

MICHAL NETUŠIL, PAVEL DITL*

AUTOMOTIVE CATALYST PRODUCTION – CHALLENGES FOR CHEMICAL ENGINEERS

PRODUKCJA KATALIZATORÓW SAMOCHODOWYCH WYZWANIEM DLA INŻYNIERÓW CHEMIKÓW

Abstract

The goal of this paper is to explain the chemical engineering backgrounds for operations participating on catalyst production in the automotive industry. It is shown that chemical engineering knowledge can help to a better understanding and optimisation of the production process. Besides the contribution mentioned above this paper brings the description of the up to date and interesting technology developed and patented by the worldwide leader in the chemical engineering - BASF. The car catalyst production process consists of two steps. Firstly, the coating slurry is produced and secondly, it is applied to the substrate. This paper focuses on the slurry production especially with regard to its dispersion, mixing, particle size reduction, and the influence of parameters affecting this process.

Keywords: plant design, automotive catalyst, process control

Streszczenie

Celem niniejszego opracowania jest przedstawienie podstaw inżynierii chemicznej procesów stosowanych przy produkcji katalizatorów w przemyśle motoryzacyjnym. W pracy przedstawiono opis nowoczesnej technologii opracowanej i opatentowanej przez światowego lidera w inżynierii chemicznej - BASF. Proces produkcji katalizator samochodowy składa się z dwóch etapów: produkcja zawiesiny i nanoszenie na podłoże. W pracy opisano wytwarzanie zawiesiny ze szczególnym uwzględnieniem dyspersji, mieszania, zmniejszenia rozmiaru cząstek i oddziaływania parametrów procesowych.

Słowa kluczowe: projektowanie instalacji, katalizator samochodowy, kontrola procesu

DOI:

* PhD. DSc. Eng. Michal Netušil, Prof. PhD. DSc. Eng. Pavel Ditl, Department of Process Engineering, Faculty of Mechanical Engineering, Czech Technical University in Prague.

1. Introduction

The process and control of slurry production are described in general without detailed information. The details depend on a vendor selection. The block diagram in Fig.1 below displays the basic configuration of a catalyst coating plant. The main steps in slurry preparation are colour coded in accordance with the key.

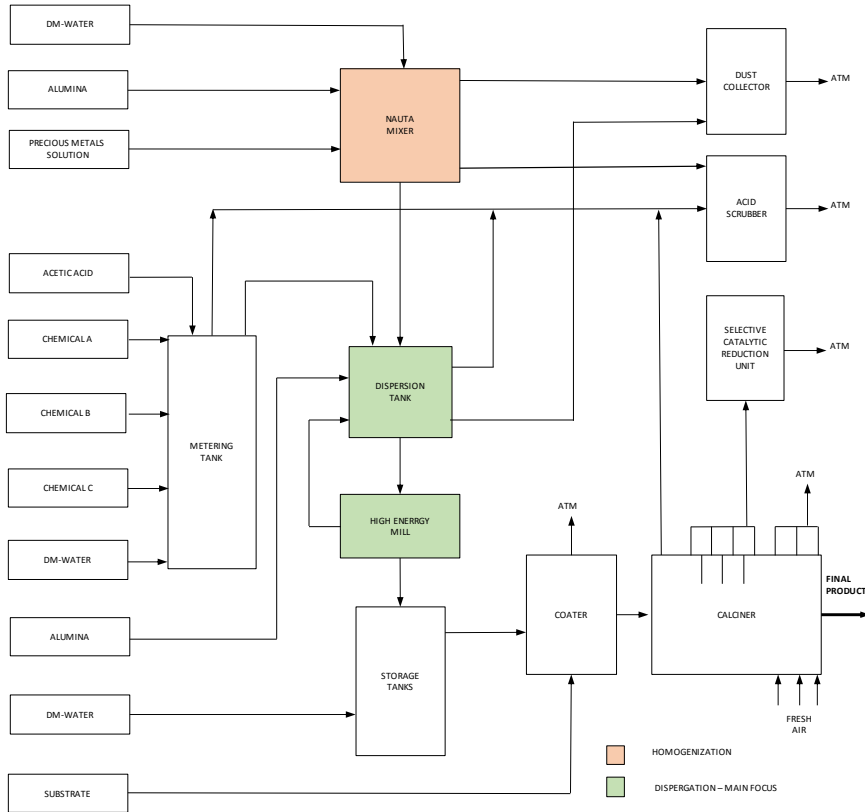


Fig. 1. Slurry preparation and coating block diagram

With respect to the material flow, the slurry preparation is set up in a building containing the ground, the first and the second floor. On the second floor, the raw material is dosed and mixed in Nauta mixers. Mixing occurs with the minimal addition of fluids. On the same floor, high-speed shear machines are placed. These machines are used for the purpose of reducing the size of ingredient particles. From the second floor, the mixture flows to the first floor where dispersion tanks are located. In the dispersion tanks, solutions are added and homogenisation proceeds. From the first floor, the mixture flows to the ground floor where it is milled by high-energy mills. The mixture from the mill is circulated back to the dispersion tank until the desired particle size is achieved. The ready mixture (slurry) is pumped to storage tanks located on the first floor. From the storage tanks

the slurry is dosed into portable tanks on the ground floor. The portable tanks containing the slurry are manually transported to the production area where they feed the coating lines.

Coating lines coat the substrates. The substrates are dipped into the slurry and dried. The new types of coating lines have also a pre-drying step. After drying, the substrates continue to the calciner. The calciner is of a tunnel type, it is a circulating hot air oven consisting of heating and cooling zones. The maximum temperature is 600°C and the overall residence time is around 90 mins. During calcination, residual moisture evaporates and the organic ingredients of the wash coats are oxidised. In the case of precious metal (PM) coats, the composition of the ammine solution used for stabilising the precious metal solution leads to the release of oxides of nitrogen (NO_x). Each zone is equipped with its individual circulating fans and burners. Substrates covered with a calcined coat leave the oven and are loaded onto pallets.

For gas treatment, two different units are needed. The acid scrubber treats acid gases. These gases are created as a result of acetic acid evaporation (acetic acid is one of the base chemicals used in slurry preparation). The principle of gas treatment is chemical absorption by means of the spraying of a base solution whereas selective catalytic reduction (SCR) mainly treats the NO_x created within the high temperature zones of the coater. Principle is reduction of NO_x to nitrogen by ammonia. The reaction occurs within the presence of O_2 . The by-product is H_2O .

2. Control description

The process control of automotive catalyst plants consists of three major sections. Slurry preparation, coating section, and the scrubber and SCR system. All the system cabinets, including power distribution panel and marshalling panels, are installed in a control room. All operator stations have monitors for the visualisation of the process flow and recipe management. The interface of the programmable logic controller (PLC) panels with the drives in motor control center (MCC) is through interposing relay panel/profibus.

2.1. Slurry preparation

Slurry required for coating is prepared on demand as per the relevant confidential recipe. The equipment involved in slurry preparation is a Nauta mixer and the associated raw material handling system, dispersion tanks, milling and slurry storage. Slurry preparation is monitored and controlled by PLC and supervisory control and data acquisition (SCADA) system. The remote terminal unit is in the plant operation room. Terminals are used for the operator's manual interventions – access is password-protected. The recipe management is implemented for both the batch and discrete parts of the process. The batch recipe management stores information about the dynamic configuration of the recipe and works for batch functions with pre-programmed batch cycles and compositions. The system enables changing the batch recipes as required. Based on actual compositions, mix ratios and quantities the formula settings are derived. The formulas for each batch are stored. Data stored also contains the time record of vessels charging.

A wireless type barcode reader system enables exact material charging according to the PLC system of the slurry section. The input from the barcode reading system is verified by

the recipe management system to ensure that the correct material is charged into the equipment as per the recipe.

A radio-frequency identification (RFID) system is implemented for the connection of hoses. The RFID system is installed in field providing information about the connection of each hose to the equipment. The system is comprised of the RFID controllers and RFID tags and it is connected to the main control system. The RFID controller is mounted at the flange of the equipment. The RFID tags are at both the ends of the hoses. The RFID controller reads the RFID tag number on the hose and the information is cross-referenced by the control system – if the numbers match, the equipment valves are opened.

In the functional area of the Nauta mixer (Fig. 2) is the PM solution tank, the dosing pumps, the Nauta mixer and the vacuum conveying system for alumina dosing. The raw material is barcoded and a barcode scanner sends the information before charging. Any mismatch in the barcode cross-referencing will not allow the batch to proceed. Remotely operated switches for all drives are shown on screen in the operation room. Based on the batch preparation recipe, the operator takes a premeasured amount of PM from the PM vault. The PM vault contains a CCTV surveillance system and an intrusion detection system. The PM solution is manually added into the PM solution tank. Use of barcode reader avoids adding the PM into wrong solution tank. The PM solution tanks are refilled regularly. Refilling of PM solution tanks is allowed only if the scrubber suction valve is open and scrubber blower is switched on. A weight measurement is displayed both in field and on the remote display panel. PM solutions are charged to the Nauta mixer using the dosing pumps. When the batch starts, the inlet valves of dosing pumps opens. Material is charged to the Nauta mixer. Charging of material to the Nauta mixer is controlled by weighing scale. The speed of agitation is automatically controlled. Mixers are fully automated and the sequence of operations follows the required recipe. The sequences involve a dust collection system, the switching on and off of valves, the addition of alumina through a vacuum conveyor, agitation, PM addition, suction to the acid scrubber system, PM solution tank rinsing, and drainage to the dispersion tank. Alumina is usually received in bulk bags which are fed into the Nauta mixer by a vacuum conveying system. Before starting alumina charging, the operator has to ensure that the dust collection system is switched on. Alumina is added in accordance with the recipe and the weighing system on the Nauta mixer trips the vacuum conveyor after the required amount is added. Powder from bags is transported through flexible hoses and charging is performed in multiple cycles with various quantities of powder according to the recipe. When the batch in the Nauta mixer is ready, the operator connects the Nauta mixer to the selected dispersion tank. Based on the connection check, the operator in the control room initiates the transfer operation. The weighing system informs the operator about the state of transfer.

The functional area of dispersion contains the base chemical storage tanks, the metering tank, the dispersion tank (Fig. 4) and the vacuum conveying system. There are usually 4-5

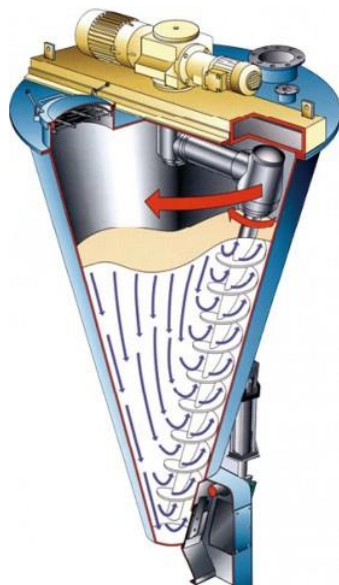


Fig. 2. Nauta mixer

base chemical storage tanks. To avoid mixing different loads in the base chemical tanks, charging of chemicals from the drum does not proceed if the barcode doesn't match. Level switch is provided to stop the air operated double diaphragm (AODD) dosing pumps when the required level is reached. Fixed quantities of base chemicals are added to the metering tank based on the selected batch recipe. On/off valves at the inlet of the metering tank close after pre-set quantities of base chemicals are added. Flexible hose connections are provided from the demineralized (DM) waterline for rinsing of the metering tank. The dispersion tank is a jacketed vessel with an agitator. The agitator is provided with a variable frequency drive (VFD) for agitation speed adjustments. The sequence of dispersion tank operation starts with filling the dispersion tank jacket with cold water. Cleanliness of the tank is checked and chilled DM water is added to the dispersion tank. Dust collection and acid scrubber suction are turned on. The Nauta mixer output is transferred into the dispersion tank and mixing with the base chemical proceeds. Agitation lasts at least 20 minutes. Slurry from the dispersion tank is fed to the energy mill via a peristaltic pump. The mill outlet overflows into a small tank and is recirculated back to the dispersion tanks. The temperature control loop is connected to the chilled water system. The vacuum conveying system for alumina dosing works in the same way as for the Nauta mixer – alumina is added in multiple steps.

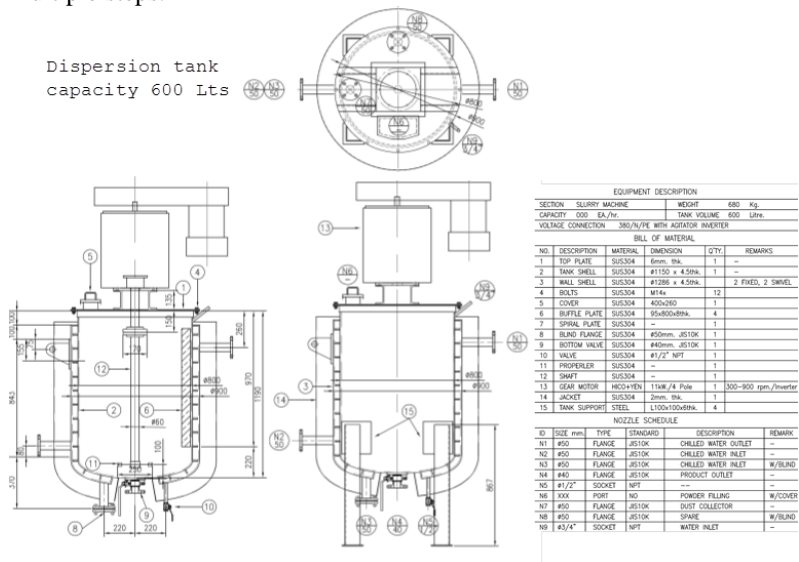


Fig. 3. Technical drawing of 600L dispersion tank with equipment description and nozzle schedule

Equipment involved in functional area of the high-energy mills do not require the recipe management. The energy mill is regulated with speed controls using VFD. The mill operation is controlled from the operation room. The sequence of milling operations starts with connecting the dispersion tank to the mill peristaltic pumps. The mill outlet pumps are connected to both the storage tanks and the dispersion tanks. The level of seal liquid for the mill is checked and flow rate is set. The mill RMP is set and the milling operation begins. During milling, the particle size reduction is checked and when the desired particle size is

achieved, the mill outlet is discharged to the storage tanks; otherwise, it is recirculated back to the dispersion tank. The speed of agitating in the storage tanks and the chilled water flow in the tank jacket are controlled automatically. An alarm triggered by weight alerts the operator to stop filling the storage tank. Based on production requirements, the storage tank outlet is manually connected to mobile storage tanks by a flexible hose. Once the source and destination hose clamps fit the valve can be opened. Mobile storage tanks mixing has the VFD control panel. RPM is set up manually by the operator. Mobile storage tanks transfer the slurry into the coating area.

2.2. Substrate coating

The coating area consist of coating production lines. Lines are usually provided as a package including all the associated instrumentation related to the systems. The substrate is manually unloaded from pallets on to a conveyor belt. The substrate marked with barcodes is conveyed to the coating machines. The substrate can be placed manually or by robots onto a rotating index table. Prior to coating, the dry weight of the substrate is measured. The substrate is rotated into the dip pan. The lower part of the substrate is dipped into the slurry. Applying a vacuum to the upper part of the substrate allows sucking in a predefined quantity of slurry. After coating, the weight gain of the substrate is measured. The coated substrate is placed horizontally on the conveyor belt by which is fed into the dryer. The substrates are dried by passing a large quantity of air heated to 150°C through the cells until the moisture content is removed. The substrate spends around 10-12 minutes in the dryer.

After drying, the substrates are rotated to a vertical position and aligned on the feeding conveyor belt to the calciner, either by robot or manually. The calciner is tunnel type oven in which hot air is circulated. Calciners consist of 7-9 different heating-cooling zones. The max temperature is 600°C and the overall time spent in the calciner is around 90 mins. During calcination, residual moisture evaporates and the organic ingredients of the wash coats are oxidised. In the case of PM coats, the composition of ammine solution used for stabilising the PM solution leads to release of NO_x. The oven is heated by burners placed in each section. The sections are also equipped with individual circulating fans. The calcined substrate leaves the oven on the conveyor belt and is manually loaded onto pallets.

2.3. Gas treatment, utilities

The acid scrubber system is provided to scrub out any volatile organic compound (VOC) or acetic acid vapour in the off-gas sucked from both the slurry preparation and coating section. A NaOH solution is used for scrubbing. A blower at the scrubber outlet maintains a slight draft in the system and vents to the atmosphere. Fresh raw water makes up the portion of stream routed to wastewater treatment plant. For acid scrubber operation, standby pumps and blowers are recommended. The scrubber usually has its own control panel. Only the information about the pressure drop across the packed column and the run/trip status of blowers is send to the SCADA. A visual alarm for a high pressure drop across the scrubber is provided in the coater area.

The SCR (DeNO_x) system processes off-gas from the calciner and consists of two types of catalysts a DeNO_x catalyst to remove the NO_x and an oxidation catalyst to remove the total organic carbon and CO. The off-gas is filtered and heated up to the working

temperature of the catalyst (the SCR unit is preheated to a minimum of 350°C). NH₃ is required for DeNO_x reaction while the O₂ content in the off-gas is sufficient for the oxidation reaction. The mixture of the off-gas and the NH₃ reacts on the catalyst surface. NH₃ sorbs to the V₂O₅ molecules of the catalyst and reacts with the NO_x, forming N₂ and H₂O. After desorption of the reacted products, the reduced catalyst is re-oxidised to the active initial state. Hydrocarbons and unreacted NH₃ are partially oxidised after the DeNO_x catalytic reaction. Downstream the catalyst oxidises the pollutants to harmless chemicals. O₂ and VOC migrate to the catalyst surface by gas diffusion and are adsorbed onto the catalyst active sites on the surface of the catalyst where oxidation occurs. The oxidation reaction products are then desorbed from the active sites and transferred by diffusion back into the gas stream. The fan installed at the outlet provides the static pressure to overcome the total pressure drop of the system and provides a constant pressure at the inlet of the system. The cleaned off-gas goes to stack. In the stack NO, NO₂ concentration is measured. Based on the NO, NO₂ concentration results the feed of the NH₃ is controlled. The SCR usually has its own PLC to control the operation.

The utility packages commonly have their own control system. The compressed air, chilled water, DM water, wastewater treatment plant and NG are basic utilities of the process. There is only few hardwire interfaces with SCADA. Hardwired are usually flow or pressure indicators. A dedicated uninterruptible power supply shall be provided for entire instrumentation system. Redundancy is provided for the field instrument and the control system. Back-up time 30 minutes is sufficient.

3. Dispersion and milling

The theoretical background for the dispersion step present in the slurry preparation process is applied. For the determination of the final dispersion size, the balance between force from dynamic turbulent stresses and surface tension force is defined according to [1] as follows:

$$\frac{d_{32}}{D} = C_1 (1 + C_2 \cdot c^V) \cdot Po^{-0.4} \cdot \left(\frac{T}{D}\right)^{1.2} \cdot We^{-0.6} = C_3 \cdot We^{-0.6} \quad (1)$$

where

- d_{32} – Sauter mean particle size [mm], ($d_{32} = 0,67 \cdot d_{\max}$)
- D – diameter of the impeller [mm],
- C_1, C_2 – constants depending on the system geometry [-],
- c^V – volumetric concentration of dispersed phase [-],
- Po – power number [-],
- T – diameter of the tank [mm],
- We – Weber number [-].

Details for deriving the constant C_3 are shown [1]:

$$C_3 = f(Po, T/D, c^V, \zeta, Vi) \approx 0.063 + 3.3 \cdot c^V \quad (2)$$

where

- ζ – ratio of local dissipation energy related to its maximal value; $\varepsilon_{max}/\varepsilon_{mean}$,
 Vi – square root of viscosity ratio of dispersed and continuous phase; $(\mu_d/\mu_c)^{1/2}$.

By combining the previous equations, the final result is obtained:

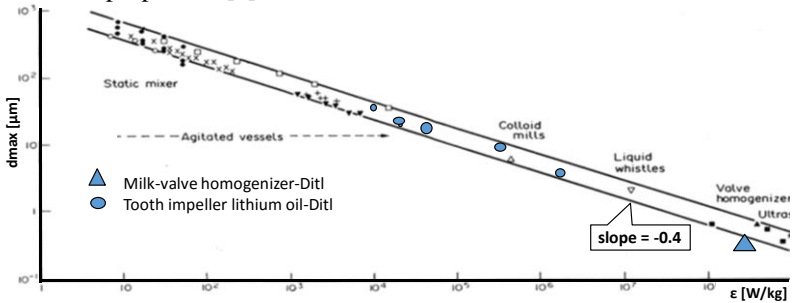
$$d_{32} \approx C_3 \cdot \rho^{-0.2} \cdot \sigma^{0.6} \cdot \varepsilon^{-0.4} \approx \varepsilon^{-0.4} \quad (3)$$

where

- ρ – density of mixture [kg/m³],
 σ – interfacial surface tension [N/m],
 ε – local energy dissipation per unit of mass [W/kg]

The result relates the final particle size to local dissipation energy. The graphical dependence of d_{max} [μm] vs. ε [W/kg] is shown on the graph below (Fig. 4).

From the balance of surface and shear stress forces, it is seen that the maximal shear stress and ε define d_{32} . If equipment with the uniform ε distribution and long enough dispersion time is applied, then the required particle size with narrow particle size distribution is achieved. Shear stress and circulation generated by an impeller in dispersion tanks should be in proportion [1].



○ to the agitated tanks of Calabrese *et al.* (1986a,b) and Wang and Calabrese (1986); □ to the agitated tank of Sprow (1967). Points ▼ and + refer to the agitated vessel of Davies *et al.* (1986) for the dispersion of cyclohexane and decalin respectively. Points ● refer to the data for a Kenics mixer, calculated (as d_{0max} values) by the present author from the data of Berkman and Calabrese (1985). They refer to xylene, silicone oil and paraffin oil. Points △, ▽ and ▲ refer to local P_{Mf} data calculated (Davies, 1985) from the specifications and operating conditions of a colloid mill, a liquid-whistle homogenizer, and a fine-clearance valve homogenizer, respectively. Points ■ are deduced from data of Walstra (1974) for a valve homogenizer, and * refers to his ultrasonic homogenizer.

Fig. 3. Generalisation of dispersion results d_{32} vs. ε

The homogenised slurry from dispersion tanks is milled. In mills at temperature 20°C, its specific gravity varies from 1.0 to 1.8. Slurry with a nominal feed size of P95 is 2-3 mm and has an extremely high viscosity of 20,000 – 4 cP. Milling is used to increase the surface area and induce defects in the particles. Milling increases the proportion of regions of high activity in the surface. If a cubic solid is broken down into smaller cubes, each of side $1/n$ of the original cube, the specific surface area is increased n -times, the broken down mass contains n^2 -times the original length of edges and n^3 -times the number of corners [2]. The most conventional mechanical milling methods are shown in Fig. 5.

Attritors are very effective for the milling of slurry, these consist of a cylindrical grinding chamber with a drive shaft that has multiple impellers protruding from it (Fig. 6). The power input is not used for rotating or vibrating a heavy grinding chamber but it goes

directly to agitating the media. The rotating shaft stirs the fine media, beads and liquid. The impellers energise the beads' charge, causing powder size reduction thanks to their mutual impact [3]. 10-800 μm ZrO_2 beads with a density of 5.7 g/cm^3 and very good abrasion resistance are used and the shaft rotates up to 4,200 rpm. Use of milling beads of the same size has been shown to produce tracks. Consequently, the beads roll along a well-defined trajectory. Therefore, it is necessary to use a combination of smaller/larger beads to randomise their motion [3, 4]. In the attritors 70-80% of the milling chamber is filled. Attritors processing hard-to-mill materials like slurry are operated in batches. There is a loop between the attritor and the dispersion tank for material circulation. Milling in attritors assures high shear stress, uniformity and short milling time.

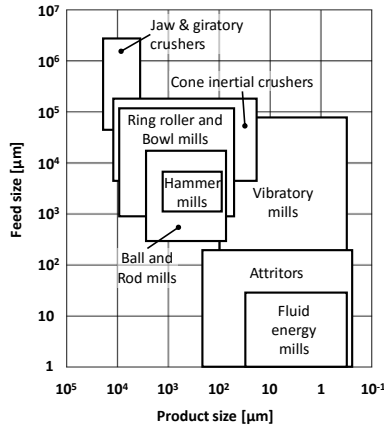


Fig. 5. Application range of mechanical milling methods

Thorough investigation of milling process has shown that three milling stages can be clearly distinguished: the Rittinger stage, the aggregation stage, the agglomeration stage. In the Rittinger stage, the energy input is approximately proportional to the new surface area formation. During the aggregation stage, particles adhere to each other – the degree of dispersion is still increasing significantly and the adherence takes place in consequence of van der Waals forces of the magnitude $0.04\text{-}4 \text{ kJmol}^{-1}$ [5]. These aggregates can be dissolved by slight mechanical intervention. During the agglomeration stage, the surface area may even decrease because of particle agglomerate growth. Growth proceeds thanks to solid bridges, interfacial forces and capillary pressure on freely movable liquid surfaces, adhesion/cohesion and attraction forces. The distance between particles and the number of contacts plays an important role in the appearance of adhesion. The presence of fine particles along with coarse particles promotes the formation of aggregates. Plastic deformation at contact points increases the area of the adhesion forces and, thereby increases the strength, compactness, and resistance to mechanical effects of the agglomerates [2, 5]. Particles in the nanometer size range have a strong tendency to agglomerate owing to their large specific surface area which accentuates their van der Waals interactions. They must be stabilised against aggregation into larger particles by adding surfactants into the system.

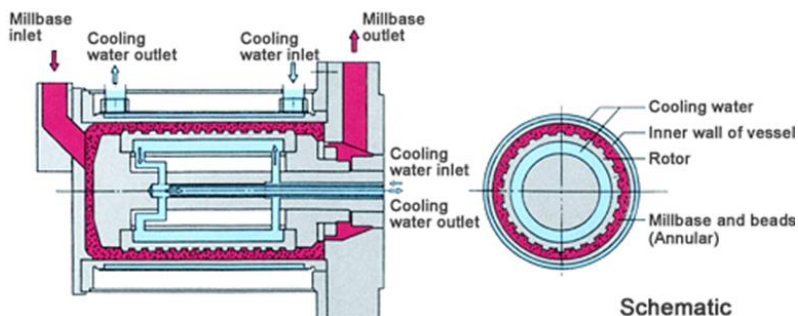


Fig. 4. Attritor scheme

In high-energy milling, surfactants have been used at a level of about 1–5 wt.% of the total powder charge into the mill. The nature and quantity of surfactants used and the type of powder milled would determine the final size, shape, and purity of the powder particles. Use of a larger quantity of surfactants normally reduces the particle size by an order of magnitude of 2–3 [4].

5. Conclusion

On the example, it is shown that chemical engineering affects many branches. Historically, theoretical principles were developed mainly in the chemical industry. Therefore, it is useful to apply this knowledge in newly evolving non-traditional areas. It can be seen in the example that it is essential to analyse the process in the first step and divide the process into separate physical operations. Following the application of already derived dependences in chemical engineering and their synthesis helps the production assessment and optimisation. Professor Ditl jokes about the role of a ‘postal pigeon’ in this knowledge transfer process. In the article knowledge obtained from the process department at Czech Technical University in Prague was applied on the example.

References

- [1] Ditl P., *Selected Problems in Dispersion Mixing*, DECHEMA, Proceedings of Annual Meeting on Extraction and Mixing Processes Working Groups, Heidelberg, 15-17 March 2015.
- [2] Welch A., *The reaction of crystal lattice discontinuities to mineral dressing*, Developments in Mineral Dressing, 1953, The Institution of Mining and Metallurgy, London, 387-392.
- [3] Rhodes M., *Introduction to Particle Technology*, John Wiley and Sons, 1998.
- [4] Suryanarayana C., Ivanov E., Boldyrev V., *The science and technology of mechanical alloying*, Materials Science and Engineering A, 2001, 304-306, 151-158.
- [5] Juhász A., Opoczky L., *Mechanical Activation of Minerals by Grinding: Pulverizing and Morphology of Particles*, Ellis Horwood, Chichester 1990.