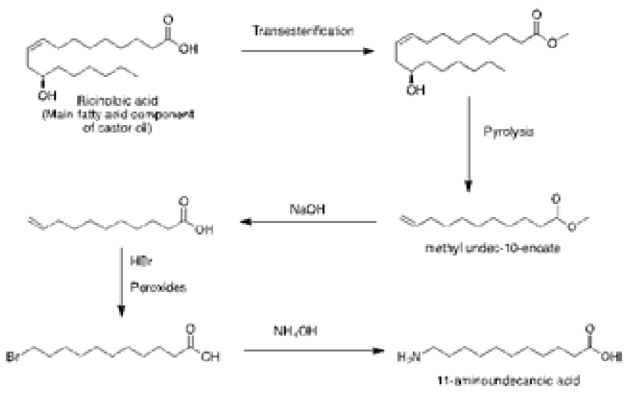


Figure 2: Examples of fatty acids studied to make renewable polyamides

Synthesis of 11-aminoundecanoic acid from ricinoleic acid is a well known industrial example for a bio-based polyamide precursor (Scheme 1). However, castor bean is the sole source for ricinoleic acid in industrial scale. Further, this plant is grown only in some parts of the world. Due to these reasons, use of other fatty acids for the synthesis of bio-based polyamide precursors are being sought.



Scheme 1: Synthesis of polyamide 11 precursor from ricinoleic acid extracted from castor beans.

Oleic acid is a frequently used fatty acid for this purpose due to its abundance in many different sources such as vegetable oil, animal fats, and algal oils. Olefin metathesis of methyl oleate with different olefin partners with right carbon lengths to make bifunctional compounds has been frequently studied as a potential route for polyamide 11 and 12 precursors. These intermediate bifunctional compounds are then can be converted to precursors of polyamide 11 and 12.

Synthesis of polyamide 13 precursor, 13-aminotridecanoic acid, is reported by starting with erucic acid as the substrate. Mustard oil and rapeseed oil are two sources that contain erucic acid. Esterification followed by ozonolysis of erucic acid produces half ester of brassylic acid. This has been successfully converted to amide ester, nitrile ester and amino ester. Finally 13-aminotridecanoic acid has been obtained by hydrolysis of amino ester.

Apart from the above-mentioned procedures, many different approaches are reported in literature to make precursors of specialty polyamides. Due to the higher unit price, synthesis of these bio-based polyamides will become economically feasible in future and replaces current syntheses from petroleum feedstock.

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Silica from Rice Husk: Value Addition to Agro-wastes

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Sri Lanka rice cultivation occupies 34 percent of the total cultivation area and produces about 1.5 to 3 million metric tons per year depending on the weather condition according to the data from rice research and development institute and the department of census and statistics in Sri Lanka. Once rice is processed the major waste is the rice husk (RH). In general, 20 percent of raw rice grain contains husk. At present RH is used in different fields such as alternative fuel, bio-fertilizers, absorbent in building materials and material for animal husbandry. However, the amount of RH used in such industries with respect to the total production is very small. Consequently more often RH dump in to landfills. Burning of RH can get good amount of energy owing to its high calorific value of about 16000 joules per gram. Even after combustion at high temperatures it generate ash, which accounts about 20 percent of the RH. Rice husk ash (RHA) contains about 90 percent silica with trace amount of other metal oxides. If we follow the above statistics, the total rice production of Sri Lanka per year produces about 300,000 to 600,000 metric tons of RH. If one assume 50% of such RH is burned it generates about 30,000 to 60,000 metric tons of RHA. Since it contains about 90% silica, it is possible to produce 27,000 to 54,000 metric tons of silica per year. This could be even doubled if all the RH is utilized. Thus, extraction of silica from RHA would be a great value addition to rice industry as well as a solution for the waste management which impact environment positively. Further this provides new business opportunity to generate additional revenues from the waste.

Silica is one of the multipurpose chemical compounds that exist in gel, crystalline and amorphous forms. The major industries where silica uses are rubber industry especially the tyre manufacturing, pharmaceuticals, cosmetics, paints, printing tonners and so on. Conventional silica production method is based on the reaction between sodium carbonate and quartz at high temperatures. However, the processes involved in traditional method are energy intensive. Considering the abundance and cheap cost as agro waste RHA, many researchers and industrialist especially in other paddy cultivation countries have focused their efforts on the possible uses of RHA to extract the silica. Being biogenic origin the author and his research team believes that the silica extracted from RHA has a high value with respect to the chemically synthesized silica. At present the author and his research team extensively studies the cheapest and most effective ways to extract silica form RHA. Further, conversion of such silica into nanosilica and surface modifications of silica to make them compatible in rubber matrices are also being investigated. In this brief, the chemical process involves in silica extraction from RHA is discussed.

Rice husk ash in fully burned condition contains high amount of silica. Thus, selection of ash is important as
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