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1. Introduction

Liquefaction of renewable solid carbon sources is a promising route for production of second generation biofuels. Due to rising acceptance of pyrolysis in biofuel production, a significant amount of the by-product biochar is available.¹⁻³ This biochar can be liquefied in the presence of Tetralin.^{4,5} Tetralin acts as a carrier for the biochar particles, as a heat transfer agent and most importantly as a hydrogen donor solvent.^{4,6} The biochar particles are thermally decomposed and the radicals of the breaking fragments need to be saturated instantaneously with hydrogen. If the availability of hydrogen is low, breaking fragments will fall into repolymerisation reactions to form unwanted tars.⁷ The solvent Tetralin provides 2 moles of H₂ by rearranging to Naphthalene. Therefore hydrogenation of Naphthalene to Tetralin is needed for usage in a chemical loop system.

A common way to produce Tetralin is to partially hydrogenate Naphthalene with 2 moles of H_2 .⁸ Further hydrogenation with 3 moles of H_2 leads to formation of fully saturated Decalin,



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Liguefaction of biochar from liguid-phase pyrolysis was carried out in the solvent Tetralin. Tetralin is able to act as hydrogen donor during liguefaction of biochar and is itself rearranged into Naphthalene. Naphthalene must be re-hydrogenated to Tetralin to allow for further use in the liquefaction reaction (chemical loop system). Therefore Naphthalene hydrogenation was investigated, applying a full factorial design of experiments approach. The yield of Tetralin was chosen as response variable, while two-level-factors for temperature (150 °C and 200 °C), pressure (20 bar and 50 bar) and Raney-Nickel catalyst load (5 wt% and 10 wt%) were selected. The Design of Experiments approach showed a rising influence of all three factors in the order: temperature < pressure < catalyst load. The reaction kinetics of the hydrogenation of Naphthalene to Tetralin and Decalin was then investigated at 150 °C and 200 °C. The reaction proceeds stepwise and not in consecutive steps. In a first step Naphthalene reacts selectively with 96% yield to Tetralin, while the reaction of Tetralin to Decalin does not start until all Naphthalene is consumed. The rate-constant of the reaction of Naphthalene to Tetralin is one magnitude higher than that for the reaction of Naphthalene to Decalin. This is in agreement with the findings from the design of experiments approach. The results of these investigations indicate that the chemical-loop system Naphthalene-Tetralin is suitable for usage in the liquefaction of biochar.

> according to the overall balance shown in Fig. 1. Decalin does form two stereoisomeric molecules, *trans*-Decalin and *cis*-Decalin. Although Decalin has a higher H/C-value than Tetralin it is unfavourable because it does not have the ability to act as a hydrogen donor.⁹ This is due to a higher molecular stability of Decalin compared with Tetralin. The hydrogenation products of Naphthalene, dihydro-, hexahydro- and octahydronaphthalene, are not of technical relevance.⁸

> Naphthalene consists of two aromatic rings and belongs to the group of polyaromatic hydrocarbons (PAHs). Naphthalene is found in coal tars and crude oil,⁸ beside PAHs consisting of three to five aromatic rings, like pyrene, anthracene, phenanthrene and fluoranthene *etc.*, Naphthalene at ambient conditions is a crystalline/waxy white solid product with a melting point of 80 °C, while Tetralin and Decalin are liquids. The



Fig. 1 Hydrogenation of Naphthalene to Tetralin and to Decalin.

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partial hydrogenation of Naphthalene to Tetralin can be conducted in the liquid-phase and the vapour-phase. Selectivity of Tetralin over Decalin is higher for liquid-phase reactions.¹⁰ Noble metal catalysts like platinum and ruthenium but also nickel are proposed to have a high selectivity towards the products.^{8,11,12} The catalyst Red Mud, a by-product of the alumina production was investigated with minor success.¹³ Sulphur compounds¹⁴ may act as sulphided catalysts. The mechanisms of the catalytic hydrogenation of Naphthalene was investigated in ref. 15 and 16.

Several authors¹⁷ propose the hydrogenation of Naphthalene in a liquid carrier at temperatures between 150 °C and 200 °C and a hydrogen pressures of 1 to 20 atm. Cyclohexane, methylcyclohexane, dimethylcyclohexane, ethylcyclohexane, cyclopentane and methylcyclopenane are preferred liquid carriers. As the reaction temperature is as low as 260 °C,⁸ decomposition of Naphthalene, Tetralin, Decalin or the carrier is not to be expected. Under biochar liquefaction conditions above 400 °C partial degradation of Tetralin and Naphthalene is observed.

Hydrogenation of Naphthalene to Tetralin was investigated by applying design of experiments with the program JMP for data analysis. The aim of design of experiments is to obtain an accurate mathematical prediction model with as few as possible physical experiments. A full factorial design was applied to investigate the hydrogenation for a reaction time of 5 minutes. Design of experiments needs two sorts of variables: (1) response variables and (2) factor variables. The yield of the desired product Tetralin was chosen as the response variable. The temperature, hydrogen pressure and Raney-Nickel catalyst load (with respect to Naphthalene feed) were used as factor variables. All independent factor variables that influence the response variable need to be taken into account. Factor constraints were defined. In the physical experiments a temperature of either 150 °C or 200 °C, a pressure of either 20 bar or 50 bar and a Raney-Nickel catalyst load of either 5 wt% or 10 wt% were used.

Design of experiment proposes that all combinations of factor variables should be investigated, which leads to a lower experimental effort. The number of experiments for the design of experiments approach is calculated as follows: With two steps for all factor variables (temperature of either 150 °C or 200 °C) and three different factors (*k*) the number of experiments $n = 2^k$, resulting in 8 experiments. For improved accuracy a replica is recommended.

From design of experiments the optimum combination of operation conditions for investigation of the kinetics of the hydrogenation of Naphthalene to Tetralin were deduced.

2. Materials and methods

Materials

Reagent-grade Naphthalene (CAS: 91-20-3) with a purity of 99%, the carrier methylcyclohexane (MCH) (CAS: 108-87-2) with a purity of 99%, Raney-Nickel as pre-activated catalyst (CAS: 7440-02-0 from Merck) consisting of 90% Ni and 10% Al on weight dry basis (SEM image, see Fig. 2) and high grade hydrogen were used for the experiments.



Fig. 2 SEM Image of Raney-Nickel catalyst.

Experimental procedure

All design of experiments investigations were performed in a stirred 450 ml batch reactor. For each experiment 20 g of Naphthalene was added to the reactor together with 80 g of MCH and 5 wt% or 10 wt% Raney-Nickel catalyst (with respect to Naphthalene). The Naphthalene to MCH ratio was 1/4. The reactor was then sealed tightly. The stirring speed was set to 500 rpm during the experiment as well as the cooling phase. The reactor was heated with an electric heating jacket to the desired temperature. When the operation temperature was reached hydrogen was supplied, pre-set to the desired pressure by an expansion valve. The exothermic reaction started immediately and the reactor was cooled during the experiment (5 minutes of reaction time) in order to keep the reaction isothermal. Upon completion of the experiment the hydrogen valve was closed, the heating jacket removed and the reactor was cooled to below 100 °C within 3 minutes. When the temperature in the reactor reached 30 °C the pressure was relieved and the reactor was opened. The liquid product obtained was filtered through a syringe filter and analysed.

Reaction kinetics were studied in a 1100 ml reactor at two temperatures 150 °C and 200 °C over a 60 minutes reaction period. This bigger reactor allows for taking samples while the reactor is in operation at elevated temperature and pressure conditions. The hydrogen pressure applied was 20 bar. For each experiment 93 g of Naphthalene was added to the reactor together with 187 g of MCH and 5 wt% Raney-Nickel catalyst (with respect to Naphthalene). The Naphthalene to MCH ratio was 1/2. Hydrogenation of Naphthalene to Tetralin is a fast reaction. After loading, the reactor was sealed tightly. The stirring speed was set to 500 rpm during the experiment. The reactor was heated with an electric heating jacket to the desired temperature. When the desired temperature was reached the reactor was supplied with hydrogen, pre-set to the desired pressure by an expansion valve. The exothermic reaction started immediately. The reactor was cooled during the 60 minutes of reaction time to keep the reaction isothermal. Samples of the reaction mixture were taken every minute in the first 10 minutes and thereafter every 5 minutes. The samples taken were filtered through a syringe filter and subjected to analysis.

The generic reaction rate equations can be expressed according to:

$$r_{\rm N} = -k_1 c_{\rm N}''$$
$$r_{\rm T} = k_1 c_{\rm N}'' - k_2 c_{\rm T}''$$
$$r_{\rm D} = k_2 c_{\rm T}''$$

where r is for the reaction rate, subscript N is for Naphthalene, T for Tetralin and D for Decalin (*cis*- and *trans*-), k is for the rateconstants, c is for the concentration and superscript n is for the order of reaction.

Analytics

The liquid product from filtration was analysed with a GC-FID. A MXT 2887, 10 m column from Restek and a gas chromatograph, type Agilent 7890A, was used. All substances are detectible between 80 °C and 150 °C. Therefor the heating-rate was set to 10 °C per minute in this section and to 20 °C per minute in all other sections. The injection method was "cool on-column". The final temperature was 360 °C.

3. Results and discussion

Design of experiments

Detailed experimental data of the conducted experiments are illustrated in Table 1. The highest yields of Tetralin (96 mol% and 95 mol%) were observed after 5 minutes of reaction for 200 $^{\circ}$ C, 50 bar, 10 wt% catalyst. Decalin production was observed at the upper temperature level. Experiments marked grey in Table 1 were not considered in the statistics. These are

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Table 1	Design of	Dt.	experiments	data	after	5	minutes of reaction

Pattern	Temperature [°C]	Pressure [bar]	Catalyst [wt%]	Yield Tetralin [mol%]
	150	20	5	37
-+-	150	50	5	49
+	200	20	5	39
+	150	20	10	23
-+-	150	50	5	2
+-+	200	20	10	85
++	200	20	10	82
++-	200	50	5	82
-++	150	50	10	75
+++	200	50	10	96
-++	150	50	10	53
+++	200	50	10	95
++-	200	50	5	77
+	150	20	10	62
+	200	20	5	30
	150	20	5	32

experimental values which do not fit the 95% confidence interval.

The results in Table 1 were subjected to an effect screening through JMP software. During this effect screening the influence of the three factors (temperature, pressure, catalyst amount) as well as two-fold combinations (the combination of pressure and temperature has an effect) and three-fold combination of factors on the response were determined. As a result of the effect screening the factors temperature, pressure and catalyst amount have a significant influence on the yield of Tetralin. Two-fold and three-fold interactions showed no significance. With the essential effects in mind the mathematical model can be built. Results of the linear regression model are shown in Fig. 3.

Fig. 3A shows the experimental Tetralin yields on the y-axis and the predicted Tetralin yields on the x-axis. If the model would predict perfectly performed experiments, all data points would lie on the 45 degree line. The 95% probability confidence interval is plotted in red dotted lines The RSME (Root Mean Square Error) describes the average deviation of the experimental data from the model with 9.4, which is within limits. Fig. 3B-D show the influence of the factor variables on the yield of Tetralin. The impact is increasing in the following order: temperature < pressure < catalyst amount, and can be read from the slope of the solid red line. The x-axis is not scaled like the observed regressors (temperature, pressure, catalyst load) because the model doesn't consist of a simple regression of one regressor but a multiple regression. Therefore the values of the x-axis are no longer corresponding to actual data values. Points on the x-axis farther out (+1.5 and -1.5) pull on the line of fit with greater leverage than the points near the middle (0.0). The influential points in all leverage plots are the ones far out on the x-axis. This makes it possible to judge if the line of fit (red line) on the effect's leverage plot carries the points significantly better than the horizontal line (blue line) does.

The estimated regression parameters and the mean yields lead to the empirical model equation for the hydrogenation of Naphthalene to Tetralin (eqn (1)) calculated with JMP.

Empirical model equation.

$$Yield = 64.74 + 8.62 \left(\frac{\text{Temperature} - 175}{25}\right) + 11.54 \left(\frac{\text{Pressure} - 35}{15}\right) + 15.04 \left(\frac{\text{Catalyst} - 7.5}{2.5}\right)$$
(1)

The graphical display of the model equation is the prediction variance surface plot, shown in Fig. 4. By setting one factor constant (temperature, pressure or catalyst load) a surface is formed in the three-dimensional space. The Tetralin yield is displayed on the *z*-axis.

Design of experiment shows that a combination of 200 $^{\circ}$ C, 50 bar and 10 wt% catalyst lead to the best result for the hydrogenation of Naphthalene to Tetralin. Fig. 4A and B both show a significant effect of the pressure on the prediction variance surface. Fig. 4C and D (catalyst) both show the most



significant shift of the prediction variance surface to higher values of Tetralin yield and Fig. 4E and F (temperature) the least.

Investigation of reaction kinetics

Results of the kinetic experiments at 150 °C, 20 bar and 5% catalyst are shown in Fig. 5 and at 200 °C, 20 bar and 5% catalyst in Fig. 6. Both figures indicate that the reaction of Naphthalene (N) to Tetralin (T) to Decalin (D) is not classically consecutive but rather occurs stepwise. In the first step Naphthalene reacts selectively to Tetralin without the formation of Decalin until 96% of the Naphthalene is consumed. A small amount of Naphthalene remains in the reaction mixture. After this first step the Tetralin is hydrogenated to Decalin, but an order of magnitude slower than the reaction of Naphthalene to Tetralin. Compared to 150 °C the reaction of Naphthalene to Tetralin is faster at 200 °C, which can be seen by comparing Fig. 5 and 6 or from the rate-constants. This agrees to the findings of the temperature dependency through design of experiments. The reaction of Tetralin to Decalin is slower at 200 °C than at 150 °C which can be seen from the rate-constants.

In Fig. 5 and 6 no concentration dependency can be observed. The reactions are therefore zero-order reactions. The start concentration of Naphthalene is 2.6 mmol per gram reaction mixture. When Naphthalene reacts to Tetralin very fast, there is a time where only a small amount of Naphthalene is left in the reaction mixture, which is practically zero. The time where the Naphthalene concentration is zero is hereinafter defined as t_N . After the time t_N the reaction of Tetralin to Decalin starts with the rate-constant k_2 , see Table 2. For the

kinetic experiment at 150 °C, 20 bar and 5% catalyst the time $t_{\rm N}$ is 9.76 min for the experiment at 200 °C, 20 bar and 5% catalyst the time $t_{\rm N}$ is 7.92 min. As proposed through design of experiments the higher reaction temperature increases the reaction rate from Naphthalene to Tetralin. Kirumakki¹⁸ investigated continuous hydrogenation of Naphthalene and found 200 °C to be the temperature for highest conversions to Tetralin while further increase of temperature above 200 °C lead to decrease in conversion because of the exothermic nature of the reaction.

The stepwise reaction leads to the following kinetic equations:

The calculated rate-constants correspond to:

$$t_{\rm N}|_{150^{\circ}\rm C} = 9.76 \,[\rm{min}]$$

$$k_1'|_{150^\circ \mathrm{C}} = 5.71 \times 10^{-5} \left[\frac{\mathrm{mmol}}{\mathrm{g} \times \mathrm{g}_{\mathrm{ext}} \times \mathrm{min}} \right]$$

$$k_2'|_{150^{\circ}\mathrm{C}} = 4.36 \times 10^{-6} \left[\frac{\mathrm{mmol}}{\mathrm{g} \times \mathrm{g}_{\mathrm{cat}} \times \mathrm{min}} \right]$$

$$t_{\rm N}|_{200^{\circ}\rm C} = 9.76 \,[\rm{min}]$$

$$k_1'|_{200^\circ \mathrm{C}} = 7.04 \times 10^{-5} \left[\frac{\mathrm{mmol}}{\mathrm{g} \times \mathrm{g}_{\mathrm{cat}} \times \mathrm{min}} \right]$$

Fig. 3



Fig. 4 Prediction variance surface plots.

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Fig. 5 Kinetics at $T = 150 \,^{\circ}$ C, 20 bar, 5% catalyst.



Fig. 6 Kinetic at $T = 200 \degree$ C, 20 bar, 5% catalyst.

Table 2	Kinetic	Equations
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Naphthalene	$r_{\rm N} = -k_1$	N-present	$t_{\rm N} < \frac{c_{\rm N,0}}{L}$
Tetralin	$c_{\rm N} = c_{\rm N,0} - k_1 t$ $r_{\rm T} = k_1$	N-present	$t_{\rm N} < \frac{c_{\rm N,0}}{L}$
	$c_{\mathrm{T}} = k_1 t$ $r_{\mathrm{T}} = -k_2$	N-absent	k_1 $t_N > \frac{c_{N,0}}{L}$
	$c_{ m T} = c_{ m T(t=t_{ m N})} - k_2(t-t_{ m N}) \ c_{ m T} = k_1 t_{ m N} - k_2(t-t_{ m N})$		<i>K</i> ₁
Decalin	$egin{aligned} r_{ m D} &= 0 \ c_{ m D} &= 0 \end{aligned}$	N-present	$t_{\rm N} < \frac{c_{\rm N,0}}{k_1}$
	$egin{aligned} &r_{ m D}=k_2\ &c_{ m D}=k_2(t-t_{ m N}) \end{aligned}$	N-absent	$t_{\rm N} > \frac{c_{\rm N,0}}{k_1}$

$$k_2'|_{200^{\circ}\mathrm{C}} = 3.93 \times 10^{-6} \left[\frac{\mathrm{mmol}}{\mathrm{g} \times \mathrm{g}_{\mathrm{cat}} \times \mathrm{min}} \right]$$

Analysis of the samples taken during the kinetic experiments at 150 °C and 200 °C and comparison of the results led to a finding concerning the composition of Decalin. It was shown that at 150 °C reaction temperature the ratio of *trans*-to *cis*-Decalin stays constant with reaction time while the ratio at 200 °C reaction temperature rose with time. Fig. 7 shows the ratio of *trans*-Decalin to *cis*-Decalin formed with respect to time. The reason for the increase of the ratio is that at 200 °C the formation of *trans*-Decalin is thermodynamically favored but can be influenced by the used catalyst



Fig. 7 Ratio of trans-Decalin to cis-Decalin (20 bar, 5% catalyst).

materials.^{19,20} While isomerization reaction of *cis*-Decalin to *trans*-Decalin were ruled out during reaction by¹⁸ other groups found isomerization from *cis*- to *trans*-Decalin in the magnitude of *trans*-Decalin formation in the reaction stage at 200 $^{\circ}$ C.²⁰

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4. Conclusion

Hydrogenation of Naphthalene was investigated. In the first part of the study several experiments were conducted using design of experiments to investigate the influence of the factors temperature between 150 °C and 200 °C, hydrogen pressure between 20 bar and 50 bar and catalyst load between 5 wt% and 10 wt% on the yield of Tetralin after 5 minutes of reaction. In the second part of the study the kinetics of the reaction of Naphthalene to Tetralin and Decalin were investigated separately for two temperatures, 150 °C and 200 °C. A pressure of 20 bar hydrogen and catalyst load of 5 wt% was chosen for the investigation of the kinetics.

The results of the design of experiments study indicate that:

(1) Influence of the factors is increasing in the order: temperature < pressure < catalyst load.

(2) Highest yield of Tetralin in the design of experiments study was found for 200 $^\circ C$, 50 bar hydrogen and 10 wt% of catalyst.

The results of the kinetic study indicate that:

(1) The reaction of Naphthalene to Tetralin to Decalin occurs stepwise and not classically consecutive.

(2) All reactions are zero-order reactions.

(3) In the first reaction step selective hydrogenation of Naphthalene to Tetralin occurs with a yield of 96%.

(4) Only after complete consumption of Naphthalene, Tetralin is hydrogenated to form Decalin.

(5) Reaction of Naphthalene to Tetralin is an order of magnitude faster than the reaction of Tetralin to Decalin.

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