Simulated Moving Bed Reactor to Valorise Glycerol into Solketal: Coupling Green Chemicals and Process Intensification

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Highlights

- Solketal, a potential fuel additive, reduces the global glycerol gut.
- SMBR is a sorption-enhanced reactive technology able to overcome thermodynamic limitations.
- Conventional SMBR for solketal synthesis performs poorly, alternative operations work better.
- Experimental validation of SMBR solketal production is pioneering for scaling up the process.

1. Introduction

Solketal is one of the most promising solutions for glycerol valorisation due to its properties as diesel additive, with the capability of enhancing fuel octane number and oxidation stability, diminishing particle emissions and gum formation, and enhancing properties at low temperatures. Furthermore, solketal has the potential to be used as jet fuel additive due to its anti-freezing property. Reinserting solketal in the biodiesel production chain complies with the Circular Economy model, which is of great economic and environmental interest [1].

The reaction for solketal synthesis is reversible, thus the conversion is thermodynamically limited. The SMBR stands out as a sorption-enhanced Process Intensification strategy able to improve the efficiency of reactive systems by combining separation by adsorption and chemical reaction using a hybrid stationary phase with catalytic activity and adsorption selectivity between the products. This way, by adsorbing one of the products, the reaction equilibrium shifts towards product formation.

In the Conventional SMBR, a feed stream composed of a reactive mixture is fed to a four-section unit, with synchronous time switch (t*) and constant flow rates. Unlike most SMBR processes, for solketal synthesis, none of the reactants can be used as desorbent, due to miscibility issues. For this reason, two non-conventional strategies were developed, the Multifeed, where the reactants are fed in different positions, and the ModiCon SMBR, where the reactants are fed at different moments of t*. Both strategies take advantage of the different affinities of the reactants with the stationary phase to promote their countercurrent contact, maximize their interaction, and, consequently, solketal's output.

In practice, to implement all these operations, it is necessary to build a highly versatile unit. The valve system strategy is a key factor in ensuring the flexibility of the unit. The distributed valve design was selected for the novel pilot scale unit built at LSRE-LCM, the Supercritical Fluid Simulated Moving Bed Reactor (SF-SMB(R)), where the experimental validation of solketal synthesis was performed.

2. Methods

The optimizations of the Conventional and Five-section SMBR were performed following the two-step procedure proposed by Faria et al. The TMBR steady-state model is used to find the feed and extract flowrates, and solid velocity (decision variables) that result in the maximum productivity (objective function), under the purity constraints of 97% (desorbent free) for solketal in the raffinate and water in the extract stream. In the first step, the optimal unit configuration (number of columns in each section) was defined. Then, for the best column configuration, a sensitivity analysis was carried out to the safety factor (SF) applied to sections 1 and 4 (solid and liquid regeneration sections) [2].

The ModiCon SMBR is a dynamic operation, therefore it requires the equations to be solved dynamically until reaching the cyclic steady state. This makes it unviable to reproduce the method that relies on the steady-state model. The rigorous SMBR must be used instead. Thus, the column configuration and SFs that achieved the highest productivity in the Conventional SMBR and the t* that achieved the highest in the Five-section SMBR were used as inputs for the ModiCon. The model equations were solved using gPROMS ®, v. 7.0.7.

The SMBR simulation studies and the experimental validation were performed in the SF-SMB(R). This unit comprises eight fixed-bed columns with 15 cm in length and 2.12 cm in diameter.

3. Results and discussion

The best column configuration for the Conventional SMBR is the 1-2-4-1. Since acetone is carried in the direction of the fluid flow, most of the reaction takes place in Section III, and this reactant is present in significant amounts only in the column immediately before the feed port, therefore there is no need for more than two columns in Section II. The reaction thermodynamic limitation is what hinders the performance of the Conventional SMBR since it is necessary more columns in the sections where the reaction occurs. As for the regeneration sections, only one column in each section is necessary. The combination of SF that achieves the highest productivity and that provides a sufficient T/SMBR equivalence is 40% in Section I and 15% in Section IV. At this point, t* is 25.7 min, the productivity is 1.086 $kg_{Solk}{\cdot}L_{Ads}{}^{-1}{\cdot}day^{-1}$ and the DC is 26.24 $L_{Desorbent}{\cdot}kg_{Prod}{}^{-1}$.

The study on the column configuration of the Five-section SMBR reveals that the reaction and the separation of acetone and solketal take place almost exclusively in Section IIIB, and the performance is strongly driven by the available reactive region. The configuration that maximizes the number of columns in Section IIIB is 1-1-1-4-1. The combination of SF that achieves the highest productivity and that provides a good T/SMBR equivalence is 40% in Section I and 25% in Section IV. At this point, t* is 23.14 min, the productivity is 7.03 $kg_{Solk}{\cdot}L_{Ads}{}^{-1}{\cdot}day^{-1}$, with DC is 5.02 $L_{Desorbent}{\cdot}kg_{Prod}{}^{-1}$. Also, the reactants feed ratio is 1.03, which results in an excess of acetone of nearly 5%.

For the ModiCon operation, such acetone excess is granted when glycerol is fed during 49% of the t* and acetone in the remaining time. The performance of the ModiCon SMBR is slightly superior to the Five-section SMBR. Using the t* of 23.14 min and a combination of SF of 40% and 25%, the productivity reaches 8.13 $kg_{Solk}{\cdot}L_{Ads}{}^{-1}{\cdot}day^{-1}$, with DC of 4.30 $L_{Desorbent}{\cdot}kg_{Prod}{}^{-1}$.

The SF-SMB(R) was built in a way that to implement the non-conventional strategies, it is only required to select it in the software, with almost no intervention in the physical equipment. The advantage of the ModiCon SMBR over the Multifeed is that its operation is slightly more robust.

4. Conclusions

The productivity results of both non-conventional operations are within the range reported for similar processes and prove that solketal may be produced by a continuous chromatographic reactor. The major advantage of using such strategies is the possibility of operating with higher flow rates and, consequently, obtaining better performance parameters. It is noteworthy that between the proposed non-conventional operation, the ModiCon strategy can achieve a productivity 14% higher due to being able to process an even higher feed flow rate while achieving a DC 14% lower.

Despite the Conventional SMBR performing poorly, experimentally validating it is a groundbreaking step in solketal production and indeed the first step to implementing this process on a large scale.

References

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Keywords

Solketal; Simulated Moving Bed Reactor; Green Chemistry; non-conventional SMBR.