Liquid compression chemical reactors

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Maxim GlushenkovAlexander Kronbergm.j.glouchenkov@utwente.nla.e.kronberg@utwente.nl

Liquid compression reactors are novel types of multifunctional chemical reactors in which high pressures and temperatures are generated during a transient compression of a feed by a liquid directly in the reactor. During the following expansion the most energy spent on the compression is recovered whereas the dissipated energy remains in the process inside the liquid. Depending on rate of the compression-expansion cycle the process can be almost isothermal or adiabatic.

The liquid compression reactors can be used for high pressure processes - polymerization, hydrogenation, hydroformylation etc. They can also process "difficult" feeds such as coal powder and slurries, oil residues, shales or sands, biomass and biomass derived liquids and industrial wastes.

Fisher-Tropsch (FT) or methanol/DME synthesis might be promising applications of the reactors. For these processes the reactors permit to use a low pressure, low quality synthesis gas produced for instance by air-blown gasification of all solid feedstocks from coal to wastes, or by air-blown reforming of natural gas. Moreover it is expected that the compression-expansion reactor cycle can reduce a proportion of heavy hydrocarbons in the FT products or eliminate them completely. All this can make economical small- and medium-size production of synthetic fuels.

Chemical reactions requiring high pressure of reactants in many cases involve additional energy input and capital cost besides direct ones associated with compression. For instance FT-synthesis, production of methanol and DME require a high pressure already in syngas production stage because compression of syngas is too capital and energy intensive. However production of syngas at a high pressure is still very expensive, energy consuming and not safe, especially if pure oxygen is used for oxidation.

At the same time existing safe and simple low-pressure air-blown processes produce a relatively inexpensive synthesis gas which, however, can be used only for burning in boilers, gas engines and furnaces.

Liquid compression reactors outlined below are high pressure reactors which do not need high pressure feeds. The high process pressure required is generated during unique cycle of transient compression-expansion of reactants by liquids locally in the reactors

In these reactors a feed in form of gas or two- or three-phase mixture is introduced into the reaction space at a low pressure, compressed there, and reacts; the product expands in the same reaction space so that they s leave the reactor also at a low pressure. Therefore the reactors combine functions of a compressor, a chemical reactor, heat exchangers and an expansion machine thus decreasing capital cost and a footprint of chemical plants, simplify and make them more energy efficient.

Basically a fundamentally new energy conversion principle is used. Instead of conventional compression and heating of reactants, at first mechanical energy (kinetic or compressional) is accumulated in a liquid and then this energy is used for compression of the reactants. Depending on the process conditions various the pressure and temperature change may occur.

The liquid compression principle can be implemented in many different ways, e.g. by means of generation of periodic pressure pulses in the liquid, by the use of various liquid inertia effects etc. Thus a novel promising family of chemical reactors is emerging. Some examples of liquid compression reactors are elucidated below.

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Hydraulic hammer liquid compression reactor

In this reactor the hydraulic ram (water hammer) phenomenon is used to compress gas or two- or three-phase mixture by a liquid. This principle used extensively in so-called <u>hydraulic ram water pumps</u> permits to generate extremely high pressures converting kinetic energy of a low-speed liquid flow.

The reactor principle is shown in **Figure 1**. The reactor comprises a hydraulic accumulator 1, a reactor tube 2, a gas feed inlet manifold 3 with an inlet valve 4, an outlet valve 5 with a valve chamber 6 playing in this particular case also a role of a product separator. The valve chamber and accumulator are communicated by a circulation loop 7 with a circulation pump 8.



Figure 1. Hydraulic hammer compression reactor: 1-hydraulic accumulator; 2reaction tube; 3-gas feed inlet manifold; 4 – inlet valve; 5 - outlet valve; 6separation chamber; 7-circulation loop; 8-circulation pump

In operation a liquid circulates through the pump 8, hydraulic accumulator 1, the reactor tube 2, and then, through outlet valve 5 into a chamber 6 and then back to pump 8.

When inlet valve 4 opens a portion of gas phase reaction component is injected in form of gas bubbles through inlet manifold 3 to the liquid flowing in the reactor tube 2. When the bubbles reach the outlet valve 5, the valve 5 abruptly closes. But the liquid column keeps on moving and compresses the bubbles generating pressure and temperature optimal for chemical reactions. Then the valve 5 opens again and the compression of the bubbles is followed by their expansion and cooling of the reaction products. Then the mixture containing reaction products is removed through the outlet valve 5 to the separation chamber 6, where gas and liquid are separated.

Liquid can also contain a solid phase – a catalyst suspended in process oil in case of three-phase slurry FT or methanol synthesis, a component of a feed in form of fine coal particles in coal hydrogenation process etc.

The catalyst in form of a packed bed or a monolith can be also placed inside the reaction tube.

The reactor permits to cover a very broad range of reaction temperatures, pressures and rates of their change depending on the design and operating parameters The achievable pressure and temperature are very strong functions of the gas hold up ε (volume fraction of the gas phase) and the liquid dynamic pressure $P_D = \rho v^2/2$,



where ρ and v are the liquid density and velocity. For example, in case of isothermal compression the achievable pressure can be estimated as:

$$P_{comp} = exp\left(\frac{P_D}{\varepsilon P_0}\right)$$

where P_0 is the initial (or inlet and outlet) pressure (for simplicity it is assumed that the gas hold up is not high, say not higher than 0.1 or 10% vol.) For process oil with density of 800kg/m³, velocity of 10 m/s and gas hold up of 0.08 the compression pressure will be about 100 bar. Decreasing of gas hold up to 5 % will result in the pressures above 2000 bar (which is already sufficient for low density polyethylene production). Further decreasing of the gas hold up, and/or increase of the liquid velocity and/or using of liquids with higher density should lead to huge, practically unlimited pressures. Of course at so high compression rates the isothermal assumption may not be valid and very high temperatures could be generated.

Application of high density liquids, for instance <u>low melting point alloys</u> with densities up to 8-9 g/cm³ and melting temperatures in range of 40-200 $^{\circ}$ C (Rose's and Wood's metal, etc.) makes it possible to increase the hold-up 8 times or decrease the speed of liquid almost three times.

Centrifugal liquid compression reactors

A basic principle of the liquid compression reactor applying centrifugal force for the compression is shown



schematically in Figure 2. The main component of the reactor is a curved channel which rotates around axis XX. A three-phase mixture (for instance syngas, catalyst and a liquid carrier) flows through the channel. The centrifugal force compresses the mixture together with bubbles entrained in the liquid when the mixture moves in radial direction to the periphery. As the mixture flows parallel to the rotational axis the pressure remains constant. This is a reaction zone, where pressure is optimal for a chemical reaction. The following radial flow of the

mixture towards the axis is accompanied with a decrease of the centrifugal force and pressure. Reaction products expand and leave the reactor. The shape of the channel and its cross-sectional area can be varied in a way that the pressure and temperature change as functions of time in optimal for the chemical reactions way.

In another version of the same principle catalyst can be placed in the tube in form of packed bed or monolith whereas a two phase mixture (syngas dispersed in process oil) is pumped through the reactor. In this case no separation of the products and solid catalyst is required.

Maximum pressure in the reactor is proportional to the reaction mixture density ρ , approximately as $\rho v^2/2$, where v is the peripheral speed. In case of typical liquid hydrocarbons, small volume gas content and v = 300 m/s it can be as high as 300-400 bar. Maximum practicable pressure is restricted only by mechanical strengths of the rotating parts. An actual rotating channel reactor is fully balanced apparatus with many channels.

Advantages and perspectives

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- The reactors solve the problem of feeding a solid phase (reactants, catalyst and/or adsorbent) into pressurized vessels since the solid, liquid and gas phase are mixed and fed to the reactor at a low pressure.
- The reactors eliminate compressors and high-pressure pumps from a process. This is especially important in case of reactions with low conversions per pass requiring multiple compression-reaction-expansion-separation stages.
- The reactors permit to increase the pressure of three-phase FT and methanol production increasing conversion per pass and making reactors more compact.
- In contrary to all contemporary processes, the products leave the reactor at low pressure together with catalyst. For FT-synthesis this may result in interruption of chain-growth polymerization reaction. Therefore a totally different product composition can be obtained, e.g. with a lower content of heavy hydrocarbons. It can also be expected that at short residence times light olefins would become the main FT products.
- The reactors can make economical the use of a low quality syngas with high nitrogen content produced, for instance, by a low pressure air-blown gasification of coal, oil shales and sands, biomass, wastes or air-blown partial oxidation/autothermal reforming of natural gas. Therefore new requirements to syngas production could be established.
- No scale up problems as known for slurry reactors are foreseen.

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• Diversity of the liquid compression methods allows selecting reactor type that suits the best for reaction kinetics, properties of multiphase mixture, pressure and temperature.

Other applications and opportunities

The liquid compression reactors can cover a very broad range of combinations of temperatures, pressures and residence times. Both compression and expansion can be near adiabatic or almost isothermal.

Since the rapid compression can be accompanied with a substantial heating of gas in the bubble the reactors can perform rapid high-temperature reactions such as pyrolysis of different hydrocarbons from methane to relatively heavy liquids, direct synthesis of nitric oxide.

The reactors with slow compression/expansion rate operate in isothermal regime and can be used for hydrogenation of "difficult" feedstocks such as coal powder and slurries, oil residues, shales or sands, biomass and biomass derived liquids, industrial wastes etc.

The use of catalytically active liquids opens opportunities for radically new chemical processes.

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