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Innovative applications of Waste Cooking Oil as Raw Material

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Abstract

The consideration toward Waste Cooking Oils (WCOs) is changing from hazardous waste to valuable raw material for industrial application. During the last five years some innovative processes based on the employment of recycled WCO have appeared in the literature. In the present review article, the most recent applications of recycled Waste Cooking Oil are reported and discussed. These include the production of bio-plasticizers, the application of chemicals derived from WCOs as energy vectors, and the use of WCOs as solvent for pollutant agents.

1. Introduction

Waste Cooking Oils (WCOs) are valuable by-products of the food chain, which can be employed as green raw materials for the production of chemicals. The amount of WCOs available worldwide is impressive, causing serious environmental, economic and social problems. It has been estimated that more than 15 million tons of waste vegetable oils are generated annually in the world, with EU close to 1 million tons per year.[1,2] Often, WCOs are discharged through public sewerages, making necessary extraordinary maintenances and increasing the water treatment costs. In fact, the presence of vegetable oil in the public conducts promotes the formation of foams, the flotation of sludges, and causes several mass transfer problems due to the adsorption of lipids onto the biomass.[3]

WCO are mainly composed of triglycerides, monoglycerides, diglycerides and variable quantities of free fatty acids (5–20% w/w) generated during the frying process.[2] The main components of triglycerides are saturated and unsaturated fatty acids, which can be used as platform chemicals for the manufacturing of added-value products in various segments of industry. More common industrial applications of WCOs are related to energy production, by direct burning ,[4,5] or for the synthesis of bio-fuels [6,7] Two additional non-negligible market segments of recycled WCOs are represented by the bio-lubricants,[8] and by the production of animal feed.[9] Many research papers, including review articles, have been reported on the above mentioned subjects during the last years.[2,10–12] As the knowledge about the average composition and about the synthetic possibilities of WCOs increases, new applications of this green and bio-compatible raw material have recently emerged. In the present review paper, a selection of recent and innovative applications of WCOs appeared during the last five years are presented. The employment of WCOs in the field of bio-materials, for the design of bio-fuels of second generation, and in the area of biosolvents for pollutants will be discussed.

2. Discussion

2.1. Waste Cooking Oils as Plasticizers

The chemical composition of WCOs is mainly constituted by a mixture of three unsaturated fatty acids: oleic, linoleic and linolenic acid.[13] The carbon-carbon double bonds as well as the acidic moiety present in these substrates are amenable of several kind of transformations, and make this mixture particularly exploitable as source of building blocks for polymer chemistry. In particular, the employment of WCO as raw material for the production of bio-plasticizers has been recently reported. Plasticizers are important polymer additives and have been used extensively in plastics, rubbers and adhesives. Nevertheless, a number of notable controversies and concerns were associated with the use of common plasticizers, namely phthalate esters, since they exhibit a migration phenomenon from the polymer matrix to the surrounding media and they are suspected to produce bioaccumulation in the environment.[14–16] Due to these potential harmful effects on human health and the environment, they have been banned in several countries as plasticizers in fields like fabrication of toys, packing materials of food and medicine.[15–18] Looking for alternative bio-based plasticizers, several kinds of modified edible oils have been considered. The synthesis of epoxidized soybean oil (ESO), acetylated derivatives of castor oil, methyl epoxy soyate, amyl epoxy soyate, tall-oil fatty esters, di-caprylsebacate and epoxidized soybean oil fatty esters has been described.[19–21]. Unfortunately, the use of bio-plasticizers from edible oils is still limited because of the high cost of the raw material and the negative impact on the withdrawal of resources from the food and feed chain.[22] Only recently the synthesis of plasticizers for PVC from epoxidized Waste Cooking Oil has been proposed.[17,18,22] Nevertheless after prolonged times some degree of migration of the bio-plasticizer was observed, as already reported for the classic phatale esters.[21–23] A solution to this issue has been reported by Jia and coworkers,[14] who proposed the covalent bonding of the plasticizer to the polyvinylchloride (PVC) backbone. This target was reached by preparing a Mannich base of Waste Cooking Oil Methyl Ester (WCOME), which was used as non-migration plasticizer for self-plasticization PVC materials. The internally plasticized PVC film showed no migration in n-hexane, which is essential to ensure a long-term stability of the physical and chemical properties of PVC products.[14]

2.2. Syngas production from Waste Cooking Oils

For many years crude and used vegetable oils have been used as ingredient for bio-diesel or bio-fuels, or for heat production through direct burning (first generation bio-fuels).[24,25] Recently, some research activity has been dedicated to the development of second generation bio-fuels derived from WCOs, more precisely hydrogen-rich synthesis gas (or syngas). Syngas can be directly burned or further converted into other chemicals using the Fischer–Tropsh process. It can be for instance transformed into liquid hydrocarbons, mostly diesel and kerosene or into Dimethyl Ether (DME). Bio-SNG (Synthetic Natural Gas) and Bio-DME (Dimethyl Ether) are fuels that can be used in gasoline or diesel vehicles, respectively, with slight adaptations.[25] Several papers report on the use of lignocellulosic biomass as raw materials for second generation of bio-fuels, more precisely for syngas production.[25–27] On the contrary limited literature is available on the utilization of waste cooking oil as a feedstock for syngas.[28,29] Only very recently the extraction of molecular hydrogen and carbon anhydride from WCOs has been discussed in the literature. The syngas produced can be employed as energy carrier or as precursors of other chemicals. The production of hydrogen-rich syngas from Asian WCOs subjected to supercritical water gasification has been reported by Nanda and co-workers.[28]

The long chain fatty acids contained in the WCO were subjected to C-C bond cleavage through thermal cracking to give short chain fatty acids, converted into H_2 and CO_2, CO and H_2O by reforming process. Such conditions promote the water-gas shift reaction between CO and H_2O to generate CO_2 and H_2,[26] and the dehydrogenation of saturated compounds to form H_2.[30]

From this mixture is possible to obtain methane, ethane, ethene and other gases. The same products can be generated directly from the mixture of fatty acids by increasing the temperature of the thermal treatment.

When crude WCO is employed, the feed concentration must be taken into account as influences the production of H_2, which decreases with the amount of feed dispersed in the oil. The process described by Nada and co-workers from WCO is depicted in figure 1.

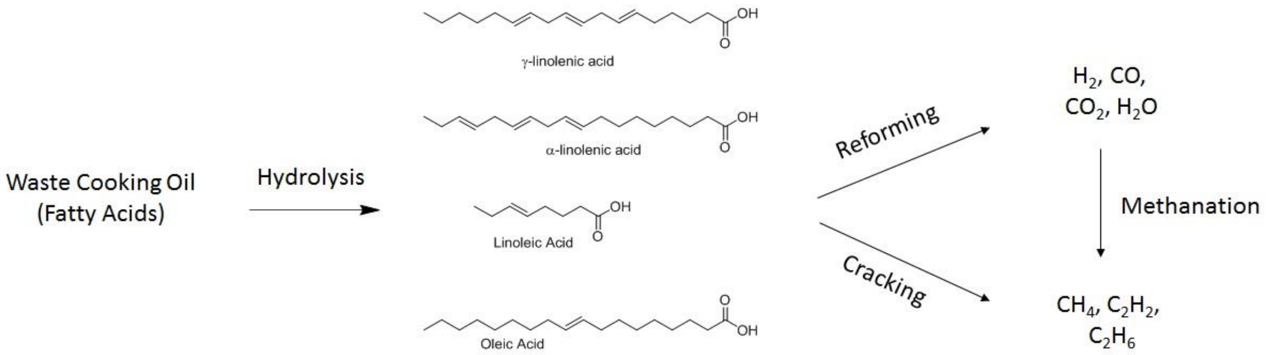

Figure 1. Schematic route for obtain energy carriers and building blocks for synthesis from Waste Cooking Oils.

2.3. Biosolvents for pollutants

Another exploitable property of the vegetable oil is the tendency to solubilize small organic molecules. When the vegetable oil arises from waste and the small organic molecules considered pertain to the family of the hazardous Volatiles Organic Compounds (VOCs), the matter becomes of general interest. Lhuissier and coworkers developed a non-aqueos phase (NAP) bioreactor for the capture and the biodegradation of VOCs.[31] The Authors tested some mineral and vegetal (from food industries) WCOs as solvents for *n*-heptane, ethyl-acetate, 2-propanol, methylisobutylketone (MIBK), toluene, *m*-xylene and 1,3,5-trimethylbenzene. The oleic phase enriched by the organic pollutants was then treated in a Two-Phase Partitioning Bioreactor (TPPB), where the VOCs degradation was achieved by selected microorganisms. Tarnpradab and co-workers employed WCOs for treat the emission produced during the rice husk pyrolysis. In particular, WCO was able to reduce the content of organic hydrocarbon contaminants with a molecular weight larger than benzene (TAR). In particular, the Authors claimed that heavy tar was absorbed by WCO through a dissolution mechanism and several data about the saturation levels were reported (Thanyawan Tarnpradab, Siriwat Unyaphan, Fumitake Takahashi & Kunio Yoshikawa, Tar removal capacity of waste cooking oil absorption and waste char adsorption for rice husk.[32] The possibility to trap small molecules with vegetable oil was also exploited by Worthington and coworkers in the realization of a mercury sorbent device, made through the co-polymerisation of sulfur and unsaturated cooking oils.[33] It is already known that mercury metal and inorganic mercury bind to reduced organic sulfur groups in dissolved organic matter (Hg-DOM),[34,35] and sulphur-based polymers recently showed to be able to remove the Hg^{2+} from water.[36–38] Searching for an abundant, inexpensive and easy to handle material, Worthington *et al.* exploited the double bonds present in the fatty acids fraction of WCOs as crosslinking points for an inverse vulcanization process of polysulfides. The Authors described and characterized different polymers obtained by combination of sulphur and canola, sunflower and olive oil, and demonstrated mercury removal from air, water and soil. With respect to previous studies,[36–38] these new rubbers are effective not only in purifying water containing inorganic $HgCl_2$, but also in capturing common forms of mercury pollution including liquid mercury metal, mercury vapour, inorganic mercury and organomercury compounds.

3. Conclusion

The availability of building blocks which arise from the transformation of wastes for modern chemical application represents one of the main research lines nowadays. The necessity to recycle Waste Cooking Oils combined with their specific chemical composition brings to the exploration of new applications in the fields of material science, energy and environmental chemistry. Some early results on these topics have been reviewed and discussed taking in consideration the bibliography of the last five years. Such results represent the starting point for the further development of new technologies.

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