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Design and operation of a radio-frequency heated micro-trickle bed reactor for consecutive catalytic reactions

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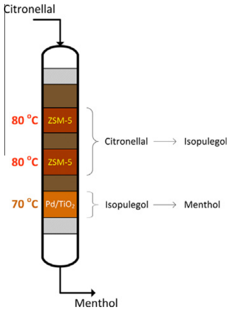
HIGHLIGHTS

- A multi zone micro-trickle bed reactor has been designed and constructed.
- RF heating creates two isothermal zones in a 40 mm long fixed bed reactor.
- The positions and the length of heating zones influence the product yield.
- A good agreement between the theoretical and experimental values was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

A radiofrequency heated micro-trickle bed reactor with two adjacent thermal zones was designed. In the first thermal zone, citronellal is converted to isopulegol over a H-ZSM-5 catalyst at 80 °C. This is followed by the second thermal zone where hydrogenation isopulegol to menthol occurs over a Pd/TiO$_2$ catalyst at 70 °C. The two catalytic zones are separated by heating zones made of nickel ferrite particles that produce heat under radiofrequency field at 180 kHz. The position of the catalytic zones was determined based on a one dimensional heat transfer model, in which the actual flow pattern was approximated. Such configuration allows achieving desired temperatures in the catalyst beds whereas the inlet and outlet gas temperatures are close to ambient temperature which increases energy efficiency of the system. The overall product yield was increased by 9 times as compared with a single thermal zone configuration.

1. Introduction

Trickle bed reactors are employed in many chemical and fine chemical applications [1,2]. Conventional trickle bed reactors suffer from the non-uniform temperature distribution and the formation of hot spots [3]. Recently we have presented an isothermal micro trickle bed reactor operated under radiofrequency (RF) field [4]. In magnetic materials, the Néel and Brownian relaxation processes result in energy dissipation, which is the dominant mechanism for RF heating [5]. Catalyst regeneration and testing was proven at both laboratory and industrial scale under RF heating [6,7]. In the RF heated reactor, catalytic zones are separated with several nickel ferrite heating zones. This configuration creates a possibility to make a few reaction zones with different temperatures, while still being compact enough to use in a single fixed bed reactor. Such configuration has an inherently large surface area-to-volume ratio, offering high heat and mass transfer rates, which is beneficial for attaining high selectivities and conversions

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Nomenclature

a	external wall area per unit of the reactor volume, m^{-1}
A_c	cross sectional area, m^2
C_i	concentration, mol m^{-3}
C_p	fluid specific heat capacity, J kg^{-1} K^{-1}
d_p	diameter of particles, m
E_i	activation energy, J mol^{-1}
F_V	volumetric flow rate, m^3 s^{-1}
$F_{m,i}$	molar flow rate of species i, mol s^{-1}
h_{ext}	external convective heat transfer coefficient, W m^{-2} K^{-1}
$\Delta_{R1}H°$	standard enthalpy of reaction 1 (cyclisation of citronellal), J mol^{-1}
$\Delta_{R2}H°$	standard enthalpy of reaction 2 (hydrogenation of isopulegol), J mol^{-1}
K	bed permeability, –
k_i	pre-exponential factor, s^{-1}
L	length, m
L_{Hi}	length of heating zone i, m
p	pressure, Pa
q'''_V	volumetric heat generation rate, W m^{-3}
q_A	heat released in catalyst bed 1, W, $q_A = \Delta_{R1}H^{deg} \times F_{m,A} \times X_A$
q_B	heat released in catalyst bed 2, W, $q_B = \Delta_{R2}H^{deg} \times F_{m,B} \times X_B$
q_{Hj}	heat released in heating zone j, W, $q_{Hi} = q_V^{tprime} \times A_c \times L_{Hj}$
T	temperature, K
T_∞	ambient temperature, 293 K
$\bar{T}_i$	average temperature in zone i, K
V	superficial velocity, m s^{-1}
X_i	conversion, –

Greek letters

δ_i	temperature non-uniformity parameter, %
ε_b	porosity of bed, –
λ_{eff}	effective thermal conductivity of the bed, W m^{-1} K^{-1}
μ	fluid viscosity, Pa s
ρ	fluid density, kg m^{-3}

Superscripts

0	initial

Subscripts

A	citronellal
B	isopulegol
C	menthol
1, 2, 3	heating zone index

and enables optimum control of residence time and temperature distribution. It also holds large promise for the development of miniature chemical synthesis devices, where several catalytic zones are integrated with microstructured sensors and actuators.

In the last decade, consecutive catalytic reactions have become one of the most active research areas in pharmaceutical and fine chemical industries [8–10]. During a consecutive reaction, just one reaction solvent, one operation procedure, and one purification step [10] are needed, thus significantly increasing synthetic efficiency. However a single pot synthesis could not be an efficient tool when two consecutive reactions require different temperatures [11]. Mass transfer limitations in stirred tank reactors make it difficult to transfer the developed protocol to industrial scale [12].

Consecutive reactions can spatially be separated in a trickle bed reactor which also simplifies the separation of individual catalysts [13]. The multi-zone micro trickle bed (MTB) reactor demonstrates the potential of microreactor technology to realise a compact chemical device, consisting of two catalytic zones and several heating zones. The design is based on accurate fast-calculating models describing the temperature distribution in the reactor. The success of the models stems from the well-defined flow conditions in the micro trickle beds.

In this paper, we provide a detailed description of the design and construction of a two zone MTB reactor and of the heat transfer model used in the design process. Subsequently, the performance of the device is shown in terms of menthol yield, as well as the ability of the heat transfer model to accurately describe the temperature profile in the device. Such approach provides optimum reaction conditions for consecutive reactions thus reduces the formation of side products and provides a greener synthesis alternative to single-pot synthesis. A two-step synthesis of menthol from citronellal was chosen as a test reaction. The first step, the cyclisation of citronellal, was performed over an H-ZSM-5 zeolite at 80 °C which provides high cyclisation rate due to its with high Brønsted acidity [14]. In the second step, a Pd/TiO_2 catalyst was employed at 70 °C [15–18]. The same process was carried out over a mixture of the two catalysts to compare the reactor performance.

2. Experimental

2.1. Chemicals

1,4-Dioxane (99 wt.%), citronellal (99 wt.%), isopulegol (99 wt.%) and menthol (99 wt.%) were purchased from Sigma Aldrich. ZSM-5 type zeolite was obtained from Zeolyst International (CBV 8014, $SiO_2/Al_2O_3 = 80$, 425 m^2/g) in ammonium form and used after calcination at 550 °C for 6 h. A 1.7 wt.% Pd/TiO_2 catalyst was prepared by incipient wetness impregnation of P25 titania (Evonik, surface area 50 m^2/g). The catalyst was dried at 60 °C overnight and then calcined for 4 h at 400 °C with a heating rate of 5 °C/min. The Pd loading was determined by elemental analysis by ICP-AES. The catalyst surface area was measured by N_2 sorption.

2.2. RF generator

The RF power generated in a resonance RLC (resistor, inductor and capacitor connected in series) circuit, an integral part of an Easyheat RF generator (Ambrell) was in the order between 100 and 500 W, depending on the applied current. However, only a small fraction of this power was absorbed by the nickel ferrite pellets in the heating zones which guarantied high uniformity of magnetic field in the radial and axial directions. The efficiency of an induction heating system depends on the design of the inductor (coil), the input power, and the amount of temperature change required for the application. A well-designed coil provides the proper heating pattern for reactor and maximises the efficiency of the induction heating system up to 95%. However this parameter decreases with temperature due to the changes in magnetic properties (saturation magnetisation and coercivity) of the ferrite particles [19,20]. The Easyheat induction heating system allows to adjust the operating frequency of RF field to get the maximum efficiency as the temperature increases.

2.3. Micro-trickle bed reactor

A quartz reactor (I.D. 9.5 mm) covered with a 40 mm thick glass wool insulation was placed vertically inside a nine turn induction