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# Tracing oxygen-atom relocation from carbohydrates to renewable chemicals for redox-economic and waste-minimized syntheses

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Small organic molecules bearing oxygen-containing functionalities are key chemical building units in organic chemical manufacturing industries. Biomass-derived carbohydrates are promising feedstocks for synthesizing functionalized organic chemicals with tailored molecular architectures, properties, and functions. The choice and sequence of organic transformations, reagents, synthetic auxiliaries, and other reaction conditions collectively determine the scalability, economic appeal, and environmental sustainability of the synthetic processes. The strategic relocation of oxygen atoms from carbohydrates to renewable chemicals can facilitate the development of redox-economic and waste-minimized synthetic pathways. This review introduces a conceptual framework for tracing the relocation of oxygen atoms from biomolecules to renewable chemicals, providing a quantitative basis for rational synthetic design. The redox economy index (REI), a new green chemistry metric, has been introduced to analyze and evaluate the efficacy of multi-step synthetic pathways of renewable chemicals, where redox steps are used tactically and strategically in constructing their molecular framework.

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## Sustainability spotlight

Tracing the oxygen atoms from sugar molecules in renewable chemicals can be immensely beneficial for designing redox-economic and waste-minimized synthetic routes. Various green metrics help to analyze and evaluate alternative synthetic pathways for their sustainability. This review introduces a new green metric, the Redox Economy Index (REI) which allows monitoring of the oxidation and reduction processes involved in the multi-step synthetic pathway of producing specific organic chemicals. The concept of the REI has been applied to various classes of organic products, including hydrocarbon fuels, solvents, monomers, and chemical intermediates. This work aligns with the following UN Sustainable Development Goals (SDGs): affordable and clean energy (SDG 7), industry, innovation, and infrastructure (SDG 9), responsible consumption and production (SDG 12), and climate action (SDG 13).

## 1. Introduction

The conversion of petroleum into functionalized organic chemicals and synthetic polymers requires several carefully crafted separation, purification, and chemical modification steps.<sup>1</sup> Transforming petroleum-derived hydrocarbon-based bulk chemicals into fine chemicals involves selective oxidation steps that introduce heteroatom-containing functionalities.<sup>2</sup> Although these steps have been made primarily catalytic, they continue to produce significant amounts of deleterious waste in the form of byproducts and side products.<sup>3</sup> A handful of primary petrochemicals derived from petroleum can be transformed into organic molecules that encompass virtually all major classes of commercially significant organic products.<sup>4</sup> Significant advances have been made in synthetic organic chemistry and associated fields (*e.g.*, catalysis and medicinal chemistry) over the past century, utilizing petroleum as the

primary feedstock.<sup>5</sup> However, green chemistry and sustainable synthetic practices can only extend the timeline of using petroleum, an exhaustible resource, in producing liquid fuels, organic chemicals, and synthetic polymers. At this critical juncture, when the organic chemical manufacturing industry is yearning for environmental sustainability and a circular carbon economy, alternative carbon-based feedstocks must be realized.<sup>6,7</sup> Biomass, especially the land-based and aquatic non-food vegetative biomass, has received particular attention in this regard.<sup>8</sup> Biomass is geographically diverse, renewable, available in bulk, and often part of many waste streams (*e.g.*, food waste, crop residues, forestry waste, and agro-industrial byproducts).<sup>9</sup> Among the various biomolecules, carbohydrates have received considerable interest because 50–70% (on a dry mass basis) of most biomasses contain carbohydrates, their structures are relatively homogeneous, and their derivative chemistry is relatively well-documented.<sup>10</sup> Carbohydrates are densely functionalized, heavily oxygenated, and possess straight-chain carbon skeletal systems that carry carbon atoms in diverse oxidation states.<sup>11</sup> Therefore, they are attractive feedstocks for the

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sustainable production of functionalized organic molecules using redox-economic synthetic pathways. The value-addition strategies of carbohydrates can benefit from the enormous information and expertise achieved in synthetic organic chemistry and petrorefinery processes.<sup>12</sup> Analogous to the petrorefinery setting, the biorefinery processes would require an initial separation and purification of carbohydrates from other biomolecules.<sup>13,14</sup> For example, cellulose and hemicellulose must be separated from extractives (*e.g.*, fats) and other biopolymers (*e.g.*, lignin) present in the lignocellulosic biomasses. In a carbohydrate-centric biorefinery setting, emphasis is given to the separation of carbohydrates (*i.e.*, cellulose and hemicellulose) in their native structure or transformed into the desired platform chemicals.<sup>15,16</sup> In this setting, carbohydrates are used as the primary feedstock to generate revenue, and attempts are made to maximize their utilization even at the expense of other biomass components. Carbohydrates can be transformed into a host of materials and polymers through selective modifications of the native biopolymer. Examples include cellulose acetates, alkylated cellulose, and various cellulose-based fibres.<sup>17</sup> However, the transformation of cellulose and other polymeric carbohydrates into small organic molecules requires significant chemical intervention, including a depolymerization step. The depolymerization step breaks down the polymeric carbohydrates into constituent monomers or small organic molecules, which are more amenable to downstream chemical modifications.<sup>18</sup> For example, cellulose is depolymerized into glucose through acid hydrolysis or enzymatic saccharification. Analogously, hemicellulose is depolymerized into pentose and hexose sugars. Defunctionalization steps remove excess and undesired oxygen-containing functionalities from biomolecules, converting them into chemical building blocks and reactive intermediates for downstream synthetic value-addition pathways.<sup>19</sup> Dehydration is a frequently used non-redox strategy to reduce the oxygen content in biomolecules and form the desired renewable chemical

intermediates.<sup>20</sup> Dehydration is an endothermic reaction that is promoted at elevated temperatures and under acid catalysis. The C(sp<sup>3</sup>)-OH bond strength is around 90 kcal mol<sup>-1</sup>, which decreases by around 20 kcal mol<sup>-1</sup> upon protonation. The dehydration reaction preserves the biogenic carbon atoms in the product and produces water as an innocuous byproduct.<sup>21</sup> Refunctionalization steps introduce new functionalities or chemically modify the existing functionalities (*i.e.*, functional group transformations) and rearrangement reactions.<sup>22,23</sup> The rearrangement steps involve carbon-carbon bond-making or bond-breaking reactions that restructure the carbon skeletal system of biomolecules or the chemical intermediates derived from them into the targeted organic products (Fig. 1). They also involve modifying the skeletal framework of biomolecules into the desired one (*e.g.*, a heterocycle into a carbocycle).<sup>24,25</sup>

This review discusses the renewable synthesis of selected chemicals with oxygen-containing functionalities from carbohydrates, utilizing a novel strategy that tracks the oxygen atoms in these compounds during the synthetic transformations. Such analysis enables the evaluation of competitive synthetic routes for specific molecules based on their redox economy. Representative examples of the major classes of organic compounds based on their applications, such as hydrocarbon fuels, fuel oxygenates, solvents, and monomers, have been selected and discussed. A new green chemistry metric, coined as the Redox Economy Index (**REI**), has been introduced to quantify the relative advantages and shortcomings of competitive synthetic routes and analyze the scope of developing more efficient synthetic routes. A lower **REI** for the synthetic process indicates a better redox economy and reduced waste production. The initial stage of development requires a high degree of design freedom, and green metrics, such as the **REI**, are crucial for making an informed decision at the early stages of process development with a high level of design freedom.<sup>26</sup> The tracing of oxygen atoms from the starting sugars to the renewable chemical products through the synthetic route combined with

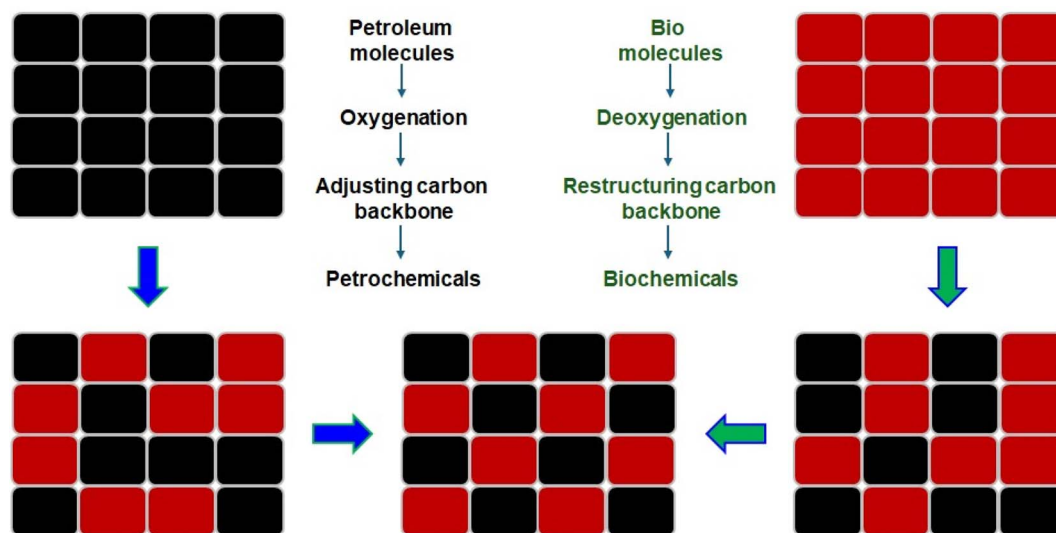


Fig. 1 Steps of synthesizing functionalized organic chemicals from anthropogenic and biogenic carbon-based feedstocks.



the REI would help to justify the choice of redox transformations and help minimize waste formation. When the REI is combined with other green chemistry metrics, it can assist in choosing the most efficient synthetic strategy for renewable organic chemicals.

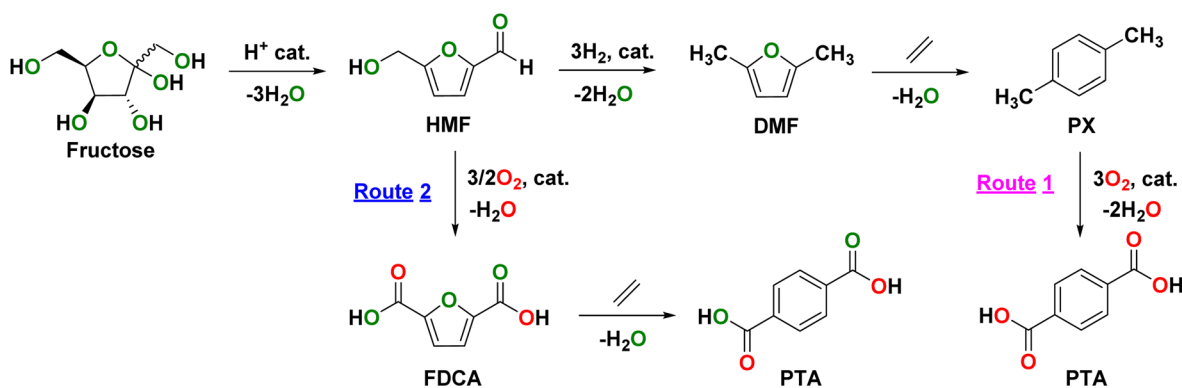
## 2. Synthesis of purified terephthalic acid (PTA)

Transformation of hexose sugars (*e.g.*, glucose) into 5-(hydroxymethyl)furfural (HMF) is a well-documented example of the defunctionalization of biomolecules through dehydration reactions.<sup>27</sup> Analogously, pentose sugars, such as xylose, can be dehydrated into furfural (FF).<sup>28</sup> Attempts have been made to produce these platform chemicals directly from lignocellulosic biomasses, eliminating the requirements for prior separation, purification, and depolymerization steps and ensuring a better pot- and step-economy.<sup>29,30</sup> The processes are elegant from several perspectives. The furanic products retain all the biogenic carbon atoms in the parent sugar molecule. The oxygen content in the sugar molecule is significantly reduced (50–60%) in the product while preserving some key functionalities. Moreover, the straight-chain carbon skeletal system of the sugar molecule is transformed into a heteroaromatic moiety (*i.e.*, furan). FF and HMF are furanic platform chemicals that can be synthetically transformed into a vast array of commercially relevant organic molecules.<sup>31</sup> Understanding the reactivity patterns of these molecules is crucial for improving existing synthetic processes and expanding the chemistry of their derivatives.<sup>32</sup>

Polyethylene terephthalate (PET) is a high-volume thermoplastic used to manufacture containers for beverages and as a synthetic fiber for clothing.<sup>33</sup> The petroleum route for making PET utilizes ethylene and *p*-xylene (PX) as the building blocks. Ethylene, primarily produced during the catalytic cracking of heavy oil, is catalytically oxidized to ethylene oxide (EO), which

is then hydrolyzed into ethylene glycol (EG).<sup>34</sup> Xylenes are produced during the reforming of naphtha or methylation of toluene, which is then purified to isolate PX.<sup>35</sup> Specially designed zeolite catalysts with a tailored pore structure favor the equilibrium towards PX.<sup>36</sup> PX is then catalytically oxidized into purified terephthalic acid (PTA) using oxygen as the terminal oxidant.<sup>37</sup> Therefore, the process involves several synthetic steps and the associated purification processes. Even with the best sustainable practices in place, this process remains unsustainable in the long run since petroleum is a non-renewable feedstock.<sup>38</sup> Therefore, serious deliberations have been made to identify a sustainable feedstock for producing PET or its functional substitutes. Biomass-derived carbohydrates have been identified as a renewable and commercially viable feedstock for producing PET. The process begins with HMF, which is produced from sugars or directly from polymeric carbohydrates. HMF is then catalytically reduced to 2,5-dimethylfuran (DMF).<sup>39</sup> Finally, DMF is reacted with ethylene by the Diels–Alder reaction, and the adduct is subjected to dehydrative aromatization in the presence of a suitable Lewis acid catalyst to form PX (Scheme 1).<sup>40,41</sup>

Ethylene can be produced renewably through the dehydration of bioethanol. The predisposition of the two methyl groups in DMF allows PX to be produced exclusively, thereby avoiding intricate separation and purification processes.<sup>42</sup> The reaction affords excellent selectivity and isolated yields of PX under optimized conditions. However, the process is not redox-economic since the HMF to DMF transformation requires three moles of hydrogen. PX must then be catalytically oxidized into PTA using the existing methodology. The redox economy of the processes can be analyzed and evaluated by combining the number of hydrogen atoms or oxygen atoms introduced in renewable chemicals through redox steps. Route 2 involves oxidizing HMF into 2,5-furandicarboxylic acid (FDCA).<sup>43,44</sup> FDCA is then reacted with ethylene, followed by dehydrative aromatization of the Diels–Alder adduct into PTA.<sup>45</sup> A lower REI



Number of hydrogen atoms required for redox steps = X  
 Number of oxygen atoms required for redox steps = Y  
**REI of Route 1: X + Y = 6 + 6 = 12**  
**REI of Route 2: X + Y = 0 + 3 = 3**

Scheme 1 Redox economy index of the synthetic strategies for the biorenewable production of terephthalic acid.



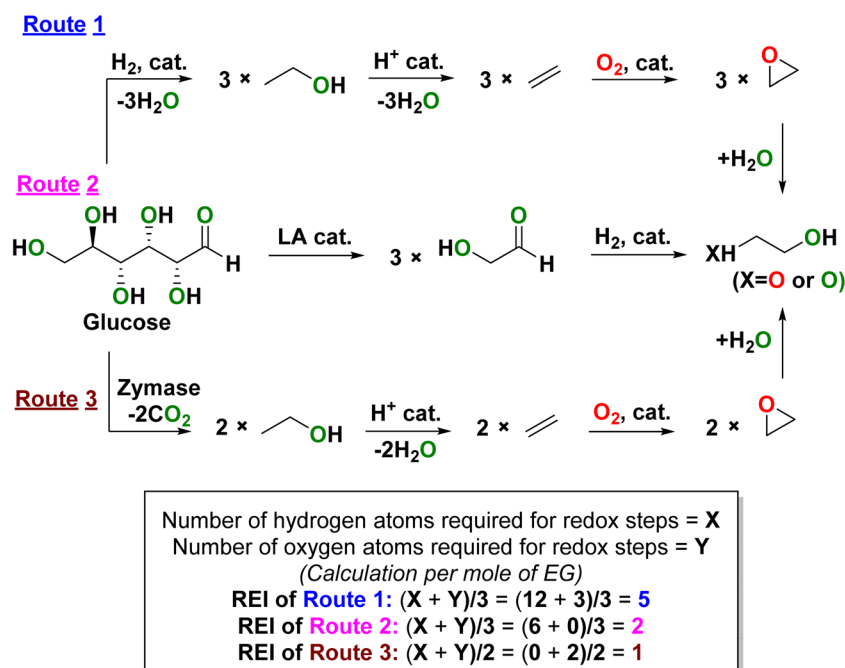
signifies a better redox economy and optimized transposition of oxygen atoms from biomolecules into the targeted renewable chemical. EG required for the process can be produced from bioethanol through the ethylene route. As shown in Scheme 1, the **REI** of PTA synthesis by Route 1 is twelve, whereas the **REI** is only three in Route 2. The reason for such a stark difference in **REI** is apparent from the redox interventions in the synthetic pathways. In Route 1, the carbon atoms in the substituents of the furan ring are in the intermediate oxidation states. The functional groups on HMF are first reduced to methyl groups to form DMF, which is then transformed into PX. The methyl groups in PX are then again oxidized to the carboxylic acid functionality to produce PTA. In Route 2, the hydroxymethyl and aldehyde groups on HMF are oxidized to carboxylic acid groups, and no hydrogenation step is required to form PTA.

### 3. Production of ethylene glycol (EG)

EG is a crucial chemical intermediate for producing value-added chemicals and formulations, and is used as a monomer for high-volume homopolymers and copolymers (*e.g.*, PEG and PET).<sup>34</sup> The petroleum route for producing EG begins with ethylene, which is produced during the catalytic cracking of paraffins. Ethylene is then purified and catalytically oxidized into EO.<sup>46–48</sup> Finally, EO is hydrolyzed in a significant excess of water (to prevent the formation of oligomers) to form EG. The global market value of EG is nearly 34 billion USD, which is expected to rise with a respectable compound annual growth rate (CAGR) over the next decade.<sup>49</sup> EG can be produced renewably from sugars and carbohydrates following various alternative pathways. Bioethanol is presently produced by a fermentative route using zymase as an enzyme.<sup>50</sup> Glucose or

cellulose can be transformed into bioethanol by the well-documented fermentative pathway. Bioethanol can then be dehydrated into bioethylene through an acid-promoted intramolecular dehydration reaction, which can subsequently be transformed into EG following the established petrorefinery pathway.<sup>51</sup> Redox economy of the renewable production routes of EG is depicted in Scheme 2. The **REI** for the bioethanol route through the fermentative pathway (Route 3) is calculated as one per mole of EG. If bioethanol is produced by the chemical-catalytic route, then the index for EG synthesis increases to 5 (Route 1).<sup>52</sup> Production of EG *via* the hydrogenation of glucose-derived glycolaldehyde is calculated as two (Route 2).<sup>53</sup> Therefore, Route 3 is the most redox-economic and waste-minimized route for EG production. However, other green metrics must also be taken into consideration for more informed decisions at the initial stages of technological development.<sup>54</sup> Route 3 loses one-third of the biogenic carbon atoms in glucose as CO<sub>2</sub>, resulting in only two moles of bioethanol for every mole of glucose, unlike the other two routes, where all the biogenic carbon atoms are converted into bioethanol. The oxygen atoms in the feedstock, intermediates, and product have been color-coded to enhance clarity of the redox steps. The oxygen atoms of the biomolecules preserved in the product are shown in green, whereas those introduced by oxidation reactions have been colored red.

Interestingly, the redox metric in Route 1 is 5, whereas that of Route 3 is only 1. The higher value of the **REI** in Route 1 compared to Route 3 is because more moles of hydrogen are required to retain all the biogenic carbon atoms in glucose during conversion into bioethanol in Route 1. Route 2 forms three moles of glycolaldehyde by the retro-aldol reaction of glucose, which, on catalytic hydrogenation, forms EG. In this



Scheme 2 Renewable production routes for ethylene glycol and their comparison using redox economy.



route, the redox metric is two for every mole of EG produced, and the oxygen atoms in EG are those of the glucose molecule.

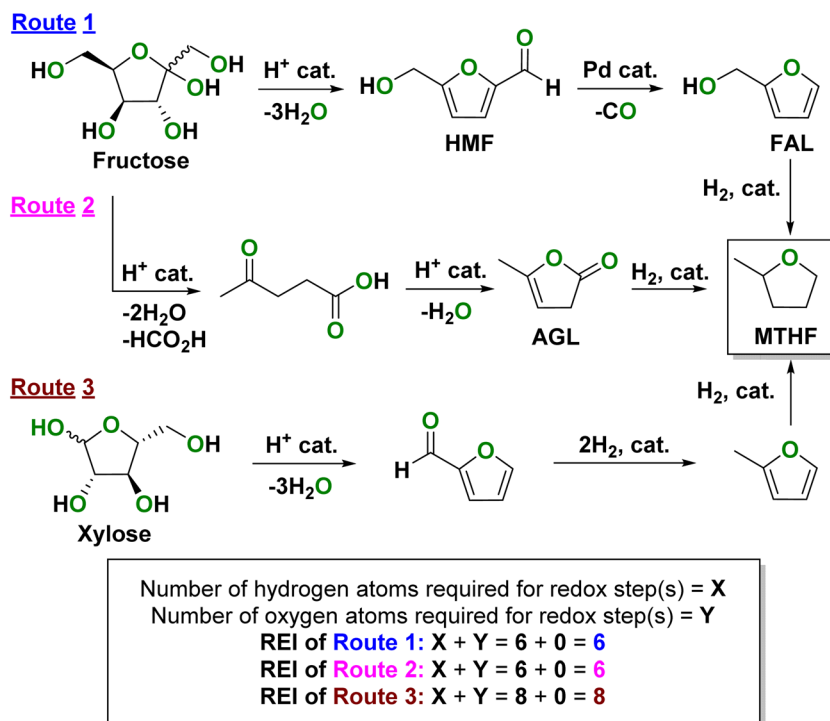
## 4. Production of 2-methyltetrahydrofuran (MTHF)

2-Methyltetrahydrofuran (MTHF) is typically prepared by the catalytic hydrogenation of hemicellulose-derived FF.<sup>55</sup> MTHF is a promising biorenewable solvent (greener alternative to THF) and fuel oxygenate.<sup>56,57</sup> The applications of MTHF as a sustainable solvent are steadily increasing and its market potential as a substitute of petroleum-derived THF is enormous. Scheme 3 analyzes and evaluates the three synthetic pathways commonly followed for producing MTHF from sugars. In Route 1, hexose sugars like fructose (or glucose) are first dehydrated into HMF. HMF can be catalytically decarbonylated into FAL. Finally, FAL is catalytically hydrogenated into MTHF. Only the third step involves the use of molecular H<sub>2</sub>, which includes both hydrogenolysis of the C–OH bond and hydrogenation of the furan ring.<sup>58</sup> In Route 2, sugar-derived LA is used as the starting material. The intramolecular dehydrative lactonization of LA leads to angelica lactones (AGLs).<sup>59</sup> AGLs can also be produced from FAL *via* rehydration and rearrangement reactions that involve cleavage of the furan ring.<sup>60</sup> AGLs are a mixture of three positional isomers based on the position of the olefinic group, and  $\alpha$ -AGL is usually present as the major component.<sup>61</sup> Finally, the catalytic hydrogenation of  $\alpha$ -AGL yields MTHF. In both Route 1 and Route 2, a C–C bond–cleavage reaction is involved, since a C5 product is derived from C6 substrates. One carbon atom is lost as CO during the decarbonylation of HMF in Route

1, whereas one carbon atom is lost as FA during the production of LA in Route 2. In Route 3, pentose sugars (*e.g.*, xylose) can be dehydrated into FF. FF is then catalytically hydrogenated selectively into MTHF, where furanic intermediates like FAL and 2-methylfuran (MFU) are transient intermediates.<sup>62</sup> This pathway does not involve a C–C bond–cleavage reaction.

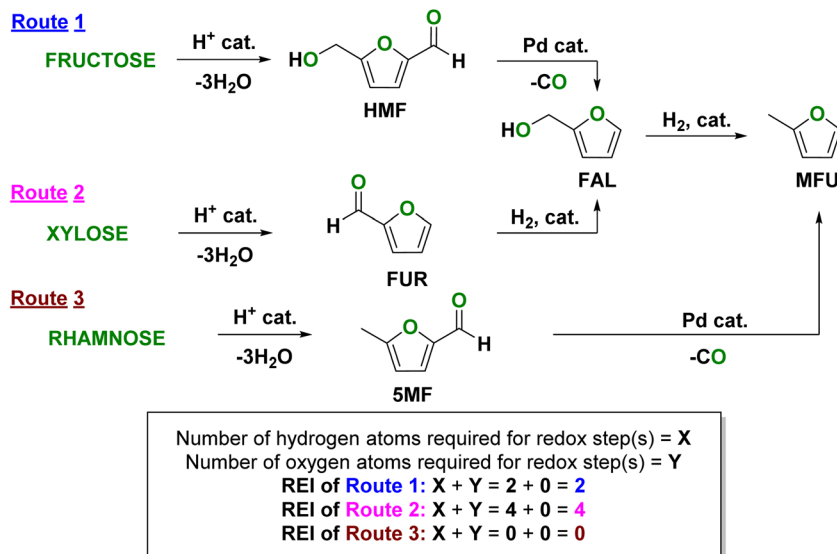
## 5. Synthesis of 2-methylfuran (MFU)

MFU has potential applications as a fuel oxygenate, but it is more important as a renewable chemical intermediate for downstream value-addition pathways.<sup>63</sup> For example, MFU can be hydrogenated into MTHF for use as a renewable cyclic ether-based industrial solvent, and also a promising fuel oxygenate.<sup>64</sup> The Diels–Alder reaction between MFU and ethylene, followed by the dehydrative aromatization of the oxanorbornene intermediate, leads to toluene.<sup>65</sup> The use of propylene as the coupling partner results in the formation of *ortho* and *meta*-xylenes.<sup>66</sup> MFU is used as a coupling partner with suitable biogenic carbonyl compounds (*e.g.*, butanal and acetone) in the Friedel–Crafts reaction, which leads to fuel precursors with an extended carbon chain length and framework. Complete hydrodeoxygenation of these fuel precursors can lead to jet- and diesel-range hydrocarbon-based liquid fuels.<sup>67</sup> Scheme 4 illustrates various pathways for synthesizing MFU starting from different furanic platform chemicals. In Route 1, hexose sugar-derived HMF is used as the starting material. HMF is catalytically decarbonylated into FAL, which is then subjected to a selective hydrogenolysis reaction of the C–OH bond to form MFU.<sup>68</sup> In Route 2, pentosan-derived FF can be used as the



Scheme 3 Redox-economic renewable synthesis of 2-methyltetrahydrofuran as a potential industrial solvent and fuel oxygenate.





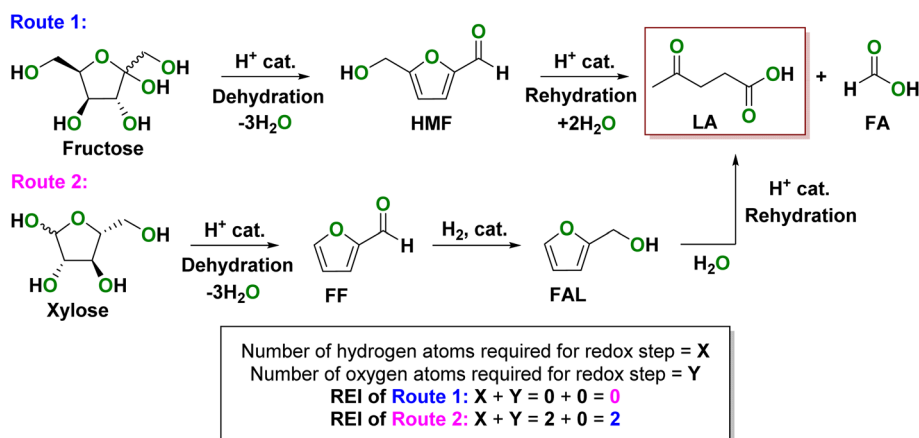
Scheme 4 Alternative synthetic routes for 2-methylfuran with their redox economy index.

starting material. FF is catalytically reduced to MFU, going through the same FAL intermediate. The REI in Route 2 is predictably higher than that in Route 1 since FAL is the intermediate in the former route. In Route 3, the starting material can be 5-methylfurfural (5MF). 5MF is typically produced by the partial reduction of HMF.<sup>69</sup> However, it can also be made directly by the acid-promoted dehydration of specific sugars, such as L-rhamnose.<sup>70</sup> The catalytic decarbonylation of 5MF can then lead to MFU. In terms of the REI, Route 3 is most favored since no hydrogen is required for the entire transformation.

## 6. Synthesis of levulinic acid (LA)

HMF can be subjected to rehydration followed by the ring-opening rearrangement to form LA and an equivalent amount of formic acid (FA).<sup>71,72</sup> LA is at the forefront of the carbohydrate-centric biorefinery movement, serving as a crucial chemical building block. The two reactive functional groups in LA,

namely ketone and carboxylic acid, can be employed individually or in combination to form a wide range of derivatives of commercial significance.<sup>73</sup> The derivative chemistry of LA is complementary to that sourced from the furanic platform chemicals.<sup>74</sup> The three oxygen atoms in LA originate from glucose, and the overall process does not involve any redox step. LA can also be produced from pentose sugars, such as xylose. Pentose sugar-derived FF is partially hydrogenated into furfuryl alcohol (FAL), which is then hydrolyzed into LA (Scheme 5).<sup>60</sup> The REI is higher for this process due to the hydrogenation step, but it does not form any byproducts containing carbon atoms. However, the choice of the most favored route is governed by a combination of other parameters. Polymeric carbohydrates containing hexose sugars (*e.g.*, cellulose, chitin, and starch) are more abundant and inexpensive than pentosans. On the other hand, the high-yielding production and purification of HMF remains challenging even after decades of research.<sup>75</sup> Therefore, the production of LA should be attempted without isolating the



Scheme 5 Comparison of the production strategies of levulinic acid by dehydrating hexose and pentose sugars.



HMF intermediate.<sup>76</sup> Pentose sugars are mainly obtained from the hemicellulose component of the lignocellulosic biomass, which is less abundant and more expensive. However, FF is more stable and easier to isolate from an aqueous reaction mixture than HMF.<sup>77</sup>

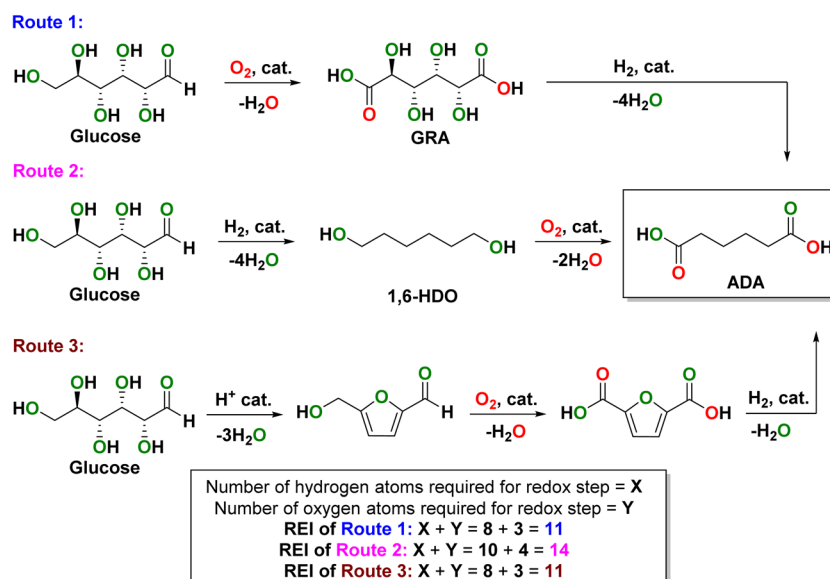
## 7. Synthesis of adipic acid (ADA)

Adipic acid (ADA) and 1,6-hexamethylenediamine (HMDA) are the monomers of nylon-6,6, a high-volume synthetic thermoplastic.<sup>78</sup> ADA is produced by the oxidation of a cyclohexanone-cyclohexanol mixture, called KA oil.<sup>79,80</sup> The world production of ADA is around 2.6 million metric tons (MMT) with a market value of 5 billion USD.<sup>81</sup> Therefore, significant interest has been shown in producing adipic acid (ADA) renewably from biogenic carbon.<sup>82</sup> Glucose has been selected as an abundant and inexpensive feedstock for the sustainable production of ADA from economic and environmental perspectives.<sup>83</sup> Glucose can be produced by depolymerizing polymeric carbohydrates, such as starch and cellulose.<sup>84</sup> The transformation of glucose, a C6 starting material, into ADA would not require any carbon-carbon bond-forming or bond-cleavage reactions. The transformation would require the oxidation of the terminal carbon atoms into carboxylic acids, whereas the carbon atoms in between must be reduced into methylene groups. According to the balanced chemical equation for transforming glucose into ADA, it is a reduction reaction that requires one mole of H<sub>2</sub> for every mole of glucose. Moreover, the transformation involves extensive redistribution of the oxidation states of carbon atoms in glucose. Scheme 6 illustrates three major pathways for producing ADA from glucose through chemical-catalytic processes. In Route 1, glucose is selectively oxidized into gluconic acid (GRA), where the terminal carbon atoms are transformed into carboxylic acid without affecting the oxidation states of the internal carbon atoms.<sup>85</sup> GRA is then selectively

reduced under catalytic hydrogenation conditions to form ADA.<sup>86</sup> Four moles of H<sub>2</sub> are required to reduce GRA into ADA, coproducing four moles of water as the byproduct. The REI of Route 1 has been calculated to be 11. In Route 2, glucose is first reduced to 1,6-hexanediol (1,6-HDO).<sup>87</sup> The primary alcohol groups (attached to the terminal carbon atoms) in 1,6-HDO are then oxidized to form the carboxylic acid functionality, resulting in ADA.<sup>88</sup> The REI of Route 2 is higher than that of Route 1, as the aldehyde carbon in glucose is initially reduced and then reoxidized in the latter route. In Route 3, glucose is dehydrated into HMF under acid catalysis. HMF is then catalytically oxidized into FDCA.<sup>89</sup> Finally, the furan ring in FDCA is catalytically reduced without affecting the carboxylic acid functionalities, forming ADA.<sup>90,91</sup> The REI of Route 3 is the same as that of Route 1. Although Route 3 involves three distinct synthetic steps, the first two steps can be performed in a single pot. The relative ease of producing and purifying the intermediates in the three routes is not taken into consideration. The chemical intermediates in all three routes have distinct advantages and challenges during their preparation and purification. The renewable synthesis of ADA has also been attempted using novel routes, such as the reduction-carbonylation of 2-furoic acid.<sup>92</sup>

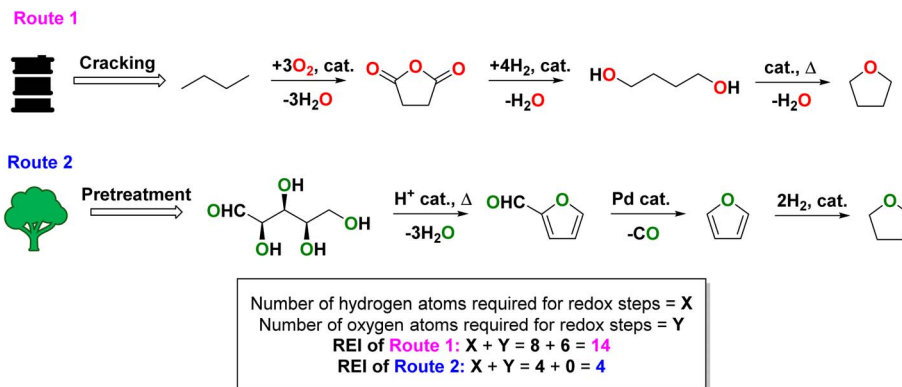
## 8. Synthesis of tetrahydrofuran (THF)

Tetrahydrofuran (THF) is a high-volume industrial solvent and a precursor of polymers. Approximately 1–1.4 MMT of THF are produced worldwide with a market valuation of around 5 billion USD, with BASF, Germany, being the largest single producer.<sup>93</sup> The synthetic route to THF from petroleum begins with *n*-butane, which is produced by cracking paraffins. *n*-Butane is catalytically oxidized to maleic anhydride (MAN). MAN is catalytically hydrogenated into 1,4-butanediol (1,4-BDO). Finally, the intramolecular dehydration reaction of 1,4-BDO leads to



Scheme 6 Comparative analysis of the biorenewable synthesis of adipic acid from sugars using the redox economy.





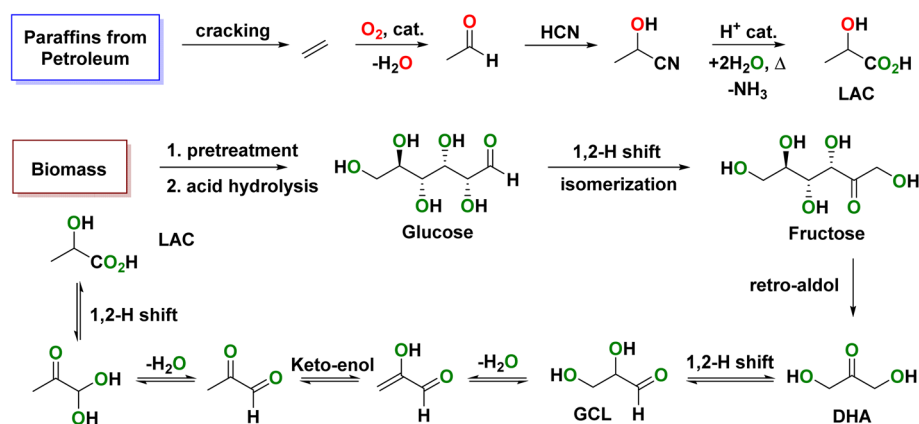
Scheme 7 Synthesis of tetrahydrofuran, an industrial solvent, from anthropogenic and biogenic feedstocks.

THF.<sup>94</sup> The process requires three moles of O<sub>2</sub> and five moles of H<sub>2</sub> for every mole of THF produced (Scheme 7). The oxygen atom in THF originates from the oxidant (*i.e.*, O<sub>2</sub>). Another route for producing THF from anthropogenic feedstock involves reacting acetylene with two moles of formaldehyde. The intermediate is then reduced to 1,4-BDO, which is then dehydrated into THF. However, the acetylene route has been largely superseded by the *n*-butane route. Over the past few decades, significant interest has been shown in sourcing THF from sustainable biogenic carbon. One important route starts with FF, a C<sub>5</sub> furanic platform chemical produced by the acid-catalyzed dehydration of pentose sugars (*e.g.*, xylose and arabinose) in hemicellulose. FF is decarbonylated at elevated temperatures in the presence of a suitable metal-based catalyst (*e.g.*, Pd) to form furan.<sup>95</sup> Finally, furan is catalytically hydrogenated into THF. The process avoids the catalytic oxidation step and uses fewer equivalents of H<sub>2</sub> compared to the *n*-butane route. Therefore, the REI is significantly lower in the FF route of synthesizing THF compared to the *n*-butane route, indicating greener synthetic transformations in the former route.

## 9. Synthesis of lactic acid (LAC)

Lactic acid (LAC) can be produced from acetaldehyde by reacting it with HCN, followed by hydrolyzing the resulting

cyanohydrin intermediate.<sup>96</sup> Acetaldehyde is produced by the selective oxidation of ethylene using metal salt-based catalysts. In addition to being a chemical building block, LAC is a promising monomer for producing high-performance, biodegradable polymers, such as poly(lactic acid) (PLA).<sup>97</sup> However, producing PLA from petroleum, an anthropogenic and non-renewable resource, using toxic reagents such as HCN, is counterintuitive from a sustainability perspective. Currently, more than 90% of LAC is produced from biogenic carbon *via* the fermentative pathway.<sup>98</sup> Nonetheless, there is vast scope for producing LAC from carbohydrates following the chemical-catalytic pathway.<sup>99</sup> Catalyst systems and reaction conditions are being optimized to produce LAC with the desired selectivity and yield, starting from inexpensive and abundant feedstocks, which can economically compete with the enzymatic route. Scheme 8 illustrates the mechanistic pathway of producing LAC from glucose, which is catalyzed by acid or base catalysts. In the first step, glucose is isomerized into fructose by a 1,2-hydrate shift. Fructose is then transformed into glyceraldehyde (GCL) and 1,3-dihydroxyacetone (DHA) in equimolar quantities by a retro-aldol reaction involving the cleavage of the C<sub>3</sub>–C<sub>4</sub> bond. Dehydration of GCL followed by rearrangement leads to pyruvaldehyde. Finally, the hydration of pyruvaldehyde is followed by a 1,2-hydrate shift, leading to LAC.<sup>100</sup> An acidic medium often leads to cyclic lactide and oligomerization of LAC under the reaction conditions.



Scheme 8 Synthesis of lactic acid from anthropogenic and biogenic carbon.



Under alkaline conditions, LAC remains in the form of lactate. Protonation of lactate leads to the formation of LAC, accompanied by the coproduction of a salt stream. As evident, the catalytic transformation of glucose into two molecules of LAC is an isohypsic reaction (a redox-neutral process).

## 10. Synthesis of $\gamma$ -butyrolactone (GBL)

$\gamma$ -Butyrolactone (GBL) is a polar, non-protic industrial solvent that also serves as a chemical intermediate in the production of other solvents, such as *N*-methyl-2-pyrrolidone (NMP).<sup>101</sup> In the petroleum pathway, *n*-butane is catalytically oxidized into MAN, which is then selectively reduced by catalytic hydrogenation into GBL.<sup>102,103</sup> In the biomass pathway, carbohydrate-derived FF can serve as the starting material for GBL, where MAN acts as an intermediate. Alternatively, FF can be selectively oxidized into 2(5*H*)-furanone (2FN), which is then hydrogenated into GBL.<sup>104</sup> The pathway *via* 2FN is more redox economic than the one passing through MAN as the oxidized intermediate (Scheme 9). Moreover, the hydrogenation of MAN into GBL is relatively more challenging, requiring specific metal-based catalysts, high overpressure of molecular H<sub>2</sub>, and elevated temperature. On the other hand, the conversion of 2FN into GBL involves the hydrogenation of an olefin, which can be performed under near ambient temperature and pressure conditions. However, 2FN must be isolated from the reaction mixture during the oxidation of FF to avoid deep oxidation. A biphasic reaction mixture, a specific acid catalyst, and milder reaction conditions are typically employed to ensure a good selectivity and yield of 2FN during the oxidation of FF.<sup>105</sup>

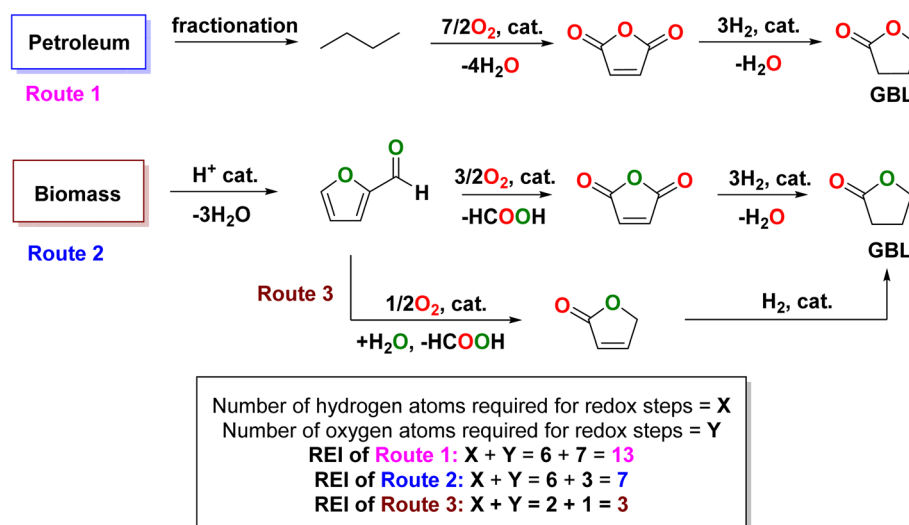
## 11. Synthesis of acrylic acid (ACA)

Acrylic acid (ACA) is one of the high-volume monomers used in the synthesis of polyacrylates, which are utilized in various

chemical manufacturing industries.<sup>106</sup> The market value of ACA is over 10 billion USD for its roughly 8 MMT of annual production worldwide.<sup>107</sup> The petroleum-derived ACA production starts with propylene, a C3 platform chemical produced by cracking. Propylene is catalytically oxidized by O<sub>2</sub> into acrolein, which serves as an intermediate in the process of synthesizing ACA.<sup>108</sup> In the biogenic route, the starting point can be glucose derived from cellulose. Glucose-derived LAC can be catalytically dehydrated into ACA, which opens up the possibility of accessing the large acrylate market in a biorefinery setting.<sup>109,110</sup> Alternatively, glucose-derived LA can be oxidized into 3-hydroxypropionic acid (3-HPA) by aqueous H<sub>2</sub>O<sub>2</sub> in an alkaline medium. Acid-promoted dehydration of 3-HPA can lead to ACA.<sup>111</sup> Novel, promising renewable synthetic routes of ACA have also been proposed.<sup>112</sup> As depicted in Scheme 10, the petroleum route of producing ACA through propylene (Route 1) has a REI of three since oxidation steps are involved. Interestingly, the REI is zero in Route 2, as no oxidation or reduction steps involving external oxidizing or reducing agents are involved. Route 3 has an REI of one since the intermediate 3-HPA must be produced *via* the oxidation of LA using chemical or enzymatic catalysis, where one mole of O<sub>2</sub> is required for producing two moles of 3-HPA.

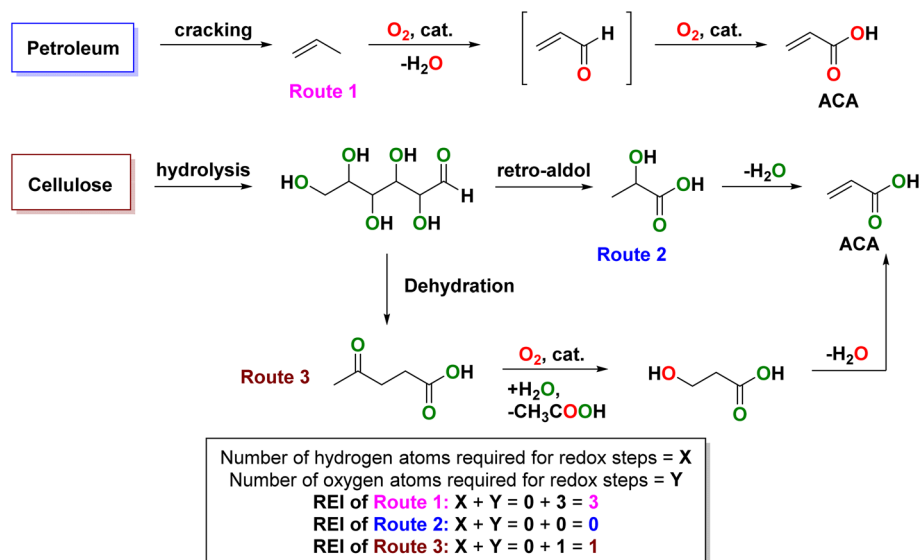
## 12. Synthesis of cyclopentanone

The synthesis of carbocyclic compounds from sugars has garnered considerable interest over the past decade, enabling access to a broader class of organic compounds of commercial value.<sup>113</sup> Sugars are typically converted into heterocycles (*e.g.*, furanics) or straight-chain compounds (*e.g.*, LA). Converting these heterocycles or straight-chain intermediates into carbocycles requires condensation, cyclization, and rearrangement reactions involving C–C bond-forming steps.<sup>114</sup> Cyclopentanone (CPN), a critical carbocycle used in synthesizing high-value compounds, is produced from petroleum-derived cyclohexane.



Scheme 9 Petroleum- and biomass-derived synthetic routes of GBL.



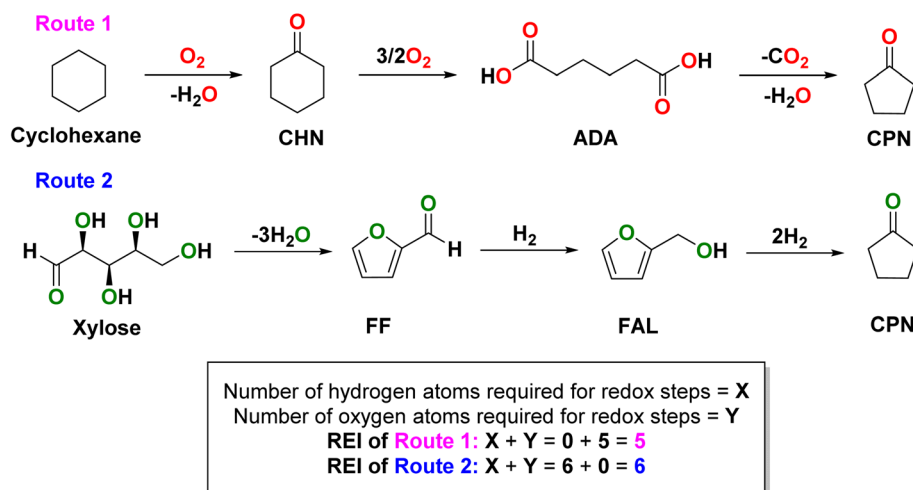


Scheme 10 Synthesis of acrylic acid from petroleum and carbohydrates.

In the first step, cyclohexane is selectively oxidized into cyclohexanone. Further oxidation of cyclohexanone using nitric acid as an oxidant produces ADA. Finally, ADA is subjected to decarboxylative ketonization to form CPN (Scheme 11).<sup>115</sup> The production of renewable CPN from FAL was first reported in 2012, involving the Piancatelli rearrangement under catalytic hydrogenation conditions.<sup>116</sup> Three moles of H<sub>2</sub> are required for converting xylose-derived FF into CPN *via* the FAL intermediate. Since 2012, the synthesis of CPN from FF has been established with a focus on the selectivity, process parameters, mechanistic details, and reaction kinetics.<sup>24</sup> Interestingly, the REI for the petroleum route is five, whereas that of the biomass route is six. However, the index is due to reduction reactions in the case of FF, whereas the index is due to oxidation reactions in the case of cyclohexane. Moreover, there is a loss of carbon atoms in the petroleum route in the form of CO<sub>2</sub>, whereas the carbon efficiency on the biomass route *via* FF is 100%.

### 13. Synthesis of hydrocarbon fuels

The synthesis of hydrocarbon-based liquid biofuels from carbohydrate molecules requires extensive deoxygenation of the latter. For example, glucose or even cellulose can be transformed into *n*-hexane under catalytic hydrogenation conditions.<sup>117</sup> The REI for the glucose to *n*-hexane transformation is calculated to be 14. However, this section focuses on the selective synthesis of aviation-, diesel-, and gasoline-range hydrocarbons from carbohydrates, with precise control over the molecular architecture and physicochemical properties of the fuel molecules. The concept of REI has been applied to rationalize the selection of organic transformation and their sequence in the synthetic pathway. The oxidizing and reducing agents are chosen as molecular O<sub>2</sub> and H<sub>2</sub>, respectively, for consistency and a more accurate comparison. Liquid transportation fuels are invariably a mixture of hydrocarbons, but

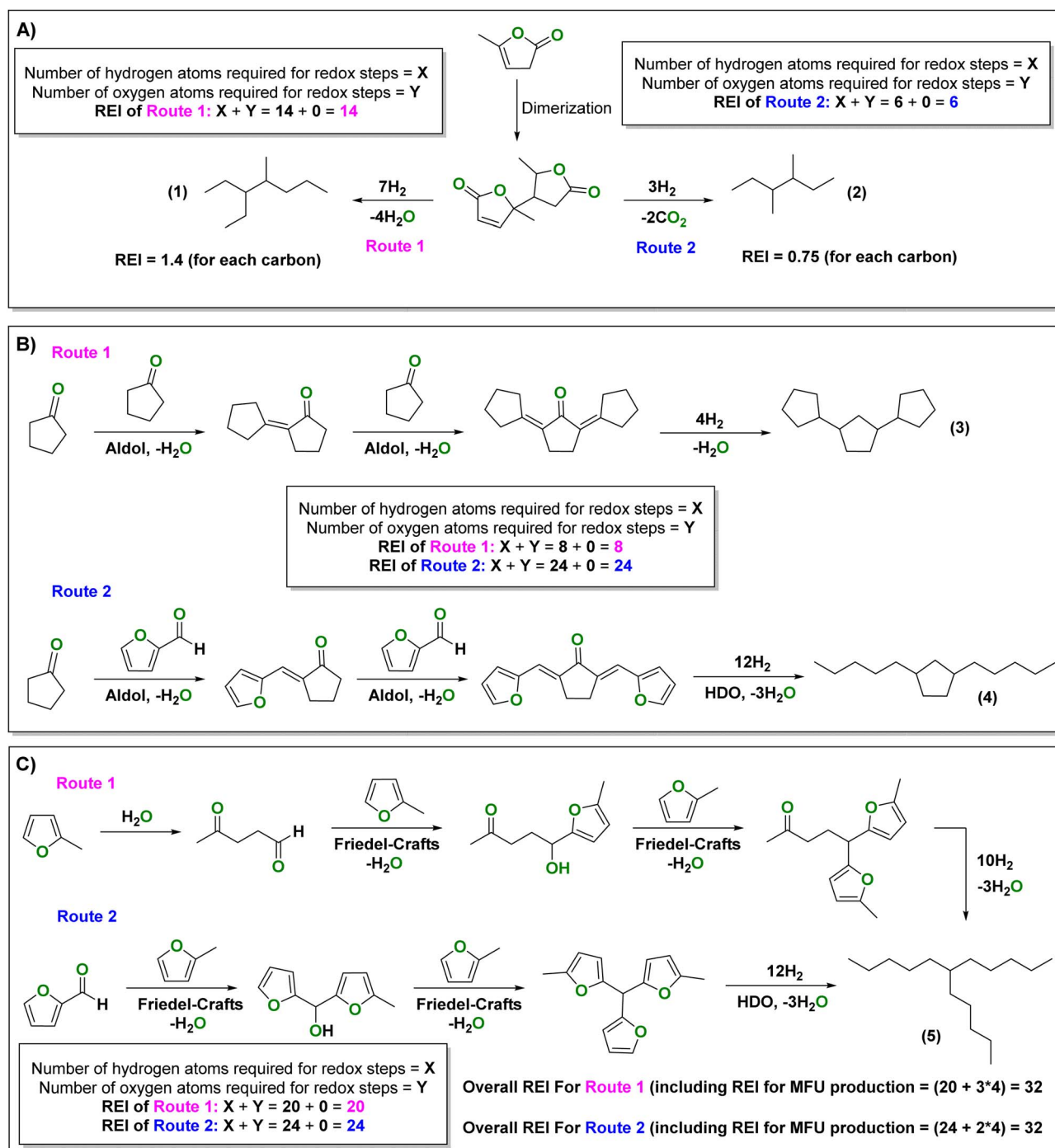


Scheme 11 Synthesis of cyclopentanone from petroleum and carbohydrate-derived molecules.



their molecular structure differs based on the engine and furnace designs. Straight-chain or mildly branched paraffins are major components in aviation and diesel fuels. Alicyclics have garnered significant interest recently as potential high-density aviation fuels. Gasoline fuels primarily consist of heavily branched alkanes in the C6–C10 range, monocyclic aromatics, and various additives (*e.g.*, octane boosters).<sup>118</sup> The synthesis of aviation- and diesel-range hydrocarbon fuels from carbohydrates has been attempted over the past few decades, and numerous fuel molecules have been synthesized. The processes

typically consist of three major steps: (1) transformation of sugars and polymeric carbohydrates into functionalized platform chemicals, (2) building/extending the desired carbon skeletal system by condensation of two or more platform chemicals, and (3) catalytic deoxygenation of the oxygenated fuel precursors produced in step 2. The target-oriented synthesis of gasoline fuels from carbohydrates is a relatively new development, first reported in 2014. However, since then, several successful attempts have been made in sourcing gasoline-range hydrocarbons from sugars and carbohydrates.



Scheme 12 Renewable synthesis of gasoline (A) and diesel-like (B and C) hydrocarbon fuels from carbohydrate-derived chemicals.



The strategy involves selecting the appropriate chemical building blocks and organic transformations that introduce the necessary branching in the carbon framework of the target hydrocarbon.

Mascal *et al.* reported the synthesis of C6–C10 highly branched gasoline-range hydrocarbon fuels from LA-derived AGLs. The major product was 3-ethyl-4-methylheptane (**1**), which was produced by the hydrodeoxygenation of angelica lactone dimer (ALD).<sup>119</sup> The **REI** is 14 for the transformation of ALD to **1** as depicted in Scheme 12A. The same research group deoxygenated ALD by a catalytic decarboxylation reaction in a later report, allowing a more hydrogen-economic synthesis. However, the major product, 3,4-dimethylhexane (**2**), is two carbon atoms shorter (lost as CO<sub>2</sub>) than **1**.<sup>120</sup> Therefore, the calculation of the **REI** was performed for each biogenic carbon in the products for better clarity. The calculation shows that the **REI** for each carbon atom in **1** is 1.4, whereas that for **2** is only 0.75. This calculation shows the effectiveness of using the **REI** as a green metric in synthesis involving redox steps.

The synthesis of aviation- and diesel-range hydrocarbon fuels from carbohydrates has been attempted, especially starting from furanic and levulinic building blocks.<sup>121</sup> The strategy is to extend the carbon skeletal system by involving various C–C bond-forming reactions, such as aldol condensation, Friedel–Crafts alkylation, Diels–Alder reaction, *etc.* Finally, the oxygenated fuel precursors are extensively deoxygenated by HDO, hydrodecarboxylation, decarboxylative ketonization, *etc.*<sup>122</sup> Scheme 12B illustrates two examples where CPN and FF serve as the building blocks for synthesizing hydrocarbon-based liquid transportation fuels. CPN can be condensed with itself by the aldol condensation reaction to form a C15 oxygenate, which is then subjected to the HDO chemistry to form **3**. Alternatively, CPN can be condensed with two molecules of FF to form a C15 oxygenate, which can then undergo HDO chemistry to form C15 hydrocarbon **4**. The **REI** for synthesizing **3** and **4** have been calculated to be 8 and 24, respectively, exclusively due to the HDO chemistry involved in their preparation. Apparently, the preparation of **3** is more redox-economic compared to **4**. However, the **REI** of producing CPN from FF must also be adjusted in the calculation to better understand the **REI** of the overall process. Since three molecules of CPN are required to prepare **3**, the total **REI** for the process would become  $[8 + (3 \times 6)] = 26$ . In the case of **4**, the total **REI**, due to the involvement of one CPN molecule, is calculated to be  $[24 + (1 \times 6)] = 30$ .

Scheme 12C illustrates the alternative routes for preparing 6-pentylundecane (**5**), a mildly branched diesel-range hydrocarbon fuel derived from sugar-based furanic platform chemicals.<sup>67,123</sup> Route 1 involves the hydrolysis of MFU into an aldehyde, which is then coupled with two molecules of MFU by the Friedel–Crafts reaction. The **REI** calculated for synthesizing **5** through this pathway is 20. Alternatively, **5** can be synthesized by condensing FF with two moles of MFU *via* the hydroxyalkylation/alkylation reaction. Finally, the C15 oxygenated is completely deoxygenated by HDO chemistry (Route 2). The **REI** calculated for this pathway is 24. Interestingly, the **REI** calculated for synthesizing MFU from FF is 4. Since three molecules of MFU are involved, in Route 1, the total **REI** of

synthesizing **5** through this route is  $[20 + (3 \times 4)] = 32$ . The **REI** calculated for Route 2 for synthesizing **5**, involving two molecules of MFU, comes out to be  $[24 + (2 \times 4)] = 32$ .

## 14. Scope, advantages and limitations of the REI

Since the institutionalization of green chemistry in the early 1990s, a series of green metrics have been developed to analyze and evaluate the synthetic pathways both qualitatively and quantitatively for designing superior processes at early technology readiness levels (TRLs).<sup>26</sup> The molar yield of the product has always been a useful metric since the dawn of organic synthesis for determining the efficiency of an organic transformation. While a high isolated molar yield of the product promises resource efficiency, it does not guarantee overall sustainability of the process. A reaction can provide a high product yield but produce substantial amounts of deleterious byproducts as waste. Atom economy (AE) is a green metric of a theoretical construct proposed by Barry Trost in 1991 that investigates the relocation of atoms in the starting materials and reagents to the product using a balanced chemical equation.<sup>124</sup> AE allows evaluation of alternative synthetic schemes for their sustainability without performing them. The *E*-factor is another green chemistry metric (proposed by Roger A Sheldon in 1992) that measures the mass of waste produced per unit mass of product.<sup>125</sup> While the *E*-factor is experimentally determined, it can also be used theoretically to estimate the relative greenness of alternative synthetic pathways with respect to waste formation. Various other green metrics have been developed over the years, such as process mass intensity and carbon efficiency. All green metrics have their advantages and limitations, and often a combination of them is more impactful in determining the overall efficacy of organic transformations and processes. Redox economy has been popularized by the pioneering studies of Phil S. Baran, among others.<sup>126</sup> Redox economy is a theoretical construct in which the scheme of a multistep organic synthesis is studied for the tactical and strategic use of redox steps in constructing the molecular framework of the product molecule. Unnecessary derivatization or protection/deprotection steps are avoided to ensure good redox economy, in line with the 8th principle of green chemistry. However, the redox economy metric remained largely qualitative in nature. This work introduces the desirable quantifiability of the redox economy metric to improve its scope and applicability in organic synthesis and sustainable chemistry. Even though AE or the *E*-factor has no direct formulaic relationship with the **REI**, a low **REI** in a multistep synthesis promotes high AE and a low *E*-factor. The **REI** values have been calculated using H<sub>2</sub> and O<sub>2</sub> as the reducing and oxidizing reagents, respectively. However, fundamentally, the **REI** values for organic transformations involving various stoichiometric reducing and oxidizing agents can also be calculated. In such a scenario, a conversion factor may be used that consists of the ratio of the molecular weights of the reagent and the model reagent (*i.e.*, H<sub>2</sub> for reduction and O<sub>2</sub> for oxidation), and the



molar ratio of the stoichiometric reagent to the model reagent. For example, the **REI** value of HMF to FDCA has been calculated to be 3. If  $\text{HNO}_3$  is used as the stoichiometric oxidant for the same transformation, the conversion factor  $[(\text{MW of HNO}_3/\text{MW of O}_2) \times (\text{mole of HNO}_3/\text{mole of O}_2)]$  is calculated to be 7.87. Therefore, the **REI** of the HMF to FDCA transformation using  $\text{HNO}_3$  for stoichiometric oxidation is 31.5 ( $7.875 \times 4$ ). Such analyses can help determine the relative advantages and disadvantages of various stoichiometric redox reagents in terms of sustainability. For example,  $\text{H}_2\text{O}_2$  is the best alternative to  $\text{O}_2$ , being close in molecular weight and providing the oxidant required for the transformation. The **REI** for the oxidation of LA into 3-HPA using  $\text{H}_2\text{O}_2$  as the oxidant is 2.12  $[(34/32) \times (1/0.5)]$ , whereas the **REI** using  $\text{O}_2$  as the oxidant was 1, as depicted in Scheme 10.

As depicted in Fig. 2, the conversion of the starting material into a product of desired structural complexity *via* an isohypsic (redox-neutral) process is idealistic but is often not achievable in practice. The rearrangement and coupling reactions can fulfil such criteria. The synthesis of LAC from glucose under hydrothermal conditions is a good example of a redox-neutral process, where the oxidation states of the carbon atoms in the starting material are redistributed without an overall change in the oxidation state. The redox-economic steps linearly modify (*i.e.*, increase or decrease) the oxidation states of skeletal atoms in the intermediates. The redox economy can be improved by accelerating changes (exponentially) and improving the step economy of the overall synthesis. Non-redox economic processes would involve a multistep synthesis, in which the oxidation states of the skeletal atoms fluctuate in intermediates. For petrochemicals, the starting materials are primarily non-functionalized hydrocarbons. The heteroatom-containing functionalities are introduced in the carbon skeletal system *via* redox steps to form reactive intermediates. In contrast, the

synthesis of reactive intermediates from biomolecules (*e.g.*, carbohydrates) mandates the removal of the excess heteroatoms (*e.g.*, N and O) by stepwise reduction steps. The **REI** concept presented in this work will assist in quantifying the improvement in redox economy in organic synthesis, particularly from the perspective of biorenewable chemicals. A lower **REI** value implies better redox economy and promises an accelerated (or step economic) and waste-minimized synthesis of the product molecule. Finally, it must be pointed out that the **REI** metric, as a theoretical construct, does not include the experimental outcome of an organic transformation. Therefore, a lower **REI** in a reaction scheme does not automatically make it superior and other process parameters and green metrics (*e.g.*, molar yield) must be consulted. For example, the synthesis of renewable PTA from FDCA has a lower **REI** than that through the DMF route. However, the synthesis of PTA from FDCA and ethylene is extremely challenging with negligible yields.

## 15. Conclusions

The presence of oxygen-containing functionalities in sugars and polymeric carbohydrates should not be considered as an inconvenience, but rather an advantage for designing their chemical-catalytic value-addition pathways. The carbon atoms in sugar molecules remain in various oxidation states, which enables the synthesis of functionalized molecules by avoiding redox steps and the associated waste formation. The challenge is to shed excess oxygen atoms during transformations and rearrangements of functional groups. The presence of several oxygen atom-containing functionalities in carbohydrates complicates the mechanistic pathways since several competitive reaction pathways with comparable energetics can lead to the formation of a mixture of products. Therefore, suitable reagents and reaction conditions must be designed to improve the selectivity towards the desired product. Tracing the oxygen atoms from sugars to renewable chemicals assists in analysing the competitive synthetic pathways and developing more efficient routes. Sugars and carbohydrates are typically transformed into a handful of small organic molecules, termed platform chemicals, which act as nodal points for branching out into renewable products of diverse structural characteristics, properties, and markets. HMF, LA, and LAC are some of the most promising carbohydrate-derived platform chemicals. Over the past few decades, research on carbohydrate-centric biorefineries has evolved from first-generation biomass-derived sugars to second-generation cellulosic biomass and, more recently, to the third generation of aquatic biomass-derived carbohydrates (*e.g.*, chitin and carrageenan). The availability, cost competitiveness, and environmental sustainability increase from the first to the third generation of biomass. However, the structural complexity of carbohydrates also increases, which often requires more demanding reaction conditions and purification steps. The oxygen content of sugars can be lowered by involving dehydration and condensation reactions that are redox-neutral. Other reactions include the hydrodeoxygenation reaction that requires a source of molecular hydrogen and a suitable metal-based catalyst. Deoxygenation reactions, which involve the loss of

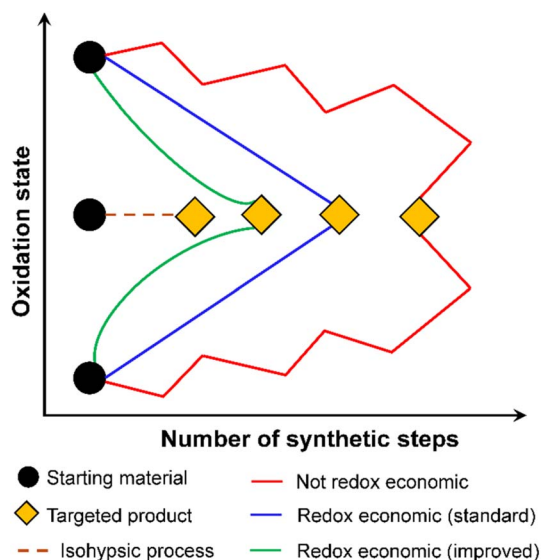


Fig. 2 Pictorial representation of redox economic and non-redox economic synthesis, adapted from ref. 126 with permission from John Wiley and Sons [*Angew. Chem., Int. Ed.*, 2009, 48(16), 2854–2867], copyright 2009.



biogenic carbon, include decarbonylation and decarboxylation reactions. The combination of deoxygenation steps applied to the sugar or polymeric carbohydrates depends on the targeted molecular framework and functionalities in the product. For synthesizing hydrocarbon-based drop-in fuels, the oxygen atoms in them must be extensively eliminated. The process also involves building an appropriate carbon framework using various C–C bond-forming reactions (*e.g.*, aldol, Friedel–Crafts, and Diels–Alder).

At early TRLs, when design freedom is at its maximum, attention must be focused on process efficiency to avoid complications later. Design freedom is lower at late TRLs, while significant knowledge is acquired about products and processes, and the focus shifts to life-cycle environmental impacts. In general, adhering to the green chemistry principles (and metrics) ensures favorable life-cycle environmental impacts.<sup>127</sup> The **REI**, the green metric introduced in this work, can assist in choosing the most redox-economic and waste-minimized synthetic design for converting carbohydrates into renewable chemicals. The **REI** can be used along with other green metrics to select the appropriate synthetic strategy for a renewable chemical.

## 16. Future perspectives

The concept of tracing the heteroatoms from carbohydrates to renewable chemicals can be extended to other biomolecules and biopolymers. For example, the synthesis of phenolics from lignin can follow such a strategy to develop more efficient synthetic processes. Chitin-derived platform chemicals can contain a nitrogen atom, which can then be valorized into renewable chemicals with N-containing functionalities. The strategy can be more useful when different moieties of a structurally complex renewable molecule are sourced from separate biomass components. Tracing the heteroatoms in the starting materials and the final product can give insights into the alternative synthetic strategies and their relative advantages and challenges. Tracing of other heteroatoms is also possible and could be beneficial for synthesizing renewable products of increasing structural complexity that contain functionalities with a combination of heteroatoms (*i.e.*, N, O, and S). Nitrogen atoms can be introduced into biorenewable molecules using inorganic sources, such as ammonia. Alternatively, amino acids can be renewable reagents with a nitrogen-containing functionality. The green chemistry metric **REI**, introduced in this study, can potentially be extended to the chemistry of renewables and synthetic organic chemistry in general.

## Conflicts of interest

The author declares no conflict of interest.

## Abbreviations

ACA	Acrylic acid
ADA	Adipic acid

AGL	Angelica lactone
BHMF	2,5-Bis(hydroxymethyl)furan
GBL	$\gamma$ -Butyrolactone
CHN	Cyclohexanone
CPN	Cyclopentanone
DFF	2,5-Diformylfuran
DMF	2,5-Dimethylfuran
DMTHF	2,5-Dimethyltetrahydrofuran
FDCA	2,5-Furandicarboxylic acid
2FN	2(5 <i>H</i> )-Furanone
FF	Furfural
GRA	Glucaric acid
GCA	Gluconic acid
1,6-HDO	1,6-Hexanediol
3-HPA	3-Hydroxypropionic acid
HMF	5-(Hydroxymethyl)furfural
LA	Levulinic acid
LAC	Lactic acid
5MF	5-Methylfurfural
MAN	Maleic anhydride
PTA	Purified terephthalic acid
<b>REI</b>	Redox economy index
SA	Succinic acid
PX	<i>para</i> -Xylene

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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