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Chemical and biological-based isoprene production: Green metrics

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ABSTRACT

Green metrics is a methodology which allows the greenness of either new or already existing processes to be assessed. This paper is a part of a special issue devoted to green metrics in which this methodology is applied to different processes to assess bio and petrochemical routes. In this work, green metrics were used as a tool to validate and compare the petrochemical and biological processes of isoprene production. The Sumitomo process has been selected for this comparison as it is beneficial because of it using less expensive C_1 components as well as the fact that it has lower investment costs for a single-step process. The production of isoprene through a modified *Escherichia coli* bacterial process has been selected for comparison with the fossil pathway. The green metrics evaluation was performed for both processes to produce isoprene and to target 50,000 tonnes of isoprene yearly.

Although, the calculated costs for the bio-isoprene are slightly higher than the actual market price of its fossil counterpart, the results obtained reveal that the bacteria-based isoprene production is able to substitute the petrochemical process, with material and energy efficiency. This conclusion has also been proved by the increasing number of industrial interest in bioisoprene. The challenge comes from the land use needed for the production of a carbon source which might be solved by the use of waste and residues which are rich in carbohydrates or lignocellulosic biomass which can be converted to simple sugars.

1. Introduction

Isoprene (C_5H_8, 2-methyl-1,3-butadiene) is a hydrocarbon, which is colourless and a volatile liquid at room temperature. Isoprene occurs extensively in nature at very low concentrations being metabolised by several organisms such as animals, plants (including macro- and microalgae), fungi and bacteria [1–3].

Isoprene is a key chemical commodity required to manufacture a diverse range of industrial products, including (in over of 95%) a wide variety of elastomers used in surgical gloves, motor mounts, rubber bands, golf balls, condoms and shoes. However, the most important use of isoprene is the production of synthetic rubber (*cis*-polyisoprene) in tire manufacturing (cars and trucks). Furthermore, 5% of the worldwide production of isoprene is dedicated to produce chemicals, which are used as intermediates for pharmaceuticals, vitamins, flavourings, perfumes, and epoxy hardeners [2,4,5].

Isoprene was first synthesised in 1860 by C.E. Williams through the pyrolysis of natural rubber. Nowadays, most isoprene production comes from fossil fuel resources. The three major producers of high-purity isoprene are Nizhnekamskneftekhim, Synthez-Kauchuk and Togliattikauchuk from Russia with a production of 427,500 tonnes in 2011. The next largest world producers of isoprene are Goodyear and Shell (USA) [6]. Dehydrogenation of isopentane as well as synthesis of isoprene from isobutylene and formaldehyde are commonly used in Russia, whereas direct isolation of isoprene from C5 stream by extractive distillation is executed in the USA [7]. Global industrial production of synthetic isoprene from petrochemical feedstocks is close to 1 million tonnes per year and currently isoprene consumption is around 850,000 tonnes annually [8]. A large amount of the isoprene produced annually is liberated by plants which collectively release approximately 500 million tonnes of carbon per year [9], making isoprene the dominant gaseous hydrocarbon produced by vegetation. This amount of isoprene is sufficient to produce 60 billion car and truck tyres, which is 50 times the current global manufacturing of 1.2 billion tyres [2]. However, the use of isoprene from plants and animals for commercial purposes is still economically

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unfeasible, although the use of latex produced by Hevea (rubber trees) to produce rubber is one example of economically efficient biological production [10].

Taking into account the growing demand for isoprene, the recent pressure on fossil fuels, and the environmental concerns related to global warming, there is an increased need for the production of chemicals such as isoprene from renewable sources. Both, the materials and processes should be more efficient, sustainable, cost-effective and environmentally friendly (e.g., using biological processes).

An industrial production of bioisoprene is an interesting option and for this reason many leading tyre producers perform advanced studies in this direction [11]. Goodyear, a well-known tyre manufacturer that produces around 200 million tyres a year, works with Genencor to engineer bacteria which will produce bioisoprene [12]. Bridgestone is also co-developing bioisoprene in collaboration with Ajinomoto, through fermentation [13]. The Michelin Company has a joint venture with Amyris to develop the bioisoprene process [14].

The goal of this work is to compare the petrochemical and biological (bacteria-based) processes for isoprene production using green metrics (material and energy efficiency, economic evaluation, and land use).

2. Production

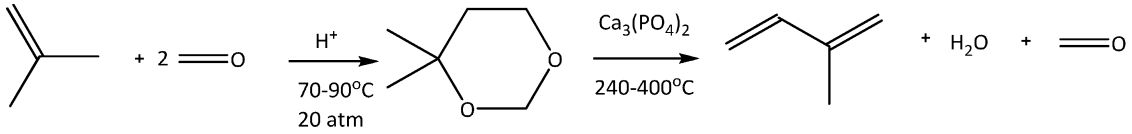
2.1. Petrochemical processes

Over the years many technological processes of isoprene production have been proposed and studied. Today the main world isoprene production occurs via separation from C_5 cracked fractions obtained as a by-product in the pyrolysis of hydrocarbons to ethylene. There are two possible technologies available to produce isoprene from C_5 streams (after separation of cyclopentadiene). The first one is isolation by extractive distillation (with N-methylpyrrolidone (BASF), dimethylformamide (Nippon Zeon) or acetonitrile (Shell, Goodrich-Arco); isoprene productivity of ca. 30,000 tonnes per year) or fractional distillation as an azeotrope with *n*-pentane (Goodyear; not yet commercialised). The second assumes the dehydrogenation of isopentane and isopentenes (methylbutenes) using Fe_2O_3–Cr_2O_3–K_2CO_3 catalyst at 600 °C with a yield of 85% (CIS, Shell, Arco, Exxon). Direct isolation allows obtaining of isoprene without additional synthetic steps thus making this method more preferred since isoprene concentration in a typical C_5 stream is 14–23 wt% [4,5,15].

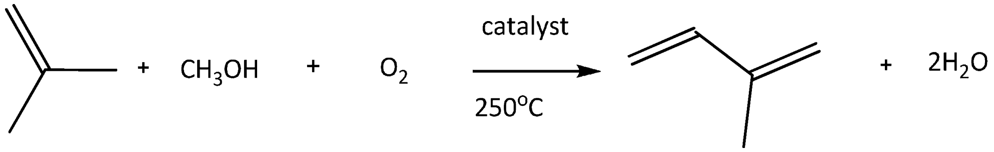
The isoprene production yield is typically very low and is in the order of 2%–5% of the ethylene yield [15]. The efficiency of the process might be increased by converting gas oil as a starting material instead of naphtha. On the other hand, recovery of isoprene from C_5 cracking fractions is considerably more efficient than the synthesis of this commodity in the chemical manner since there is enough ethylene produced to satisfy the large share of isoprene demands [4].

Due to the limited availability of isoprene as a by-product in the production of ethylene, much effort has been devoted to develop synthetic methods of isoprene production. There are main four synthetic routes leading to isoprene [4,15]: (i) addition of acetone to acetylene to form 2-methyl-3-butyne-2-ol and subsequent partial hydrogenation and dehydration (Snamprogetti process) used by ANIC and Karbochem, (ii) dimerization of propene to isohexene followed by demethanation (Goodyear – Scientific Design process), (iii) dismutation of isobutene and 2-butene to form 2-methyl-2-butene followed by dehydrogenation, (iv) double addition of formaldehyde to isobutene resulting in 4,4-dimethyl-1,3-dioxane followed by dehydration and cleavage of formaldehyde.

The fourth process has been scaled up into industrial processes by several companies (Bayer, IFP, Marathon Oil, Kuraray and the CIS).



Recently this route was improved and simplified by Sumitomo Chemical through use of less expensive feedstock i.e. CH_3OH and O_2 in the presence of catalysts: H_3PO_4–MoO_3/SiO_2 and mixed oxide systems based on Mo–Bi–P–Si, Mo–Sb–P–Si, or H_3PO_4–V–Si [15].



This process has not been yet practiced commercially, but is similar to the commercial ones [4]. Furthermore the Sumitomo route is a subject of great interest because it has some advantages such as less expensive C_1 components used in the synthesis, as well as, lower investment costs of a single-step process. For this reason this process has been selected as a potential petrochemical route of isoprene production and was compared with the one using bacteria.

2.2. Bio-based process

Two principal pathways have been identified for the biosynthesis of isoprene by bacteria: cytosolic mevalonate (MVA) and plastidial 1-deoxy-D-xylulose-5-phosphate (DOXP) pathways [16]. Bacteria are able to produce isoprene by DOXP as well as by the MVA pathway by gene modification [17,18].

Isoprene can be produced by both, Gram-positive and Gram-negative bacteria, under facultative anaerobic conditions through the carbon source oxidation process. Among different genus, *Bacillus* seems to be the best producer of isoprene [19]. Yang et al. reported isoprene biosynthesis by a genetically engineered bacterial strain, obtained by co-expressing an optimised MVA pathway and the isoprene synthase ($IspS_{Pa}$) (from the higher plant *Populus alba*) on *Escherischia coli* [17]. This strain allowed isoprene production up to 6.3 g L^{-1} under 40 h of fed-batch fermentation. The Danisco US Inc. together with The Goodyear Tire & Rubber Company patented the isoprene production method, using *Bacillus* bacteria. A modified strain achieves an isoprene production yield from glucose of 8.9% at 40 h or even 10.7% at 59 h [20]. Other key players on the tyres market are also developing the technologies to produce bioisoprene. Ajinomoto and other tyre company Bridgestone Corp as well as Michelin with Amyris are working on the development