

Fundamentals of Chemical Technology and Chemicals Management Laboratory

Catalytic cracking of hydrocarbons

Manual for experiment

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Exercise aim

The main goal of this experiment is catalytic cracking of chosen aliphatic hydrocarbons (hexadecane, dodecane etc.) **on a solid catalyst bed**. During the experiment, the student has the opportunity to study the influence of temperature, time and dosing rate of raw material on the final products of catalytic cracking.

As catalyst are used molecular sieves (zeolite 13X) and/or Al_2O_3 . The reaction products (liquids and gases) are analyzed with gas-liquid chromatography using Hewlett-Packard GC 6890.

Installation description

A schematic diagram of device is presented in Figure 1. The process consists of two steps: reaction and catalyst regeneration.

The reaction is performed at isothermal conditions in reactor (1) filled with catalysts (4,4g zeolite 13X). Temperature inside the catalyst bed (2) is measured with thermocouple (3). Control unit (11) is a temperature regulator (involves on temperature programming). Hydrocarbon is dosing with a stable rate into reactor with calibrated syringe using infusion pump (4). Reaction products passing through condenser (8) cool down and finally liquid products condensate in receiver (9). Element (15) is filled with “dry ice+acetone” cooling mixture, and all residual products are freezing out there. Gaseous products flows through container (6) and, after through gas meter (7). Washer (16) filled with paraffin oil indicates gas flow. Air pump (5) doses air into reactor during catalyst regeneration. Gas cylinder (14) contains inert gas (Ar or N_2) which if necessary for reaction products removing from catalyst bed and at final step of catalyst regeneration for air removing is used.

During the second step – catalyst regeneration the pump (5) doses air into reactor. The mixture carbon oxide and carbon dioxide flows to afterburner (10) where reaction carbon oxide oxidation to carbon dioxide with Cu as a catalyst performs, and next CO_2 flows to absorber (19) filled with sodium hydroxide solution (NaOH) where sodium carbonate (Na_2CO_3) arises as a product.

Peristaltic pump (19) helps in gases transportation between reactor through afterburner to absorber.

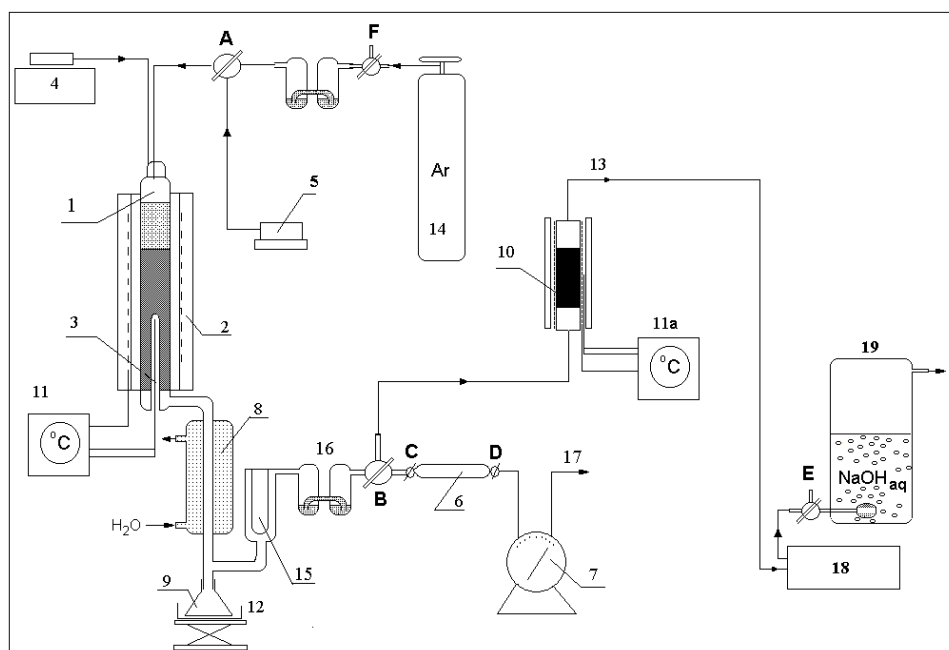


Figure 1. Installation scheme. A,B,C,D,E,F cranes; 1- flow reactor; 2- catalyst bed; 3 – thermocouple; 4- infusion pump; 5- air pump; 6- gaseous-products container; 7- gas meter; 8- Liebig condenser; 9- liquid products container; 10- afterburner $\text{CO} \rightarrow \text{CO}_2$; 11 and 11a- temperature units control; 12- cooling bath; 13- afterburners' products transport line; 14- inert gas (Ar or N_2) cylinder; 15- "dry-ice" + acetone container; 16- oil washer; 17- gases outlet; 18- peristaltic pump; 19-absorber.

Experiment steps

1. Turn on air pump (5) and temperature control unit (11) set-up 600°C for catalyst regeneration (30minutes).
2. Weight products receiver (9).
3. Decrease catalyst temperature to $450^\circ\text{C} - 585^\circ\text{C}$ according to instructor suggestion and purge catalyst bed with argon.
4. Infusion pump (4): set dosing speed on suitable value (proposed by teacher).
5. Fill syringe with undecane (or other raw material) and place needle through membrane into reactor.
6. Connect receiver (9) with Liebig condenser (8).
7. Note gas meter (7) value.
8. Fill cooling bath (12) with "dry-ice+acetone" mixture.
9. Start dosing raw material - pump "on", and note time.

10. Reaction time suggests instructor.
11. Time over, turn off dosing raw material, take out needle.
12. Note gas meter (7) value and disconnect gaseous products container (6).
13. Purge catalyst bed with Ar (gas cylinder 14).
14. Disconnect liquid products receiver, and when its temperature become to room temperature weight it.
15. Make glc of liquid and gaseous products.
16. Obtained results note in suitable results table.
17. Regenerate catalyst bed (30minute) in an air flow.
18. Increase temperature till 220°C in afterburner (10) using temperature control unit (11a).
19. Fill absorber (19) with 0.1M NaOH solution (the volume suggests instructor).
20. Turn on peristaltic pump (18).
21. Using Warder's method Na₂CO₃ contents is determined.
22. Regenerate catalyst and eventually perform process under different conditions (change temperature, raw material dosing speed,) according to points from 3 till 19.

Note! During experiment right position of all cocks/valves should be consulted with instructor.

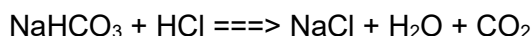
The Warder's method* description

The determination of sodium carbonate contents in 0.1MNaOH solution with Warder's method is realized through acid titration (0.1MHCl) using phenolphthalein and methyl orange as indicators. The sample of titrated solution should be cooled (in a mixture ice with NaCl) because of CO₂ loss limitation. Additionally the burette terminal position should be close to solution surface.

The first titration in the presence of phenolphthalein is till solution discoloration (whole amount of NaOH and half of Na₂CO₃ is titrated). Sodium carbonate passes to sodium bicarbonate according to reaction:



Next, to the solution a methyl orange is added and titration (with 0.1MHCl) continues till the first colour change (from yellow to orange) as a result of the reaction:



If during first titration (in the presence of phenolphthalein) a [mL] of 0.1M HCl was consumed, and during second titration (in the presence of methyl orange) b[mL] of 0.1MHCl, than the Na₂CO₃ amount (in grams) can be calculated according to equation:

$$X = 2b \cdot C_M \cdot 0.106$$

where:

C_M – HCl molar concentration [mmol/mL]

0.106 - Na₂CO₃ molar mass [g/mmol]

and finally, the carbon contents in sodium carbonate should be calculated.

* J.Minczewski, Z.Marczenko „Chemia analityczna. Analiza ilościowa
.” PWN 1973, Vol. 2 page 224

The final equation according with the amount of the Na₂CO₃ amount (in grams) is calculated is given as:

$$X = 2b \cdot C_M \cdot 0.106 \cdot 50$$

On the end, the amount of coke that has been adsorbed on catalysts should be calculated.

Experiment report should be prepared according to pattern attached to manual and contained:

- An aim of experiment,
- an experiment brief description,
- glc results description and interpretation,
- a table containing obtained and calculated data,
- Sankey diagram (if necessary prepared on basis of process mass flow balance) with suitable scale and stera legends,
- results discussion, and comments,
- conclusions (among, if the aim of experiment has been achived),
- students remarks and suggestions if there are some (for example how to improve some steps of experiments).

A results sheet signed by instructor should be attached.