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Integrated recycling of polylactide using biomass into renewable fuels: a combined experimental and computational design approach

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Across the globe, the consumption of plastics and fuels is rising steadily. Conventionally, both products are fossil-based and have a negative impact on the environment, particularly plastic pollution and CO_2 emissions. This work explores the recycling of bio-based polylactide (PLA) into renewable fuels as a strategy to mitigate both issues. To develop an efficient recycling strategy and guide process development toward the most promising pathways, we propose a systematic, three-step screening approach that combines depolymerization experiments with computational methods to estimate fuel properties, production cost, and material efficiency across alternative production routes. First, the robust, non-toxic bisguanidine TMG_2e and a zinc bisguanidine catalyst are evaluated for PLA alcoholysis using 15 different alcohols. Applying our predictive models, we rank each alkyl lactate as a potential fuel blend candidate based on its estimated fuel properties. In the final step, we analyze the most promising candidates using reaction network flux analysis (RFNA) to gain insight into the economic costs and environmental impact of their production, considering biomass alcohols as co-reactants in the alcoholysis step, which are produced from either biomass or renewable CO_2 and hydrogen. As a result of this screening approach, which is general and not limited exclusively to the selection of fuel candidates, methyl and ethyl lactate are identified as the most promising alkyl lactates. Both candidates exhibit comparable properties and a similar efficiency in the depolymerization step. However, the whole production process of methyl lactate outperforms that of ethyl lactate when methanol is produced from CO_2 and hydrogen, whereas ethyl lactate becomes favorable when ethanol originates from biomass. We thus outline a new sustainable value chain starting from PLA plastic waste and biomass to sustainable fuel candidates.

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Introduction

The demand for everyday goods like plastics and fuels is steadily rising.[1] The production, consumption, and disposal of these goods – mainly produced from fossil resources and within a linear economy – lead to severe consequences for the environment, such as the accumulation of greenhouse gases in the atmosphere and the pollution of the environment with non-degradable plastics.[2] Thus, the implementation of a circular plastics economy and the efficient integration of fuels from renewable sources in the transport sector are urgently required steps. For a more efficient and holistic approach, both problems can be viewed as interconnected. New recycling strategies for plastics need to be implemented, considering multiple renewable feedstocks and adopting a comprehensive approach that encompasses the entire waste stream, including lower-purity fractions that could find applications in the fuel sector. Polylactide (PLA) has emerged as one of the most promising bio-based polymers and as a suitable candidate to replace fossil-based plastics.[3,4] PLA is an example of a safe and green product that embodies multiple principles of green chemistry (PGC).[5] It can be produced without involving hazardous reactants or solvents (PGC3), the polymer and its degradation products are non-toxic (PGC4), PLA is produced with a low energy demand (compared with fossil-based counterparts) (PGC6)[6] and from a renewable, biomass-based precursor (lactic acid) (PGC7), and it degrades faster than conventional polymers (PGC10).[5,7–9] However, current production of PLA *via* ring-opening polymerization (ROP) is still performed with the toxic catalyst tin octoate ($Sn(Oct)_2$). Meanwhile, several environmentally friendly catalysts are being developed to replace $Sn(Oct)_2$, thereby

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addressing the concern about the release of the catalyst into the environment during PLA degradation.[10]

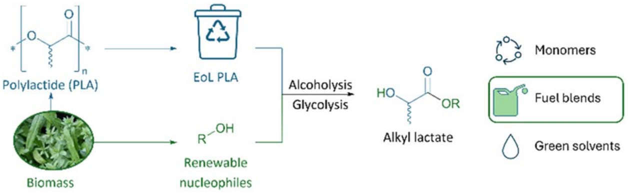
Despite its intrinsic biodegradability, a strategy to handle end-of-life (EoL) PLA to recover its valuable molecular functionality is desired.[11] Mechanical recycling allows the direct re-use of the entire molecular structure of the polymer by melting and reprocessing it.[12–14] However, it requires a high purity of the waste feedstock and only extends the linear lifetime of plastics, since it leads to quality loss of the polymer after each recycling cycle.[12] Recycling *via* pyrolysis or gasification represents, in principle, viable options to treat EoL PLA, but they require high temperatures and have, in general, poor selectivity.[15] The only recycling strategy to re-obtain virgin-quality polymer from EoL plastics is selective depolymerization and subsequent polymerization following a "closed-loop" approach.[11,16] Alternatively, selective depolymerization can be performed by transforming the polymer into valuable, low-molecular-weight chemicals, which already have an end-user market, or into platform chemicals, which can then be supplied to other value chains. This strategy is called "open-loop recycling".[17–19] Due to the interesting properties of PLA, the development and optimization of catalytic reactions to depolymerize PLA, either in a closed-loop or open-loop fashion, is a very active field of research.[11,20]

Possible depolymerizations of PLA are reductive hydrogenation to platform chemicals such as 1,2-propanediol,[21–23] hydrolysis of PLA to lactic acid at elevated temperatures or under acidic or basic conditions,[11] or alcoholysis. During the alcoholysis, the ester bonds of PLA are cleaved *via* random scission of the polymer backbone. This transesterification reaction is generally performed with PLA dissolved or finely dispersed in the corresponding alcohol and in the presence of a homogeneous or heterogeneous catalyst.[11] Compared to hydrolysis, alcoholysis benefits from better swelling of PLA in alcohols than in water, which enhances the contact of the polymer with the catalyst and alcohol. The reaction is generally characterized by high conversion of PLA, especially using short-chain, highly nucleophilic alcohols such as methanol (MeOH) or ethanol (EtOH).[11] Keeping the whole life cycle of PLA in mind, we introduced several benign Fe and Zn guanidine complexes as highly active catalysts for both the polymerization of PLA and its alcoholysis to alkyl lactates (RLas) and demonstrated their applicability in a circular plastics economy.[24–27] Such new catalytic recycling routes for EoL plastics combined with PGC are crucial to reach sustainability targets in terms of feedstock and atom efficiency.[28–30] To further realize a sustainable global economy, we investigated possible applications for the recycling products produced, considering different quality product streams. RLas represent valuable platform chemicals, which, for example, can be reconverted to PLA in a closed-loop fashion,[31–33] can serve as platform chemicals for further synthesis[34] or can be directly used as green solvents.[35,36] Even though the alcoholysis of PLA is highly selective and achieves high yields of RLas, lower quality product fractions (such as racemic or impure RLa fractions) obtained during the purification process (*e.g.*, fractions containing low amounts of alcohol) or by the use of impure or lower quality waste PLA streams (which cannot be used to remanufacture virgin PLA) need to be considered. An alternative and unexplored option for these low-quality RLa fractions is their use as fuel blend components. Examples of renewable fuel candidates that can replace fossil fuels are bio-based components derived from food crops, such as fatty acid methyl esters or ethanol, fuels from carbon dioxide and renewable electricity,[37] and bio-hybrid fuels.[38,39] Moreover, biofuels from waste streams have received considerable attention.[40,41] Gao *et al.*[42] presented a highly relevant study on the conversion of mixed and low-quality wastes into automotive fuels, discussing it as a promising strategy to valorize plastic wastes in isolated regions without local industry, such as islands. In all these cases, the carbon dioxide emitted during combustion is not accumulated in the atmosphere but used in photosynthesis or direct air capture and circulated in a closed loop.

To identify promising renewable fuels, systematic fuel screening approaches have been proposed. Fuels are defined by their properties, not by their molecular structure. Therefore, screening molecules for desired fuel properties can yield a plethora of molecules as potential fuel candidates. The molecules that are screened can be taken from a database[43] or generated during the screening using computer-aided molecular design.[44] Properties can be predicted using predictive models like group-contribution and quantitative structure–property relationships (QSPR),[45] quantum chemistry,[46] and machine learning models.[47]

Apart from fulfilling property requirements, fuels must also be produced in a cost-efficient and environmentally friendly way. To identify promising fuel production routes, rapid process screening methods were developed.[48–50] These methods only require limited data, such as reaction stoichiometry, enthalpy, and selectivity, to rapidly identify the most promising production pathway of specific products. By systematically exploring the impact of new routes early in their development, promising reaction candidates can be identified and experiments efficiently guided. Process screening methods such as Reaction Network Flux Analysis (RNFA) have been widely applied, for example, to assess processes for the production of renewable fuels[49,51,52] or bio-based plastics.[53,54] While they do not replace detailed technoeconomic analysis or life-cycle assessments (LCA), they offer a good trade-off between obtaining useful metrics at an early technology-readiness level with minimal availability of data.

So far, the implementation of a renewable, circular economy has been mostly pursued independently for plastics and fuels. One way to further improve production efficiency is to rethink recycling pathways not as isolated but rather combined with intermediates originating from other available renewable feedstocks. The latter can serve, for instance, as reactants in the depolymerization or for the direct synthesis of a specific product. An example of this strategy, combining multiple feedstocks, is provided by Beydoun *et al.*[55] who demonstrated an integrated concept of catalytic plastic recycling using diols as co-reactants, which can be produced from biomass, thus exploiting two separate feedstocks.



Scheme 1 Integrated recycling of biomass-based PLA using renewable nucleophiles (Nus) to obtain alkyl lactates (RLas) used as green solvents,[35,36] as monomers[57] or precursor for monomers,[35,36,54] and as fuel blend candidates (this work).

Herein, we refer to this approach as an "integrated" recycling strategy, meaning the combination of multiple feedstocks – with at least one stream represented by plastic waste – to produce a specific molecule. An auxiliary feed material that substantially contributes to the molecular weight of the target molecule produced by depolymerization (such as the alcohols in the alcoholysis) may dominate the economics of recycling (positively or negatively) and even constitute a bottleneck for the large-scale implementation of a recycling process.[56] This stresses the importance of assessing the economics of new recycling pathways at an early stage of their development (*i.e.*, when a catalytic reaction is still investigated on a laboratory scale).

To address these challenges, we combine the know-how of the depolymerization of PLA using guanidine-based catalysts with fuel property prediction methods and the early-stage process screening method RNFA to develop and evaluate new integrated recycling strategies for EoL PLA beyond the laboratory scale. Specifically, we consider biomass-derived alcohols combined with EoL PLA when analyzing the production pathway of the RLas, as depicted in Scheme 1. To investigate this approach, we screen 15 RLas as potential fuel candidates, considering their thermophysical and ignition properties as well as the cost and carbon efficiencies of their production pathways. This fast-screening approach enhances the effectiveness of the work in the laboratory, since we are able to identify the most promising molecules and focus further development and scale-up efforts only on these candidates.

Methodology

Fast-screening strategy of alkyl lactates as fuel candidates

We propose a fast-screening strategy with three selection steps to enable a cost-effective and time-efficient evaluation of the RLas as fuel candidates (see Fig. 1). The first step is the experimental investigation of the depolymerization of PLA *via* alcoholysis (Fig. 1, experimental analysis). This step is required to identify feasible nucleophiles (Nus) for the depolymerization and to provide quantitative selectivity values (S_{RLa}) as input for the pathway screening method (step 3 of our approach). To have a broad range of potential RLas being evaluated as fuel candidates, 15 different Nus are investigated in the first selection step. 14 alcohols and ethylene glycol (EG) are applied in simple depolymerization procedures without further isolation of the RLas. In the second step, the obtained RLas are evaluated with respect to relevant ignition and thermophysical properties using predictive models developed in previous studies[45,47] (Fig. 1, fuel properties estimation). In the third step, the most promising candidates are then analyzed using the pathway screening tool RFNA, which requires selectivity values from step 1 as input, to rank the RLas with respect to costs and carbon efficiency of their production route (Fig. 1, RFNA). While a combination of steps 2 and 3 is possible, as demonstrated in previous studies,[58,59] in this work, we decided to separate the two steps for better comprehensibility, especially with readers

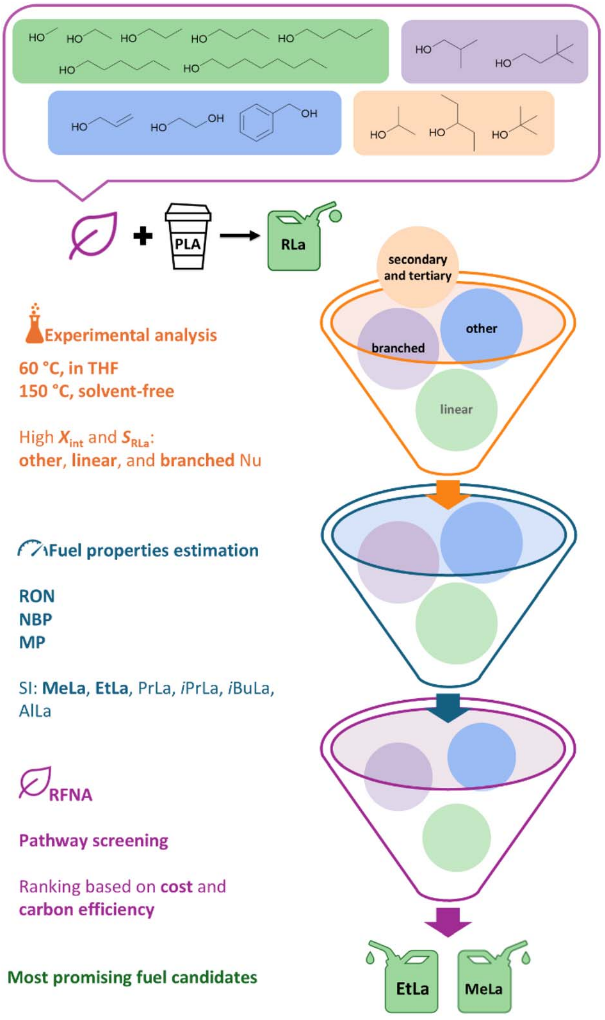


Fig. 1 We followed the methodical pathway displayed for the screening of different RLas obtained by depolymerization of PLA. First, we evaluated the PLA depolymerization using a broad range of Nus: methanol (MeOH), ethanol (EtOH), ethylene glycol (EG), propanol (PrOH), iso-propanol (iPrOH), allyl alcohol (AlOH), butanol (BuOH), iso-butanol (iBuOH), *tert*-butanol (*t*BuOH), pentanol (PeOH), 3-pentanol (3PeOH), hexanol (HeOH), 3,3-dimethyl-1-butanol (Me_2-BuOH), benzyl alcohol (BnOH), and octanol (OcOH). In the second step, computational methods were applied to predict the fuel properties of the RLas. Therefore, we considered the ignition property represented in the research octane number (RON) as well as thermophysical properties, *e.g.*, the normal boiling point (NBP) and the melting point (MP). The most promising RLas were further evaluated with respect to their economic and environmental impact using RFNA, which requires the selectivity (S_{RLa}) of the pathways determined in step 1.

from different scientific backgrounds in mind. We focus on the achievability of RLas and the technology-readiness level of chemical recycling processes behind them as well as the evaluation of these recycling products as novel fuel candidates, which are not yet established fuels. In the following subsections, each of the three selection steps is explained in detail.

Step 1: experimental investigation of PLA depolymerization *via* alcoholysis

For the experimental investigation of the PLA depolymerization through alcoholysis, we selected two highly active catalysts with distinct properties and requirements in order to ensure an effective and representative depolymerization process.

The first catalyst evaluated is the organocatalyst bis(*N*,*N*,*N*,*N*-tetramethylguanidino)-ethane (TMG_2e). The easy-to-synthesize organocatalyst is chosen due to its robustness towards impurities. TMG_2e is active in contact with water and air and was shown to be able to depolymerize post-consumer polymer waste.[60,61] Despite the high stability, an activity loss after removal of the alcohol and the RLa under reduced pressure from a polymer mix was observed, rendering the recyclability of the organocatalyst as low. A possible solution could be the immobilization of the catalyst, a milder isolation procedure or a batch-feed process.[65] Still, considering our goal to transform lower-quality waste streams into valuable fuel candidates, the organocatalyst is a good candidate for this study due to its accessibility and high robustness.

The second catalyst applied in this study is the Zn bisguanidine catalyst $[Zn(DMEG_2ch)_2](OTf)_2\cdot THF$ (**Zn1**).[62] In 2024, the alcoholysis of PLA with **Zn1** was reported using multiple alcohols and achieving high conversion of PLA as well as high selectivity for the corresponding RLas.[26] Additionally, the catalyst showed good recyclability. After the successful depolymerization of PLA using EtOH, all volatile components, EtOH and EtLa, were removed under high vacuum. Without an additional work-up, the ethanolysis of PLA could be repeated two times with only minor activation loss. In the fourth run, a more severe activity loss is observed. Still, a high conversion of PLA (X_{int}) over 80% could be achieved. Therefore, **Zn1** was chosen for this study as a promising catalyst for a sustainable circular economy, being able to polymerize LA and depolymerize PLA effectively.[26]

Besides the catalysts, 15 nucleophiles are selected. The selection criteria are based on literature research and feedback loops between step 1 and step 2. Moreover, the selection was influenced by the availability of the Nus from CO_2, hydrogen, and/or biomass. First, we selected standard alcohols used in PLA alcoholysis, since they have the highest technology-readiness level; therefore, we chose MeOH and EtOH. Second, the alcohols used should vary in different characteristics such as length (#C atoms = 1–6, and 8), branching (*i.e.*, iBuOH), and the position of the OH group (*i.e.*, *t*BuOH) to understand the influence of these characteristics on the alcoholysis and on the fuel properties.[63] Additionally, AlOH and BnOH are selected to evaluate how the allyl or benzyl group of the alcohol influences the alcoholysis. Third, after the results for the first group of linear RLas were analyzed, the focus shifted to carbon-dense nucleophiles like iPrOH, Me_2BuLa, and 3PeOH. EG is chosen as it is readily derived from biomass[64] (step 3).

For this study, we use virgin PLA to establish a baseline and secure consistent conditions throughout. Three general procedures (**GP**) for the alcoholysis of PLA are applied. For all three, PLA (250 mg, 3.47 mmol) is depolymerized using TMG_2e (8.9 mg, 35 μmol, 1.0 mol%) and 7 equiv. of the Nu. Following **GP1** and **GP2**, the experiments are performed without applying inert conditions to mimic industrially relevant conditions. For **GP1**, PLA and the catalyst are dissolved in THF (4 mL) and placed in a preheated oil bath ($T = 60$ °C). Subsequently, the reaction is started by the addition of the Nu. Following **GP2**, the alcoholysis is performed under solvent-free conditions: PLA and the catalyst are suspended in the Nu and the reaction vessel is placed in a preheated oil bath ($T = 150$ °C). **GP2*** is conducted as described for **GP2** but using **Zn1** (36.4 mg, 34.7 μmol, 1.00 mol%) under inert conditions.

Step 2: fuel property screening

To screen RLas for their suitability as fuel blend candidates, we predict and evaluate key relevant properties of feasible candidates after step 1. Specifically, we consider ignition properties – derived cetane number (DCN) and research octane number (RON) – as well as thermophysical properties – normal boiling point (NBP) and melting point (MP). We employ our Graph Neural Network (GNN) for ignition properties[47] and the QSPR model for the thermophysical properties of Dahmen *et al.*[45] Both models are developed for the prediction of the respective properties of oxygenated hydrocarbons, which include the candidates considered in this work. The QSPR model has been validated and benchmarked from a large dataset retrieved from the DIPPR database, while the GNN model was trained using a curated database containing between 479 (DCN) and 335 (RON) species. Details on the development and benchmarking of the models are provided in the respective references. Following previous studies and norms on property requirements of fuels, we impose specific limits on each property, which are predicted by the models, in order to qualify a specific RLa as a suitable fuel candidate. Accordingly, fuel candidates that do not fulfill these constraints are discarded in step 2 and are not further considered in our analysis. Fuels for compression ignition (CI) engines require a high auto-ignition propensity, while fuels for spark ignition (SI) engines require a low auto-ignition propensity. The auto-ignition propensity is proportional to the DCN, which is used to quantify the ignition quality of CI engine fuels, and inversely proportional to the RON, which is used to quantify the ignition quality of SI engine fuels. Following Dahmen *et al.*,[44] we require DCNs ≥ 40 for CI engine fuel blend candidates and RONs ≥ 85 for SI engine fuel blend candidates. Furthermore, the value of the NBP and the MP must ensure that the fuel remains liquid under ambient conditions but still has sufficient volatility. We require a maximum MP of -20 °C and a minimum NBP of 60 °C. As a volatility requirement, the European E10 gasoline norm EN 228 (ref. 65) requires a minimum of 75 vol% to be evaporated at 150 °C, using the test method described in EN ISO 3405.[66] The US SI engine fuel specification requires 90 vol% to be evaporated at a maximum of 185 °C or 190 °C, depending on seasonal climatic changes.[67] Considering these requirements and potential model uncertainties, an upper limit on the NBP of 220 °C is set.

Step 3: production pathway screening method

In the last selection step, we apply the early-stage pathway screening method RNFA[50] to analyze the production pathway from raw material (*e.g.*, EoL PLA or lignocellulosic biomass) to the respective RLas selected as promising fuel candidates after step 2. Using RNFA, the production effort for many alternative production pathways can be estimated, requiring very limited data to identify promising candidates for further economic and environmental evaluation.

RNFA builds on a reaction network that maps reactants and products (nodes) of different reaction pathways through reaction steps (edges). The molar flow of feedstocks, intermediates, products, and by-products through the network is constrained by the stoichiometry of the reaction steps. Besides the stoichiometry of the reaction steps involved, RNFA requires as input the yield vector Y, which gives the yield of each process step r (and thus determines the efficiency of the chemical transformation of the raw material), and the respective enthalpy of formation of each component in the network (which is, in turn, an input for the estimation of the investment cost). In RNFA, the stoichiometric matrix A relates the process flux vector f through the network with the vector b of positive molar flows of products and by-products leaving the network. The optimal flux vector f is determined by solving a constrained multiobjective optimization problem. Further details of the implementation of RNFA can be found in previous publications.[49,50]

We formulate a bi-objective optimization problem that minimizes the carbon loss and the specific cost with respect to the burning heat of the fuel. The carbon loss is defined as the ratio between the molar flow of carbon introduced by the feedstocks and leaving the network with the fuel. In green chemistry terms, the carbon loss can be interpreted as a measure of the atom efficiency of a process, defined for carbon.[50] The optimization problem is subject to mass balance constraints (including yield values for each reaction step, taken from the literature or own experiments) and cost functions, which entail investment and operating costs. The latter costs only cover raw material and waste disposal costs. The molar flow of one fuel component (RLa) is imposed as a constraint, while the output flow of by-products is considered as loss in the carbon loss function. The optimization problem is given by eqn (1).

$$\begin{aligned}&\min_{\bar{f}}\begin{Bmatrix}\text{carbon loss}\\ \text{specific cost}\end{Bmatrix}\\ &\text{s. t.}\quad \text{mass balance (including yields)}\\ &\qquad\quad \text{costs (raw material, disposal, investment)}\\ &\qquad\qquad \text{annual fuel production}\end{aligned}\tag{1}$$

The reaction network implemented is based on König *et al.*[59] and is extended with the alcoholysis step determined experimentally using TMG$_2$e (Table 1) and **Zn1** (Table 2), as well as with further steps for the production of AlOH. The reaction network encompasses renewable production routes from EoL PLA, biomass, hydrogen from electrolysis, and captured CO$_2$ to the corresponding RLa. The constrained optimization problem given by eqn (1) was solved in GAMS version 48.4.0 (ref. 68) using the deterministic global solver BARON version 24.10.10.[69] The epsilon-constraint method[70] was used to incorporate both objective functions in the optimization problem. All new data introduced in this work are reported in the SI.

Results and discussion

Step 1: alcoholysis of PLA to possible fuel candidates

Both catalysts (TMG$_2$e and **Zn1**) investigated in this work proved to be highly active in the alcoholysis of PLA using MeOH and EtOH.[26,60] Using inert conditions, **Zn1** shows high X_{int} and high S_{RLa} towards MeLa, EtLa, BuLa, and iBuLa in THF at 60 °C as well as fast depolymerization of PLA at 150 °C under solvent-free conditions.[26,60]

For this study, we performed multiple alcoholysis reactions yielding the respective RLas using TMG$_2$e under industrially relevant conditions. **Zn1** is applied under inert conditions to

Table 1 Overview of the obtained X_{int}, S_{RLa}, and Y_{RLa} for the depolymerization of PLA (250 mg, 3.47 mmol, 1.00 equiv.) using 15 different Nus (7 equiv.) and TMG$_2$e (1 mol%). Further details can be found in Tables S2 and S3 in the SI

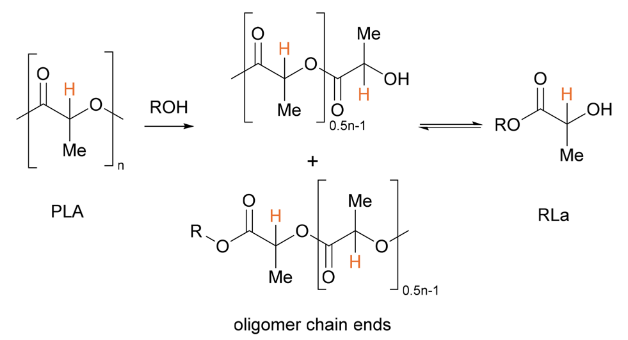
#	Nu	#C[a]	**GP**	t [h]	X_{int}[b] [%]	S_{RLa}[b] [%]	Y_{RLa}[b] [%]
1	MeOH[60]	1	**2**	0.08	100	98	98
2	EtOH	2	**1**	19.5	100	100	100
3	EtOH	2	**2**	24	100	100	100
4	EG	2	**2**	48	100	—	100
5	PrOH	3	**1**	48	100	98	98
6	PrOH	3	**2**	48	100	98	98
7	iPrOH	3	**2**	48	100	45	45
8	AlOH	3	**1**	0.5	100	100	100
9	AlOH	3	**2**	0.42	100	100	100
10	BuOH	4	**1**	48	100	85	85
11	BuOH	4	**2**	24	100	98	98
12	iBuOH	4	**1**	48	100	88	88
13	iBuOH	4	**2**	48	100	96	96
14	*t*BuOH	4	**1**	24	Low amount of oligomers		
15	*t*BuOH	4	**2**	48	Only oligomers formed		
16	PeOH	5	**1**	48	100 ± 0	91 ± 0	91 ± 0
17	PeOH	5	**2**	48	100	98	98
18	3PeOH	5	**1**	48	No reaction		
19	3PeOH	5	**2**	24	Only oligomers formed		
20	HeOH	6	**1**	24	93 ± 4	82 ± 4	76 ± 6
21	HeOH	6	**2**	24	100	98	98
22	Me$_2$BuOH	6	**1**	48	100 ± 0	61 ± 15	61 ± 15
23	Me$_2$BuOH	6	**2**	48	100	71	71
24	BnOH	7	**2**	24	99	100	99
25	OcOH	8	**1**	48	85 ± 7	82 ± 2	71 ± 7
26	OcOH	8	**2**	48	100	93	93

[a] Number of C atoms of the used Nu. [b] X_{int}, S_{RLa}, and Y_{RLa} were calculated from ^{1}H NMR spectroscopic analysis according to the literature.[20,24]

investigate if the metal catalyst and more controlled conditions have a beneficial effect on the catalysis. Thus, only selected Nus (PrOH, iPrOH, and OcOH) are tested. Scheme 2 displays the proposed reaction mechanism for the alcoholysis of PLA. First, the polymer chain is attacked, and oligomeric species with two different chain ends are formed *via* transesterification. The second step is an equilibrium reaction between the oligomers and the desired RLa. We determine X_{int}, S_{RLa}, and the yield of the RLa (Y_{RLa}) using ^{1}H NMR spectroscopic analysis. The methine proton H (highlighted in Scheme 2) enables the determination of the ratio of PLA, oligomer chain ends, and RLa.[71] Since the last step is an equilibrium reaction, small amounts of oligomeric species are still present even after complete conversion of PLA and a prolonged reaction time, often leading to $S_{\text{RLa}} < 100\%$.

Alcoholysis using TMG$_2$e

We evaluate two general procedures, **GP1** and **GP2**, for the alcoholysis of PLA using TMG$_2$e. Table 1 shows selected results of the performed depolymerization experiments. Additional results can be found in Tables S2 and S3 in the SI. Fig. 2 compares the results for the ethanolysis following **GP1** (green) and **GP2** (blue). The lower T and the larger reaction volume led to lower X_{int} and S_{EtLa}. Following **GP1**, we only achieved a Y_{EtLa} of 84% after 6 h, whereas $Y_{\text{EtLa}} = 89\%$ was achieved within 1 h under solvent-free conditions (**GP2**). Nonetheless, within 24 h, both reaction procedures yielded 100% EtLa. Comparing the results for **GP1** and **GP2** using other Nus, a similar trend is observable (Table 1). Especially, for longer chain alcohols (#C atoms ≥ 6), a sufficient S_{RLa} (≤96%) is only achieved following **GP2**. Under these conditions, complete conversion ($X_{\text{int}} = 100\%$) using 13 of the 15 Nus is observed within 24 h (SI, Table S2), and sufficient selectivity is obtained for twelve of the 15 Nus within 48 h. For two Nus (*t*BuOH and 3PeOH), we observe only the formation of transesterification side products in the form of oligomeric species under the harsher reaction conditions and prolonged reaction time. Besides the influence of the reaction conditions, we investigate the influence of the length, branching, and position of the OH-group of the Nu.



Scheme 2 Proposed mechanism for the alcoholysis of PLA. First, oligomeric species are formed in an irreversible reaction step *via* random scission of the polymer backbone. Subsequently, the oligomers are transformed into the RLa in an equilibrium reaction.

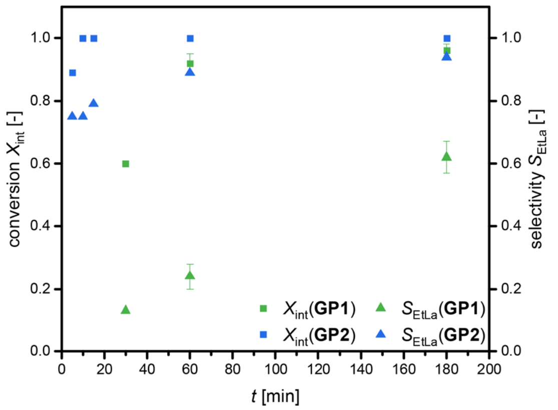


Fig. 2 The comparison of the ethanolysis (7 equiv. EtOH) of PLA (250 mg) using TMG$_2$e (1.0 mol%) following **GP1** (green, THF (4 mL), 60 °C, 260 rpm) and **GP2** (blue, 150 °C, 260 rpm) is displayed. Both reaction procedures lead to high Y_{EtLa} within 24 h ($Y_{\text{EtLa}} = 100\%$, see Tables S2 and S3). Yet, **GP2** shows higher X_{int} of PLA (blue squares) and higher S_{EtLa} (blue triangles) within a given time interval.

First, the influence of the chain length of linear alcohols, ranging from MeOH to OcOH, on the alcoholysis following **GP2** is investigated. In Fig. 3, the results obtained for X_{int} and S_{RLa} are displayed. The reaction is first analyzed as soon as a homogeneous reaction mixture is observed (blue bars, t is noted on top of bar) and after 3 h (purple bars). For all tested primary linear alcohols, high conversions ($X_{\text{int}} \geq 98\%$) within 1 h are achieved. Considering these results, we cannot identify a negative influence of the length of the nucleophile on the conversion of PLA. All alcoholysis reactions reached high conversion of PLA within 35 min. However, as shown in Fig. 3, a decrease in S_{RLa} for C$_2$ to C$_8$ alcohols can be observed. Methanolysis achieves high yields of MeLa within 5 min ($Y_{\text{MeLa}} = 98\%$). An elongation by one CH$_2$ unit to EtOH decreases the S_{EtLa} obtained after 10 min significantly. For better comparability, we determined X_{int} and S_{RLa} calculated after 3 h (Fig. 3, purple bars). We observe high selectivities for five of the seven tested ROHs ($S_{\text{RLa}} \geq 85\%$) except the C$_3$ alcohol PrOH ($S_{\text{PrLa}} = 69\%$) and the C$_5$ alcohol PeOH ($S_{\text{PeLa}} = 77\%$). However, after 24 h, all alcoholysis reactions reach a $Y_{\text{RLa}} \geq 94\%$ except octanolysis. Methanolysis is the fastest proceeding reaction, followed by ethanolysis and butanolysis, which each reach $Y_{\text{RLa}} \geq 96\%$ within 3 h. Considering these results, a significant dependency of the reaction progress on the chain length of C$_2$ to C$_8$ alcohols cannot be observed under the given reaction conditions.

Second, we investigate the alcoholysis using branched alcohols. Fig. 4 displays the results obtained from the alcoholysis of PLA (**GP2**) using PrOH, iPrOH, BuOH, iBuOH, PeOH, HeOH, and Me$_2$BuOH after 1 h. The results for *t*BuOH and 3PeOH cannot be visualized, since only very low depolymerization activity was observed. Comparing iBuOH and BuOH, a severe negative effect of the branching for **GP1** (Table 2, entries 10 and 12) is observed, leading to incomplete depolymerization of PLA within the 48 h timeframe. Following **GP2**, the effect is less severe but leads to a decrease in X_{int} and S_{iBuLa} compared to the unbranched BuOH ($t = 1$ h, Fig. 4). For the analysis of the alcoholysis using the C$_6$ alcohol Me$_2$BuOH, we had to isolate Me$_2$BuLa first, since only limited (spectroscopic) data are available. Therefore, the

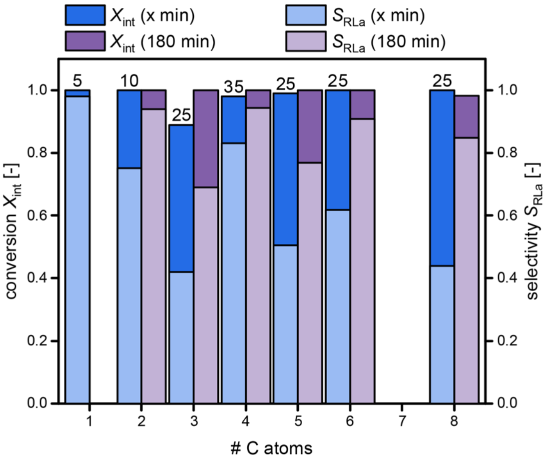


Fig. 3 Comparison of X_{int} and S_{RLa} achieved by alcoholysis of PLA using linear C_1 to C_8 alcohols under **GP2** after a homogeneous reaction mixture is first observed (blue) and after 3 h (purple).

alcoholysis using Me_2BuOH following **GP2** was adjusted to a 2.00 g-scale of PLA (27.8 mmol, 1.00 equiv.) using TMG_2e (1.03 mol%, 73.7 mg, 288 μmol). The reaction was performed at 150 °C under reflux conditions and with a reduced amount of Me_2BuOH of 3.0 equiv. (10 mL, 82.6 mmol). The adapted reaction conditions lead to similar results to those obtained in the small-scale experiments, and we could achieve a PLA conversion of 100% within 24 h ($Y_{Me_2BuLa} = 57\%$). After 48 h, the determined Y_{Me_2BuLa} amounted to 75%, which is comparable to the results of **GP2** (Table 1, entry 23). After isolation of Me_2BuLa, the compound was identified using 2D NMR spectroscopic analysis, assigning the resonances in the ^1H NMR spectrum to enable the analysis of the alcoholysis performed. After 1 h, Me_2BuOH shows comparable X_{int} and S_{RLa} to iBuOH. However, Me_2BuOH is the only primary alcohol reaching insufficient S_{RLa} after 48 h. Its linear analogue HeOH achieved a S_{HeLa} of 98%, whereas we obtained only a low S_{Me_2BuLa} of 71% after 48 h.

We propose that the increased steric complexity of the alcohol aggravates the scission of the PLA backbone. Further, the reaction between oligomer chain ends containing an iBu or Me_2Bu residue and the corresponding branched alcohol could hinder the formation of iBuLa or Me_2BuLa further due to the bulkiness of the reaction partners.

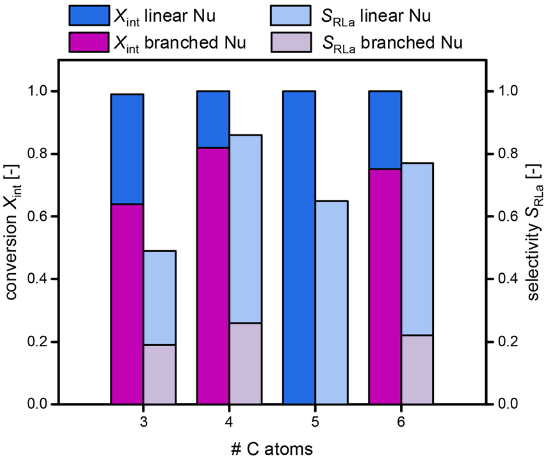


Fig. 4 Comparison of X_{int} and S_{RLa} achieved by alcoholysis of PLA using linear and branched alcohols under **GP2** after 1 h.

Third, the influence of the position of the OH group was investigated by comparing primary with secondary or tertiary alcohols (Fig. 4). The position of the OH group severely influences the alcoholysis and only low conversions can be observed. iPrOH only reaches a low S_{iPrLa} of 45% after 48 h compared to its primary isomer ($S_{PrLa} = 96\%$). For the secondary alcohol 3PeOH and the tertiary alcohol *t*BuOH, only oligomerization was observed within a 72 h timeframe.

The ^1H NMR analysis was complicated by resonance overlapping of the different species. Although gel permeation chromatography could provide further insight into the species formed, the low reactivity of both alcohols rendered them unsuitable for further investigations. Consequently, no additional analytical methods were applied. Changing the structural properties of the alcohol not only influences S_{RLa} but also decreases X_{int}.

We conclude that using TMG_2e, the reactivity is mostly influenced by the steric encumbrance of the alcohol, especially if secondary or tertiary alcohols are used. The chain length has only a smaller influence on the PLA conversion.

Furthermore, AlOH, BnOH, and EG as Nus for the depolymerization of PLA are investigated. A yield of $Y_{AlLa} = 100\%$ within 30 min following **GP1** and within 25 min following **GP2** is achieved. The double bond accelerates the reaction significantly: the C_3 alcohol performes better than EtOH. High BnLa yields are achieved following **GP2** within 25 min ($Y_{BnLa} = 85\%$). We cannot observe oligomer formation using BnOH. Thus, we propose that BnOH attacks the end of the polymer chain directly and only BnLa is formed.[72] The glycolysis using EG shows promising results. However, due to overlapping resonances in the ^1H NMR spectrum, a quantitative analysis is not feasible in $CDCl_3$. Yet, we are able to determine $Y_{EGLa} = 100\%$ after 48 h using ^1H NMR spectroscopic analysis in DMSO-d_6. These results are in good accordance with prior studies.[61,63] To summarize, primary linear nucleophiles are more suitable for industrial applications, but changing the structure of the alcohol, *e.g.*, implementing a double bond, can yield a positive influence on the depolymerization reaction using TMG_2e.

Alcoholysis using $[Zn(DMEG_2ch)_2](OTf)_2 \cdot THF$ (Zn1)

Besides depolymeriozation using an organocatalyst, the metal-catalyzed alcoholysis of PLA under inert conditions was investigated. The alcoholysis was performed according to **GP2** using Schlenk techniques (**GP2***) to avoid air and water contamination. OcOH is chosen to gain insight into the influence of a long alkyl chain on the alcoholysis using a metal catalyst.

Using **Zn1** leads to high Y_{RLa} within a short time span ($t = 1$ h) for all investigated RLas (Table 2). Compared to TMG_2e, EtOH and MeOH show similar results. The alcoholysis using **Zn1** is not significantly hindered by the elongation of the chain length from a C_2 to a C_8 alcohol or using the secondary alcohol iPrLa following **GP2***. **Zn1** is able to depolymerize PLA selectively to PrLa, OcLa, and iPrLa within 1 h ($S_{RLa} \geq 98\%$). Thus, the metal

Table 2 Overview of the obtained X_{int}, S_{RLa}, and Y_{RLa}, for the depolymerization of PLA (250 mg, 3.47 mmol, 1.00 equiv.) using five Nus (7 equiv.) and **Zn1** (1 mol%) under inert conditions

#	Nu	#C[a]	GP	t [h]	X_{int}[b] [%]	S_{RLa}[b] [%]	Y_{RLa}[b] [%]
1	MeOH[26]	1	**2***	0.8	100	98	98
2	EtOH[26]	2	**2***	0.25	100	100	100
3	PrOH	3	**2***	1	100	98	98
4	iPrOH	3	**2***	1	100	98	98
6	OcOH	8	**2***	1	100	98	98

[a] Number of C atoms of the used Nu. [b] X_{int}, S_{RLa}, and Y_{RLa} were calculated from ^1H NMR spectroscopic analysis according to the literature.[20,24]

catalyst **Zn1** is better suited for the depolymerization of PLA using more challenging alcohols than the organocatalyst.

Discussion of experimental results

The performed fast-screen alcoholysis and glycolysis of PLA show that unbranched, shorter chain Nus are the most promising candidates for PLA depolymerization. **Zn1** proves to be more effective using branched iPrOH as well as OcOH (C_8) and shows higher selectivity within 1 h compared to TMG_2e for all investigated Nus except MeOH. Nonetheless, TMG_2e is highly effective in the alcoholysis of PLA, reaching high conversion ($X_{int} \geq 98\%$) for all linear Nus within 1 h (Table S2) under industrially relevant conditions.

From a synthetic standpoint, we see fast conversion of PLA for all primary alcohols within a reasonable time frame. Considering the successful scale-up of the ethanolysis using TMG_2e, the robustness of the catalyst against post-consumer waste, the range of applications, and the aspects of green chemistry, EtLa is one of the most promising RLas with a high technology-readiness level. Overall, twelve RLas qualify as feasible candidates from our preliminary experimental analysis, using both TMG_2e and **Zn1**, and are therefore further analyzed in the subsequent fuel property evaluation (step 2) and production pathway analysis (step 3).

Table 3 Ignition properties and selected thermophysical properties of the fuel candidates considered in this work

#	RLa[a]	DCN	RON	NBP [°C]	MP [°C]
1	MeLa	13	110	169	−39.5
2	EtLa	13	111	179.1	−43.6
3	EGLa	12	104	259.3	3.9
4	PrLa	14	104	194.2	−45.7
5	iPrLa[b]	14	110	185.9	−27.5
6	AlLa	11	104	195	−39.9
7	BuLa	17	97	215	−39.2
8	iBuLa	14	105	205.5	−31.4
9	PeLa	21	88	234.9	−39.3
10	HeLa	26	74	249.5	−23.5
11	BnLa	12	109	293.8	25.8
12	OcLa	37	44	282.6	−28.2

[a] Applied values received using TMG_2e as the catalyst. [b] Applied values received using **Zn1** as the catalyst.

Step 2: evaluation of the alkyl lactates as fuel candidates

Following our fast-screening strategy, from the 15 RLas investigated experimentally in step 1, the twelve promising candidates are investigated considering relevant fuel properties in step 2. Each candidate is evaluated through predictive models that map the chemical structure of the components with relevant properties. The properties calculated in our analysis are shown in Table 3. The predicted values of the ignition and thermophysical properties in Table 3 follow specific structural correlations, which confirm the physical soundness of the employed models. Considering linear RLas (*i.e.*, from MeLa to OcLa), the predicted RON decreases with increasing chain length of the alcohol substituent, which is expected and known, for example, from the RON value of linear alkanes.[73]

All the branched, aromatic, and oxygenated RLas give higher values of the predicted RON than RLas with long-chain substituents, which can be explained by their more compact structure. The same interpretation can be drawn for the NBP, which is correctly predicted to increase with increasing size of the considered molecules and is higher for linear molecules than for their branched or compact counterparts.

Fuel property screening results

Considering the limit imposed on the ignition properties, none of the RLas listed in Table 3 satisfy the DCN requirement, whereas almost all RLas satisfy the RON requirement, except for HeLa and OcLa. Notably, eleven RLas exhibit RON values greater than 100. Given that the common European SI engine fuel standard requires a RON of 95,[65] the RLas are promising candidates to balance more low-octane blend stocks.

Most of the RLas satisfy the MP criteria, except for EGLa. All RLas exhibit the minimum NBP. However, the upper limit of 220 °C for the NBP further excludes PeLa as a fuel blend candidate and yields the final list of suitable fuel blend

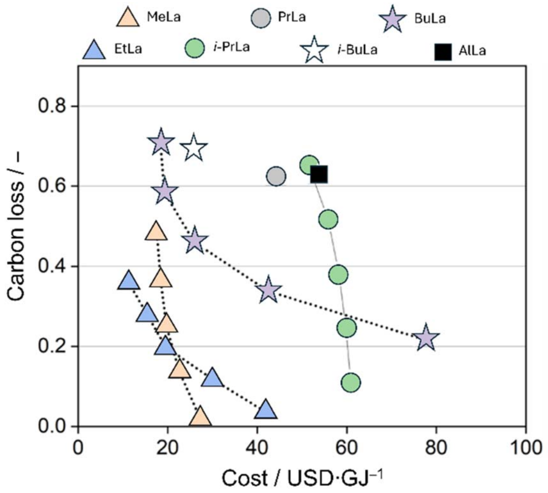
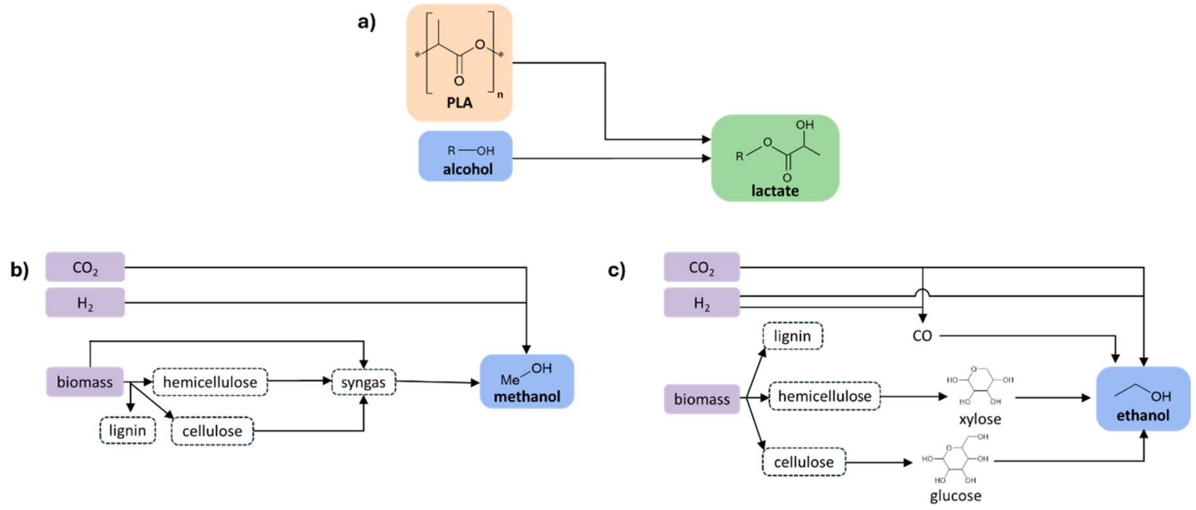


Fig. 5 Collection of the Pareto front for each of the RLas determined by RNFA as a solution to the optimization problem given by eqn (1). Values of the selectivity are taken from the experiments with the organocatalysts, with the exception of iPrLa, for which data from experiments with the **Zn1** are considered.



Scheme 3 Optimal production pathways determined by the optimization algorithm as a solution to the bi-objective optimization problem given by eqn (1). (a) General scheme of the alcoholysis of PLA; (b and c) reaction subnetworks to produce the respective alcohols for the methanolysis and ethanolysis. A more comprehensive scheme including all alcohols investigated in step 3 is available in Scheme S2 in the SI. Each solution on the Pareto front corresponds to one or a combination of multiple pathways through the network from raw materials (biomass, CO_2, and hydrogen) through the respective alcohols to the final RLa.

candidates for the subsequent RFNA analysis: MeLa, EtLa, PrLa, iPrLa, BuLa, iBuLa, and AlLa.

Step 3: early-stage pathway screening from raw materials to fuel candidates

Fig. 5 shows the results of the bi-objective optimization problem given by eqn (1) in the form of a Pareto front for each of the seven most promising fuel candidates. In general, there are multiple pathways from raw materials to form the final RLa, with each pathway having its own value of the objective functions in eqn (1). Each point along a Pareto front corresponds to a specific flux combination that leads to the final RLa in the reaction network. A constant RLa production is imposed as a constraint in eqn (1), while the required amount of feedstock varies among the pathways and is reflected in the respective carbon loss. For the products MeLa and EtLa, the collection of all pathways from the raw materials to the products is shown in Scheme 3. While the alcoholysis reaction step (Scheme 3a) is the same for all RLas and only differs by a slightly different reaction selectivity (Table 1), the production pathway of the respective alcohol (Schemes 3b and c) significantly determines the values of carbon loss and the cost function of a specific production pathway.

Discussion of pathway screening results

In general, production pathways that use CO_2 and hydrogen as raw materials are characterized by a lower carbon loss (*i.e.*, material conversion efficiency) and a higher specific production cost than pathways that start from biomass, as observed previously.[51] Overall, MeLa and EtLa stand out as the best candidates from both an economic and environmental point of view. Other alcoholysis studies point toward the same conclusion with respect to the chosen alcohol.[42,74–76] In our study, this can be explained by the existence of an efficient synthesis pathway from renewable CO_2 and hydrogen or from lignocellulosic biomass to the required alcohols EtOH and MeOH, while the production of the higher alcohols involves several intermediates or does not use all biomass fractions, *e.g.*, lignin, cellulose, and hemicellulose. Moreover, long-chain alcohol molecules make a substantial contribution to the molecular weight of the RLa. Thus, their production pathway impacts the cost and carbon loss functions more than short-chain alcohols. According to our analysis, EtLa outperforms MeLa regarding economic and environmental criteria when biomass is used as feedstock. Being produced through biomass gasification, the biomass-based production pathway of MeOH is characterized by a poorer carbon efficiency than the biomass fermentation pathway used to produce EtOH. At the same time, production routes from renewable CO_2 and hydrogen allow a more efficient production of MeLa, particularly because MeOH production from these feedstocks is less energy intensive and has, therefore, according to the employed cost correlation in RNFA, a lower impact on the investment costs than the production of EtOH. These results partly reflect our expectations for the well-characterized EtOH and MeOH pathways, yet the RNFA offers enhanced quantitative resolution, revealing nuances and subtle differences in pathway performance among all studied candidates.

Conclusion

We evaluated and established a new integrated recycling route using PLA and biomass as feedstocks for novel green fuel candidates. By combining predictive property models (step 2) and early-stage pathway screening methods (step 3) with fast and robust depolymerization catalysts for the alcoholysis of PLA (step 1), we were able to screen 15 RLas as possible fuel candidates. The experimental results performed in step 1 established twelve alcohols as suitable Nus for the depolymerization of PLA using the organocatalyst TMG_2e and bisguanidine metal catalyst **Zn1**. Thus, we report successful recycling of PLA using multiple readily available Nus. Since the fast screening of multiple RLas on a small scale was the main goal of step 1, future work should focus on the scale-up of the most promising recycling processes as well as on catalyst recycling strategies. Another relevant factor for the transition from the laboratory scale to larger scales is testing post-consumer or post-industrial PLA waste materials or mixed waste streams containing PLA. The chemical structure analysis performed in step 2 established the seven RLas MeLa, EtLa, PrLa, iPrLa, BuLa, iBuLa, and AlLa as promising fuel candidates due to their high RON and suitable physical properties. These candidates were then analyzed in step 3, concerning cost and carbon loss following multiple production pathways of the alcohols used, resulting in MeLa and EtLa as the most promising fuel candidates for an integrated recycling strategy. MeLa and EtLa already have multiple applications, *e.g.*, as green solvents or as starting material for lactide. The usage of MeLa and EtLa as fuel expands their possible applications in a complementary way by offering a solution for low-quality product fractions. With this three-step screening approach, we present a new integrated, ready-to-scale recycling strategy for PLA to green fuel candidates using bisguanidine catalysts. LCA is generally the appropriate methodology to evaluate the full environmental impact of a molecule. However, LCA requires extensive data, which is rarely available for novel molecules and processes in the early stage of their development. In this context, our rapid screening approach enables the identification of promising fuel candidates using minimal input data. These candidates can then be prioritized for LCA, detailed simulation, property validation, and scale-up experiments. After demonstration of this approach for the design of fuel candidates and their optimal production pathway, this framework is generally applicable and not limited to a specific product. By redefining target properties and screening criteria, it can be used to design integrated recycling processes, for example, to produce virgin-grade polymers or platform chemicals for other processes.

Author contributions

L. B. and T. B. conceived, designed, performed, and evaluated the experiments in the laboratory. P. A. performed the evaluation of fuel properties of the obtained alkyl lactates. M. A. and M. P. performed the RFNA. M. A. and L. B. wrote the initial draft of the manuscript. S. H.-P. and A. M. supervised the project progress and provided the funding. All authors contributed to the final manuscript by discussion, editing, and reviewing.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

Original data (NMR spectroscopy) are available in the Chemotion Repository and are published under an Open Access model (CCBY-NC-SA 4.0 Attribution-NonCommercial-Share). The original data for step 1 can be found in the Chemotion Repository under https://doi.org/10.14272/collection/LB_2025-09-05. Further experimental data as well as data of the pathway screening method are given in the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d6se00361c.

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