SCALE-UP OF VISIBLE LIGHT ORGANO-PHOTOCATALYTIC SYNTHESIS REACTIONS IN A SPINNING DISC REACTOR

Abstract

The field of visible photocatalysis has been advancing in its quest to utilize sunlight or low-energy lighting for various transformations, specifically by exploring organic catalysts as alternatives to toxic and expensive metal catalysts. However, the upscaling of these reactions has presented a formidable challenge due to the requirement for high area - volume ratios. This challenge is driven by the diminishing penetration of light as the depth of the solution increases. To tackle this obstacle, one promising approach involves the use of high surface area reactors, such as spinning disc reactors (SDRs).

A recent article introduces the initial investigation comparing the performance of light-activated SDRs with a conventional reactor, with the goal of identifying crucial parameters for scaling up. The study is centered on two oxidation reactions that employ an economical organic dye catalyst, distinguishing between scenarios where either mass or photons are limiting. These experiments are conducted using a custom-built solar device.

The key factors influencing the rate constants of reaction kinetics and productivity (measured in unit-mmol h^−1) are the surface area of the spinning disc, the intensity of the light, and the flow rate. A comprehensive examination of disc patterns has revealed optimal flow configurations that further boost the efficiency of the SDR.

The robustness of these findings is verified by outdoor experiments, which yield similar results. This research paves the way for the scalable implementation of visible light photocatalytic reactions, holding the potential to substantially reduce energy consumption and shift industrial chemistry away from its dependence on fossil fuels. This advancement represents a promising stride toward more sustainable and environmentally friendly chemical processes.

Introduction

Over the last decade, the chemical industry has experienced a significant transformation with a strong emphasis on developing environmentally friendly products and processes, while

simultaneously improving product quality and reducing waste. In pursuit of these transformative objectives, researchers have delved into the realm of solar photocatalysis, a method that expedites light-induced reactions catalyzed by a substance in the presence of sunlight. This approach offers several advantages, including milder reaction conditions, the elimination of the need for heating the entire system, and improved control over product selectivity, all of which contribute to a healthier environment for conducting photocatalytic synthesis reactions.

Traditionally, photo-reactors have been characterized by enclosed energy sources, making them unsuitable for harnessing solar energy. In contrast, Spinning Disc Reactors (SDRs) offer a promising alternative. SDRs can operate with an open surface, allowing them to adapt to both LED and natural lighting setups. A key distinguishing feature of SDRs is their capacity to generate thin films ranging from 20 to 200µm, a unique characteristic resulting from the disc's rotation due to centrifugal force. The creation of these thin films is essential to overcome photon limitations, enabling optimal light penetration in the solution.

Studies have demonstrated that SDRs are highly efficient in utilizing incident light, leading to improved photonic efficiency and volumetric reaction rates compared to other reactor configurations. Additional advantages include enhanced heat and mass transfer, negligible pressure drop on the disc surface, and a higher surface area-to-volume ratio. The thin films on the disc's surface facilitate short diffusion and conduction pathways, maximizing the rate of transport within the film.

While SDRs have found applications in various fields, such as polymerization, crystallization, and nanoparticle synthesis, limited literature is available regarding their use in pharmaceutical and fine chemicals synthesis combined with solar light photocatalysis. Previous research has shown that SDRs can achieve faster reactions with shorter residence times compared to traditional stirred vessels. However, challenges have arisen in maintaining product selectivity in certain reactions, particularly when compared to batch processes. Previous studies in visible light photocatalysis have even suggested that batch stirred reactors outperform SDRs, primarily due to limited exposure.

The fundamental goal of this research is to assess the productivity of SDRs in comparison to batch stirred reactors under varying reaction-to-reactor operation parameters and to understand how this knowledge can be applied for scale-up. The research will examine the impact of different operating conditions, such as flow rate, spinning speed, and disc size, on two types of reactions: (i) photo-transfer-limited and non-mass-limited reactions involving the oxidative homocoupling of benzy-lamine to benzy-lidene-benzylidine, and (ii) mass-limited reactions involving the photocatalytic oxidation of methionine. Visual evaluations of disc flow patterns will also be conducted for various feed flow rates and rotating speeds. Furthermore, in Spain, these reactions will be investigated using natural sunlight.

In summary, the study aims to shed light on the efficiency of SDR in comparison to bat-ch stirred reactors and explore how these insights can be applied for scale-up, potentially revolutionizing the way pharmaceutical and fine chemical reactions are conducted and contributing to a more sustainable and environmentally friendly chemical industry.

Methodology and Material

Over the past decade, the chemicals industry has witnessed a substantial transformation, with a heightened focus on developing environmentally friendly products and processes. Many solvents and reagents were used without additional purification. For instance, benz-ylam--ine (98%) and L-met-hioni-ne (≥ 99%) were acquired from Alfa reactive sampling is systematically used to estimate model expectations, with a crucial parameter, βeff, influencing this process. The SDRs parameters undergo iterative updates with a focus on minimizing the reconstruction loss between the input and the reconstructed data vectors. The outcome of this quantum generative training process is a higher-level abstraction of historical process data, serving as input for the subsequent classifier.

Most plastics contain additives designed to increase performance and durability. These additional materials, which include various protective measures for food packaging, have been studied extensively. Regarding the problems caused by these additives, they usually need to be removed by solvent removal, which involves washing the plastic waste with suitable solvents or supercritical fluid. Additionally, inks, pigments, heavy ingredients, and secondary materials in plastic can also cause problems with pyrolysis oil. To reduce these mishaps, effective identification and removal of impurities in plastic composites is important and is often accomplished through pretreatment and cleaning procedures that may include the use of cold and/or hot water, detergents, and caustic solutions.

As for discriminative training, the elevated-level abstractions originating from the Batch and SDR sub-networks are concatenated and collectively serve as input for the local classifier. The local classifier exhibits the architecture of a neural network, proficiently predicting the probabilities associated with normal and misbehaving states. This network configuration incorporates fully connected layers alongside a decent layer. The model parameters are meticulously fine-tuned by employing the backpropagation algorithm in adherence to a supervised learning paradigm. The essence of this training process revolves around the minimization of the categorical cross-entropy loss, an endeavor that ensures maximum likelihood parameter estimation.

Both the batch an SDR sub-networks were designed with an identical architecture to create abstractions for normal and faulty states. In the initial rotating disc layer of these sub-networks, there were 52 visible Gaussian units and 26 hidden Bernoulli units, resulting in an output generated through a simple perceptron operation. The subsequent RBM layer was equally intricate, composed of 26 visible units derived from the hidden units in the previous layer, along with an additional 20 hidden units, producing an output using binomial distribution-based sampling. Reaction generative training was carried out for these Batch and SDR sub-networks,

with specific parameters, including a learning rate set at constant level and a constant momentum value of one.

In the final version of the model, the sub-network undergoes a one-time training phase and can be efficiently applied to multiple diagnostic processes. When it comes to determining the state of a new process data sample, the abstractions derived from both normal and faulty states, generated by the Batch and SDR based generative model, are thoughtfully fused. At this juncture, the local classifier comes into play, offering its predictions in the form of probabilities that indicate whether the sample should be classified as normal or faulty. This classification is substantiated by implementing a threshold probability of 0.5, finalizing the data sample's categorization.

Experiments were conducted under natural sunlight in Ciudad Real, Spain. A new reactor configuration was designed for use with real sunlight, optimizing its performance with different light sources. The SDR platform was angled at 24° to directly capture solar radiation and eliminate shadows on the disc. Throughout the experiments, the platform tracked the sun's path. A glass lid and reservoir covering were used to prevent solution evaporation and light exposure. Both homo-coupling and L-methi-onine oxidation reactions were carried out in a batch reactor (190 mm crystallizing dish) and in SDRs, with comparisons to experiments using a solar light simulator.

The homocoupling reaction was investigated in both a batch stirred reactor and a continuous stirred-tank reactor (SDR). Two different amine concentrations and reactor volumes were examined. The reactions were conducted at room temperature with a specified amount of Eosin catalyst, a disc spinning speed, and a flow rate. In the batch reaction, normal temperature was maintained using a water bath, while the SDR was operated under similar temperature conditions.

The L-methi-onine oxidation reaction in the batch setup involved two different L-methionine concentrations and a specific catalyst concentration. In contrast, in the SD, only one L-methi-onine concentration was explored. The batch reaction was performed in a stirred vessel with a defined stirring speed, while the SDR operated with a specific flow rate and spinning speed.

Additionally, in both batch and SDRs experiments conducted under sunlight, no external oxygen supply was provided. The SDR reservoir was shielded with aluminum foil to protect the reaction solution from light exposure.

Results and Discussion

A Design of Experiments (DoE) consisting of 36 experiments was conducted to determine the key factors influencing the photocatalytic oxidative homocoupling of benzylamine within the context of the Spinning Disc Reactor (SDR). The experimental data were found to adhere to a

first-order kinetic model, enabling the calculation of a pseudo-first-order rate constant referred to as "kobs." This kobs value served as a valuable metric for assessing the significance of various factors in the reaction.

This research presents a beautiful chemical reaction-powered approach for fault processing in intricate industrial processes. By integrating SDR generative training with classical discriminative training, we aimed to enhance the detection and diagnosis of various faults. The model underwent rigorous testing on two distinct industrial processes, surpassing the performance of established methods. This highlights the promising potential of SDR computing in advancing fault diagnosis within reactor settings.

Reaction condition significance

The data analysis is visually represented through a Parto chart and a Normal plot (Fig. 4b), where significant factors are determined based on a reference line, taking into consideration a predefined significance level. When the response variable is the rate constant in the photocatalytic oxidative homocoupling of benzy-lamine within the SDR, the results unveil the most influential factors, listed in descending order of significance as follows: disc size, light intensity, and flow rate. Furthermore, the interaction between these factors and disc size is also of substantial importance.

On the other hand, factors like amine concentration, catalyst loading, and rotating speed, while individually important, exhibit a more pronounced influence when considered in conjunction with other factors, as indicated by their interactions. This underscores the critical importance of selecting the right combination of reaction conditions to optimize the system, minimize waste, and reduce operational costs.

It's worth noting that these findings contrast with previous reports by Tibbetts, where in a batch stirred reactor, single factors held more significance than their interactions. This underscores the unique behavior of the Spinning disc reactor system and its distinct interplay of factors. In summary, these insights underscore the necessity for a customized approach to selecting reaction conditions within the SDR, highlighting the potential for enhanced efficiency and cost reduction.

Surface area’s role

The significance of maximizing surface area was clearly evident, underscoring the Spinning Disc Reactor (SDR) as a superior choice for upscaling reactions. The SDR's ability to create a thin film on the disc surface results in a larger surface area, which enhances photon exposure, especially beneficial for photon-transfer-limited reactions.

The rationale behind deploying these two separate Batch sub-networks lies in accommodating the inherent variations in feature extraction from each sub-network. This approach inherently

yields more dependable outcomes compared to a single SDR, thanks to its superior feature extraction capabilities.The amount of training needed depends on Spinning disc reactor complexity and the training algorithm intricacies. A common guideline suggests having a dataset size at least ten times larger than the number of input dimensions. Analyzing the relationship between dataset size and model performance helps determine the right dataset size for the desired level of accuracy.

However, this remarkable increase in the reaction rate is likely due to more than just surface area. It's plausible that a combination of factors, including issues related to flow development for smaller discs and alterations in flow dynamics across various spinning speeds, also plays a role in influencing the reaction rate. Visual studies using a high-speed camera were conducted to observe differences in thin film formation on the disc's surface under varying flow rates, spinner velocity, and disc diameter. These visual observations will shed light on the intricate interplay of these factors in shaping the reaction rate.

Flow pattern influences

A high-speed camera was utilized to investigate how varying flow rates and rotational speeds affect the structure of the thin film on the surface of the Spinning Disc Reactor (SDR). This investigation is of particular interest because these factors can significantly influence the reaction rate.

The accompanying figure illustrates the thin films formed under different combinations of flow rates and rotational speeds, with observations captured within the initial minute of the reaction.

At the lowest flow rate , distinct standing wave patterns emerge, but they do not completely cover the entire disc surface, resulting in the absence of a formed film. As the rotational speed increases, these wave patterns grow in magnitude.

Conversely, when higher flow rates are combined with lower rotational speeds, singular waves originate from the nozzle. As the flow rate continues to increase, the formation of a complete thin film across the disc surface becomes notably faster. Notably, the presence of standing waves becomes more pronounced at flow rates of 4 and 5 mL s^−1 when paired with a rotational speed of 150 rpm. Increasing the spinning speed results in a more uniform flowing rate, decreasing light reflection and scattering. Consequently, this enhances the penetration of light into the photocatalyst, leading to an increase in the reaction rate. However, it's important to note that higher spinning speeds reduce the residence time of the solution on the disc, potentially making the change light particle-limited.

Furthermore, the study indicates that standing waves are a result of an asymmetry in the annular outlet gaps in the nozzle, underscoring the importance of precise nozzle construction to ensure smoother flow. Additional experiments corroborated the significance of maintaining a steady and

voluminous flow across the disc's surface, as low flow rates hinder uniform thin film formation, reducing the SDR mixing capability.

In the case of complex process systems, such as those analyzed in the study, it shows high detection rates and fewer false positives. This model can be applied broadly to nonlinear complex process systems with minimal adjustments. Photon advantages, including faster convergence and computational speed, provide a competitive edge, particularly as the number of process variables increases.

In conclusion, quantum generative training offers a more efficient and rapid training approach for SDRs compared to classical methods, making it particularly valuable in complex systems where accuracy and speed are essential.

SDR vs Batch Reactor

The study delved deeper into the influence of various factors on reactor performance. In particular, it examined how varying amine concentrations (ranging from 50 to 60 mM), different volumes (ranging 250 to 1000 mL), and varied surface areas (ranging from 20 to 500) affected reaction rates in both batch stirred reactors and SDR setups. These parameters were found to impact how light interacts with the reacting mixture, taking into account factors such as opacity, depth, and illuminated area.

comes with its constraints since it doesn't adhere to a particular function's gradient and mandates multiple iterations to achieve convergence due to the influence of noise in Gibbs sampling.In contrast, quantum generative training offers a solution to some of these challenges. It quantifies a quantum advantage in terms of computational effort and time required to achieve a specific model performance. You can compare quantum training to classical techniques by examining the loss curves of RBM layers in the DBN-F sub-network. The quantum approach demonstrates faster convergence, representing a quantum advantage. Importantly, the computation time required for quantum techniques is negligible and doesn't increase with network size, making it especially advantageous for larger networks.

The results indicated that, even with a 3.5 cm film depth, light penetration was possible in a batch stirred reactor. However, it was suspected that light could only penetrate the solution to a certain depth. Stirring the solution had a positive effect on homogeneous irradiation. Moreover, considering that the reaction was photon-transfer-limited, the longer exposure time in the batch stirred reactor compared to the SDR with the 50 cm disc (60 minutes vs. 21 minutes, 35% of light exposure) could explain the observed differences.

Molecular dynamics simulations offer a powerful approach to understanding the behavior of molecules at the atomic and molecular scale. In this research, simulations were conducted to study the interactions between lead ions and polyprpylene at the molecular level. Various

parameters were examined, including gyration radius, root mean square deviation , root square fluctuation , van der Wals energy, electrostatic energy, and total energy. These parameters were examined to acquire a deeper understanding of the structural and energetic characteristics of the system.

These findings emphasized the importance of optimizing the reaction with the specific reactor setup and highlighted the significance of productivity and photon-specific turnover (PSTY) when comparing different reactors. PSTY values for the SDR showed the potential for scaling up visible light reactions, outperforming batch reactors under certain conditions.
It's worth emphasizing that this level of accuracy outshone traditional methodologies typically applied for similar fault detection tasks.

Nevertheless, it's crucial to acknowledge that the model did exhibit a false rate of 18.41%.This implies that, in certain instances, it erroneously identified issues even when none were actually present. While this false alarm rate represents a noteworthy limitation, the study underscores the substantial potential of merging quantum computing and deep learning techniques to enhance the detection of faults within intricate systems, such as the SDR.To sum it up, the research initiative involved a series of experiments conducted with a Batch, focusing on the identification of operational anomalies and issues. A quantum computing-based model was meticulously trained using data originating from both normal and faulty operations, yielding a remarkable 86.08% accuracy in the realm of fault detection. Despite the existence of a 18.41% false alarm rate, the study effectively spotlights the promising outlook for harnessing quantum computing and deep learning to advance the fault detection capabilities in complex systems akin to the SDR.

The impact of light intensity on L-meth-ionine oxidation is less significant than for the benzylamine homocoupling reaction. Variations in solar light intensity during the reaction had minimal effects on performance. This phenomenon could be attributed to the exceptionally high solar irradiances, which render the reaction rate less dependent on light intensity and more on mass transfer. In the SDR, the smaller size and extended exposure to natural sunlight explained the faster reaction rates, highlighting the potential of photoreactors optimized for solar photocatalysis over traditional batch reactors, particularly for environmentally friendly processes using natural light.

Conclusion

In this research, the performance of the Spinning Disc Reactor (SDR) was meticulously examined and compared to that of a batch stirred reactor in two distinct types of reactions: one constrained by photon transfer and the other by mass transfer. The optimal conditions were identified as involving a large surface area, high light intensity, and flow rate, combined with a low rotational speed. This configuration led to a larger volume treated per illuminated surface area and a longer residence time of the solution on the disc. Visual studies revealed that high flow rates and spinning speeds created irregular waves, which improved liquid distribution across the disc compared to the interference caused by standing waves.

The reactor generative training procedure made use of an adiabatic quantum computer for quantum sampling, enabling the estimation of model expectations. In this process, the Wave 1000 L per sec-processor was employed, equipped with an impressive array of 2,148 qubits and 5,600 cou-plers. These quantum resources were accessible through a cloud-based remote operation framework. Each computational run adhered to a carefully designed anneal schedule, with a fixed duration of 20 micro-sec . To maintain consistency and facilitate the effective management of the temperature-dependent parameter, denoted as βeff, an embedding scheme tailored to the energy function of each Restricted Boltzmann Machine (RBM) instance was thoughtfully established. It's noteworthy that βeff was intentionally set to a unity value to simplify the model.