

# The Green Chemistry

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## 1 Introduction and Principles

An early conception of “green chemistry was developed in 1990 by P. Anastos and J. Warner<sup>1</sup> through 12 principles ranging from prevention and atom economy to pollution prevention and an inherently safer chemistry. These principles, described below, offer a protocol to adhere in developing novel chemical processes.

1. **Waste prevention:** by prevent waste production, rather than clean up and treat wastes after having produced. Plan to minimize waste at every process’ stage.
2. **Atom economy:** reduce waste by recycling the number of atoms from all reagents that are incorporated into the final product. Use atom recycling concept in order to evaluate reaction efficiency.
3. **Less hazardous chemical synthesis:** design chemical reactions’ path in order to be as safe as possible. Consider the hazards of all substances handled during each single step of the reaction, including waste.
4. **Designing safer chemicals:** minimize toxicity directly by proper design. Predict and analyze factors such as physical properties, toxicity, and environmental impact of each designed process’ step.
5. **Safer solvents & auxiliaries:** look for the safest solvent available for any given step. Optimize the total amount of solvents and auxiliary substances used in order to minimize the waste produced.
6. **Design for energy efficiency:** find the least energy-intensive chemical route, thus reducing heating and cooling, as well as pressurized and vacuum conditions (i.e. try to stay as close as possible to ambient temperature & pressure).
7. **Use of renewable feedstocks:** use feeds which are made from renewable (i.e. bio-based) sources, rather than other chemicals made from petrochemical products.

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<sup>1</sup> P. T. Anastas, J. C. Warner, The Twelve Principles of Green Chemistry, Oxford Univ. Press, Oxford – UK (1998).

8. **Reduce derivatives:** minimize the use of temporary derivatives such as protecting groups in order to reduce the waste production.
9. **Catalysis:** Look for catalysts that help to increase selectivity, minimize waste, reduce reaction times and increase energy efficiency.
10. **Design for degradation:** design products that can degrade themselves easily into the environment. Ensure that both original and degraded products are not toxic, bio-accumulative, or environmentally persistent.
11. **Real-time pollution prevention:** real time control of chemical reactions to prevent the formation and the release of any potentially hazardous or polluting products into the environment.
12. **Safer chemistry for accident prevention:** developing chemical processes and procedures that are safer to inherently minimize the risk of accidents. Evaluate all the potential risks and assess them beforehand.

Today, more than 98% of all products and materials needed for modern economies is still derived from petroleum and/or natural gas, generating substantial quantities of wastes and emissions.

An exaggerated, but illustrative, view of **twentieth century** chemical manufacturing can be written as a recipe<sup>2</sup>:

- (1) Start with a petroleum-based feedstock.
- (2) Dissolve it in a solvent.
- (3) Add a reagent.
- (4) React to form an intermediate chemical.
- (5) Repeat (2)-(4) several times until the final product is obtained; discard all waste and spent reagent; recycle solvent where economically viable.
- (6) Transport the product worldwide, often for long term storage.
- (7) Release the product into the ecosystem without proper evaluation of its long-term effects.

The recipe for the **twenty-first century** will be very different:

- (1) Design the molecule to have minimal impact on the environment (short residence time, biodegradability).
- (2) Manufacture from a renewable feedstock (e.g. carbohydrate).
- (3) Use a long-life catalyst.
- (4) Use no solvent or a totally recyclable solvent.
- (5) Use the smallest possible number of steps in the synthesis.
- (6) Manufacture the product as required and as close as possible to where it is required.

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<sup>2</sup> Based on: Woodhouse, E. J. Social Reconstruction of a Technoscience? : The Greening of Chemistry.

A typical example of the twentieth century chemical manufacturing production model is represented by plastic materials, which are also a typical example of linear economy: no-renewable resources, oil or ethane in this case, are used to produce plastic materials, which at the end of life become wastes and dispersed into environment. Today, some about 8 million of metric tons escapes into the world's oceans each year<sup>3</sup>, most of it from countries in South East Asia, where plastics use has outpaced waste management infrastructure and the situation is approaching catastrophic proportions.

The green chemistry approach is the correct way to deal with the actual environmental situation, representing a promising strategy of future economic development also for industrialized countries.

Paul Anastas, then of EPA, and John C. Warner developed the Principles of Green Chemistry (Figure 1), which help explain what the definition means in practice. The principles cover such concepts as:

- Designing processes to maximize the amount of raw material that ends up in the product.
- Using safe, environmentally-benign substances, including solvents, whenever possible.
- Designing energy-efficient processes.
- Using the best form of waste disposal: not creating it in the first place.



Figure 1: Principles of Green Chemistry

<sup>3</sup> A.H. Tullo, Fighting ocean plastics at the source. Chem. & Eng. News, 96 (16) (2018) 29-34

The following paragraphs illustrate some very innovative applications of green chemistry in novel chemical plants.

## 2 Applications

### 2.1 Bio-refinery

The utilization of biomass as input raw material in bio refineries make them an example of green chemistry application according to point 7, “*Use of renewable feedstocks*”, given in the previous section.

There exist several definitions of a biorefinery and biorefining. The preference for one over the other depends on context it is used. A definition is formulated by NREL (National Renewable Energy Laboratory): “*A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass.*” It follows that, a biomass upgrading system needs to be included in the bio-refinery plant, otherwise the novel process should not be considered a bio-refinery.

There are two main process pathways: Thermochemical Bio-refinery and Fermentative bio-refinery. The thermochemical bio-refinery is based on gasification units in which biomass is heated up to high temperature and converted into a gas mixture, similar to a syngas, through the use of gasification agent, such as oxygen. The syngas with impurities is then upgraded to valuable fuels or chemicals such as ethanol, methanol and DME (di-methyl-ether) or is used to produce electricity in conventional power plant<sup>4</sup>. In the following process scheme, biomass undergoes gasification and  $H_2$  is separated out of the gasification stream<sup>5</sup>.

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<sup>4</sup> “What is a biorefinery?” T Berntsson, BA Sandén, L Olsson, A Åsblad - 2012 - [publications.lib.chalmers.se](http://publications.lib.chalmers.se)

<sup>5</sup> García, C.A., et al., Stand-alone and biorefinery pathways to produce hydrogen through gasification and dark fermentation using *Pinus Patula*, *Journal of Environmental Management* (2016)

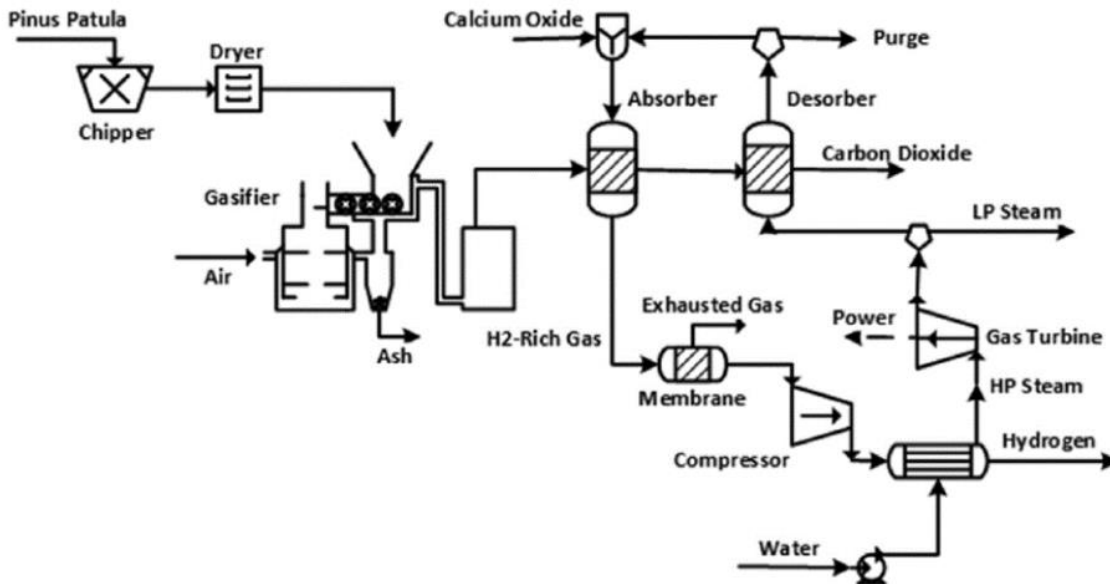


Figure 0-1 Example of a thermochemical bio-refinery. The scheme is divided in two sections: on the left takes place the biomass gasification; on the right purification steps occur to obtain as the main plant output pure hydrogen.

The fermentative bio-refinery is based on the presence of cellular bio reactor in which the monomeric sugar of the biomass is converted in ethanol. Obviously, the biomass should be pre-treated with the following steps before entering in the bio-reactor:

1. **Grinding.** It is necessary to break the cell wall membrane of the biomass and permit the release of all the cell content (carbohydrates for bio-ethanol production, lipids for bio-diesel production).
2. **Hydrolysis.** Starch, lignocellulose or better polymeric carbohydrates and poly-phenolic lignin are not directly fermentable by most yeasts to produce bio-ethanol. According to this, the hydrolysis of such compounds must be carried out in order to obtain fermentable monomeric sugars.
3. **Fermentation** It is the step in which a cell culture, having monomeric sugars as a nutrient source, generate ethanol as a primary metabolite product. Historically, the most commonly applied microbe is the yeast. For example, *saccharomyces cerevisiae*, which can produce ethanol to give concentration as high as 18% of the fermentation broth, is the preferred one for most ethanol fermentation.

All these operations are resumed in the following process scheme:

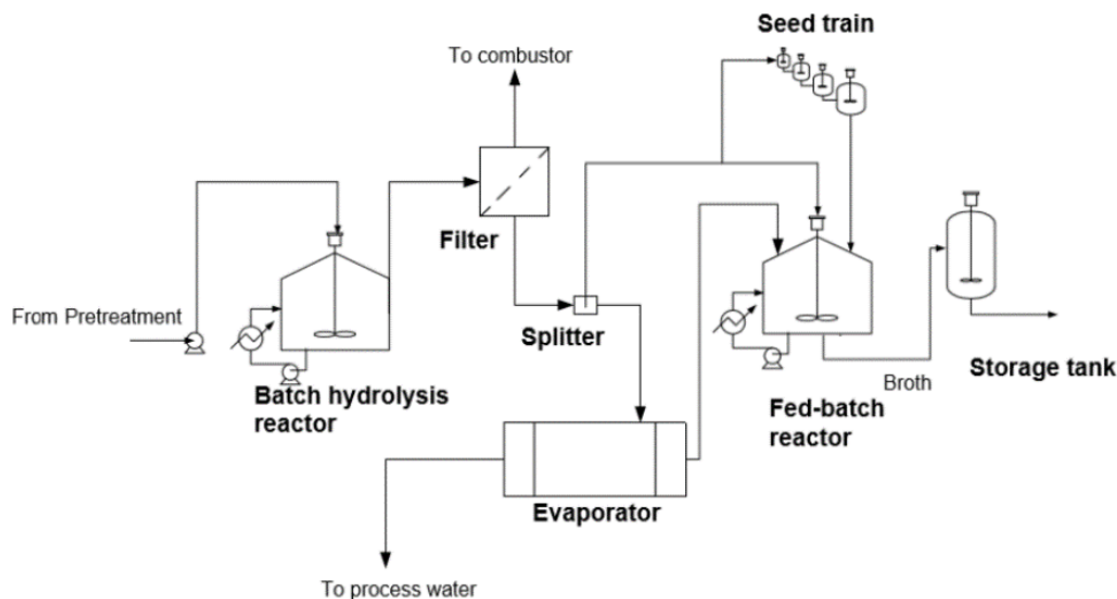


Figure 0-2 Example of a fermentative bio-refinery. In the scheme are represented the hydrolysis and the fermentation bioreactors.

The biomass upgrading fermentation plant produces a diluted ethanol stream which should be distilled and purified (using a vapor-phase molecular sieve adsorption) to reach the purity of ethanol required (99,5% ethanol concentration)<sup>6</sup>.

## 2.2 Plastic depolymerization technologies

The global plastic production has increased from 15 million tons per year in 1964 up to 359 million tons in 2018. Every year, around 8 million tons plastic are released into the oceans, and nowadays, more than 150 million tons are estimated to be accumulated there<sup>7</sup>.

This alarming situation is the result of the mono-use plastic objects: thanks to their low cost, nobody cares of re-use plastic materials and prefers to throw them away. But waste plastic still has a high economic value since it can be reused in many different ways.

Plastic, at the end of its life, can be mechanically recycled, landfilled or incinerated. When not mechanically recycled, plastic waste can be *depolymerized* via *chemical processes* in order to recover the *monomers*. Those *monomers* might be further processed to produce new “*virgin*” plastic.

<sup>6</sup> Davis, R., Kinchin, C., Markham, J., Tan, E., Laurens, L., Sexton, D., Knorr, D., Schoen, P., and Lukas, J. Process Design and Economics for the Conversion of Algal Biomass to Biofuels: Algal Biomass Fractionation to Lipid- and Carbohydrate-Derived Fuel Products. United States: N. p., 2014. Web. doi:10.2172/1159351.

<sup>7</sup> <https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/>

PET (Polyethylene terephthalate) is one of the most widely used polymers all around the world. It consists of polymerized units of the monomer ethylene terephthalate, with repeating units  $C_{10}H_8O_4$ . PET is a thermoplastic resin and because of its transparency, resistance and gas barrier properties it is particularly suitable for the production of bottles for carbonated beverages. The main PET applications are bottles, films, tubes, trays and blisters, containers, labels, etc.

Depolymerization means the polymer plastic conversion process back into its original monomers. PET depolymerization techniques are:

- **Glycolysis.** This method involves the reaction of PET, under pressure and at temperatures in the range 180-240 °C, with an excess of glycol, usually ethylene glycol, which promotes the formation of Bis(2-Hydroxyethyl) terephthalate (BHET). The reaction is described in the picture below<sup>8</sup>.

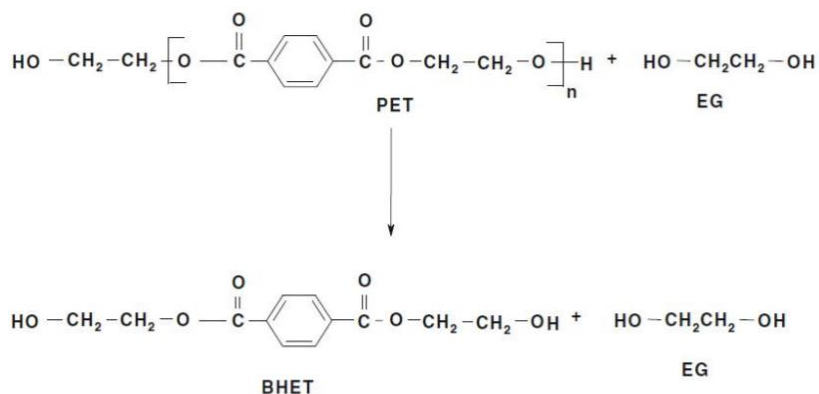


Figure 0-3 Glycolysis reaction of PET for the formation of Bis(2-Hydroxyethyl) terephthalate (BHET).

Because the reaction rate is proportional to the polymer surface, it is advisable to first reduce the size of the raw PET waste to small particles by grinding, cutting, etc.

- **Methanolysis.** PET methanolysis is based on the treatment of PET with methanol at relatively high temperatures (180-280 °C) and pressures (20-40 atm), which leads to the formation of dimethyl terephthalate (DMT) and ethylene glycol (EG) as the main products. The reaction proceeds usually in the presence of typical transesterification catalysts, the most widely used being zinc acetate<sup>9</sup>.

<sup>8</sup> ARVI Theme plastic and rubber, "Report: PET glycolysis". Subtask 4.1.1. 27.1.2017

<sup>9</sup> A.M. Al-Sabagh, F.Z. Yehia, Gh. Eshaq, A.M. Rabie, A.E. ElMetwally, Greener routes for recycling of polyethylene terephthalate, Egyptian Journal of Petroleum, Volume 25, Issue 1, 2016, Pages 53-64, ISSN 1110-0621, <https://doi.org/10.1016/j.ejpe.2015.03.001>.

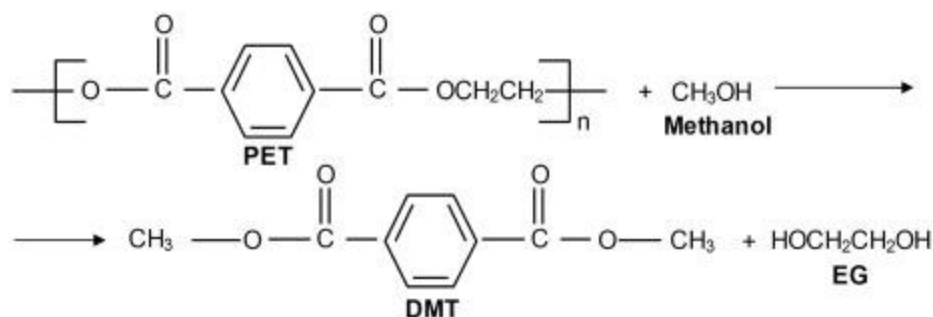


Figure 0-4 Methanolysis reaction of PET for the formation of dimethyl terephthalate (DMT).

- Hydrolysis.** Reaction of PET with water allows the polyester chains to be broken down into terephthalic acid (TA) and monoethylene glycol (MEG). The process can be carried out under neutral, acidic or basic conditions. Several patents have been filed dealing with the acid hydrolysis of PET by reaction with concentrated sulfuric acid (> 14.5 M). The process takes place at temperatures between 25 and 100°C with a duration of just a few minutes at atmospheric pressure.

The alkaline hydrolysis of PET involves treating the polyester with an aqueous solution of sodium hydroxide (4-20 wt%) under pressure at temperatures between 200 and 250°C for periods of several hours. Under these conditions the sodium salt of TA is formed and by acidification TA is recovered from the solution as a precipitate.

Neutral hydrolysis is usually performed under pressure (10-40 atm) at temperatures in the range 200-280°C. Alkali metal acetates are typically used as catalysts to promote PET hydrolysis. The reaction proceeds more slowly than the acid hydrolysis, several hours being required to achieve high PET conversions<sup>10</sup>.

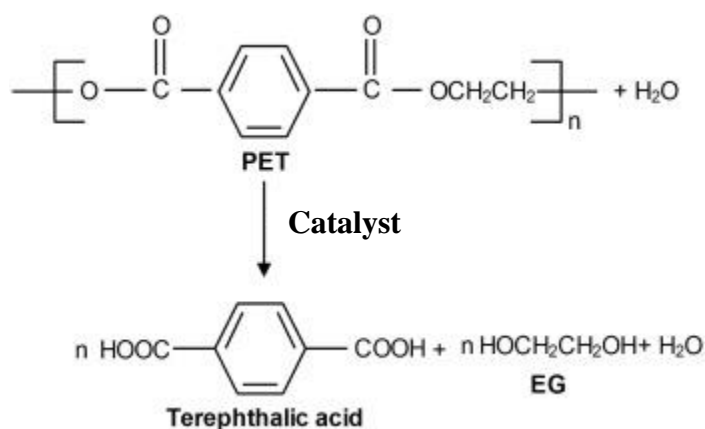


Figure 0-5 Hydrolysis reaction of PET for the formation of terephthalic acid (TA).

<sup>10</sup> A.M. Al-Sabagh, F.Z. Yehia, Gh. Eshaq, A.M. Rabie, A.E. ElMetwally, Greener routes for recycling of polyethylene terephthalate, Egyptian Journal of Petroleum, Volume 25, Issue 1, 2016, Pages 53-64, ISSN 1110-0621, <https://doi.org/10.1016/j.ejpe.2015.03.001>.



### 3 Economics

Green chemistry, as showed in the previous paragraphs, does not apply to a precise definition, whereas it represents an industrial endeavor of reacting to nowadays issues.

All the green chemistry technologies are all based on the reduction of by-products emissions and minimization of output waste streams; for this reason, it is the expansive discipline that is evolving in response to this wide array of challenges and there can be a direct economic benefit in the application of green chemistry principles at the development of new products, since avoiding hazardous or special chemicals handling and deal with by-product management means increased operating costs and decreased revenues.

Taking in consideration three different indicators, i.e. market growth, capital flows and market demand, there has been an impressive upward trajectory in the past eight years. Markets that includes biobased chemicals, green polymers, renewable feedstocks, etc., is believed to increase from \$11 billion in 2015 to about \$100 billion by 2020, as reported in the *Figure 0-1: Market figures trend of green chemistry from 2011 to 2020* in the study elaborated by Pike Research in 2011.

According to the same research, the highest penetration of green chemistry within 2020, will be in the polymer sector

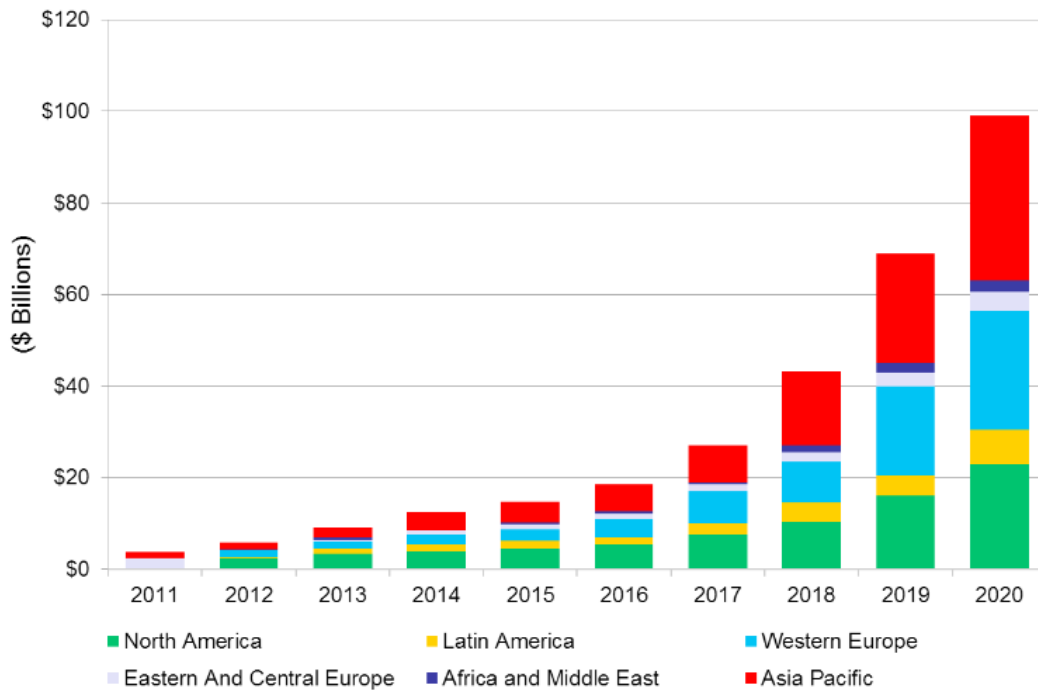


Figure 0-1: Market figures trend of green chemistry from 2011 to 2020

## 4 Conclusion

Two examples of green chemistry applications have been provided. It is believed that green chemistry will represent a winning strategy towards the development of the circular economy.

Green chemistry technologies are widely spreading in different chemical sectors such as biogas production and upgrading, bioethanol production, green catalysis, carbon capture & storage technologies (CCS), algae processing (cultivation, lipid extraction, protein extraction, etc.), plastic recycle technologies, bio-degradable plastic polymers, renewable energy sources, etc. Chemical manufactures, especially oil downstream industries, can develop stronger business advantages for green chemistry by rethinking sustainable marketing approaches.

The path to achieve a green and sustainable society is still long.

Certainly, we will take a few wrong turns along the way, but there is growing agreement on the general way forward. Although science can help move towards an ideal world of zero risk, hazard and pollution, only the society, at large, will ultimately determine what is acceptable in terms of the cost-benefit issues posed by sustainable development<sup>11</sup>.

Although, the modern ideas of sustainable and green chemistry are only around 30 years old, we should not lose sight of the fact that some of the objectives have been pursued for many years. A quote from R. W. Hofmann, the first President of The Royal College of Chemistry, London, made in 1848 is just as relevant today as it was then:

*‘In an ideal chemical factory there is, strictly speaking, no waste but only product. The better a real factory makes use of its waste, the closer it gets to its ideal, the bigger is the profit.’*

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<sup>11</sup> J. Clark and D. Macquarrie, *Handbook of Green Chemistry and Technology*. 2007