



Review article

Dispersed phase catalysis: Past and future. Celebrating one century of industrial development



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ABSTRACT

Bergius process for coal liquefaction was patented one century ago. It constituted the first application of dispersed phase catalysts in slurry reactors, considered as once-through disposable solids. Starting from waste materials as additive, the role of catalysts in the conversion of heavy carbonaceous feeds like coal of petroleum residues was progressively identified. Cracking activity was initially considered as necessary, but it was later recognized that hydrogenation activity is essential. The desired properties were established: small particle size, resistance to agglomeration and low cost. Synthesis methods for the production of dispersed phase catalysts are reviewed. Based on historical developments, prospective ways are proposed for improving efficiency of existing conversion processes.

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1. Introduction

Invoking dispersed phase catalysis, the present paper does not intend to build on a new class of catalytic acting mode. It simply refers to the use of solid catalysts, present as small particles,

maintained in a dispersed state within a fluid reacting medium. That is heterogeneous catalysis, but the main reason for establishing a distinction is more related with the design of reacting vessels and with the treatment of heavy and complex reactants, than with any distinctive mechanistic consideration. Some polymerization reactions constitute a peculiar application of dispersed catalyst in which a high value catalyst is mixed at very low concentration with the reactants. The catalyst is not recovered and is

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incorporated in the produced polymer. This application will not be considered in the present paper.

So-called slurry reactors, employed for dispersed phase catalytic reactions, are designed in order to insure an efficient contact between the reacting phases and the catalyst. In that respect, they do not need sophisticated arrangement nor do they deserve decisive breakthrough for improving efficiency; conventional mechanical mixing or gas driven bubbling systems conveniently apply. Autoclaves and batch reactors constitute the simplest type but their use is limited either to small scale production or laboratory units, so we will preferably consider dynamic flow reactors. If we now focus on the functioning of such a kind of reactor, it must be pointed out that moving a continuous flow of catalytic material has a cost, and it must be kept at a minimum, in contrast with fixed bed reactors for which the mass of catalyst is not an essential concern. The second and more critical point resides in the separation of the resulting products from the catalytic phase. If the desired product is a liquid, a simple volatilization will work, but in the case of formation of solid products or by-products, the separation step for catalyst recovery may be excessively complex and/or incomplete. This feature is decisive for the whole conception of any process involving a dispersed phase catalyst and it will dictate its main desired characteristic: high intrinsic activity and, correlatively, low concentration of circulating catalytic phase. Owing to arduous and deficient catalyst recovery, another desirable attribute is the low cost of base material and manufacture of dispersed catalytic systems. Historically, this aspect has overwhelmed any further consideration and has imposed a severe limitation to the selection of possible candidates as active phases. These considerations have restrained the scope of elaboration methods and most of the materials added as active phases are low-priced wastes. Similarly, economical considerations have limited the application of dispersed phase catalysis to cheap raw materials as reactants: coal, bitumen or petroleum residue.

1.1. History

The first patented application of dispersed catalysts to an industrial process goes back one century ago, in 1913, when Bergius patented the results of its observation concerning the production of liquid fuels from coal under hydrogen pressure [1]. This pioneering work was carried out in Bergius' own laboratory. He promptly recognized the necessity for industrial support and associated in 1914 with the firm Theodor Goldschmidt A.G. where he occupied an executive position. After World War I, several firms sponsored the work. In 1921, a 30 tons-per-day pilot plant dedicated to hydrogenation of oil and tar was in function, and 1 year later, a second plant was designed for coal hydrogenation. In 1924 the British Bergius Syndicate was created to exercise the patents rights in the UK. In 1931 a consortium composed of IG Farben, ICI, Royal Dutch Shell and Standard Oil of New Jersey merged their patent rights on hydrogenation processes. Most of commercial plants in the world were constructed in the nineteen thirties: in the USA, UK, France, China, Korea, the major capacity being established in Germany with 12 plants producing 4 millions tons of gasoline in 1943.

In the first patent, the use of an additive is not specifically mentioned. But industrial practice immediately recognized the positive influence upon coal conversion obtained through addition of "luxmasse", a by-product of alumina production consisting mainly of iron oxide. Although during this early period of development it was merely considered as a sulfur trap converting sulfur in coal to iron sulfide, it became the standard additive in coal conversion processes. Further observations evidenced a possible influence of coal mineral matter, in which iron sulfide is present as pyrite. Thus, since the very start, research and industrial developments of dis-

persed phase catalysis have intimately been correlated with coal liquefaction and later with upgrading of heavy crude and petroleum residues. Questions dealing with catalytic action as well as the conversion mechanism were intricate and hardly addressed by a systematic experimental approach. The Bergius process promptly became industrially mature, but continuous progress and further improvements relied for many years upon empirical observation. It may be argued that this is the case for many industrial processes, but this one looks exemplary in the sense that, despite being far away from rational understanding, it demonstrated its maturity and performance, allowing large scale production of gasoline.

Such a fast transposition of a chemical process from laboratory experiment to commercial production truly deserves being referred to as a success story. Bergius' merit as a prominent chemist was recognized and he was awarded the Nobel Prize in 1931, with Carl Bosch, for their contributions to the invention and development of chemical high-pressure methods. The prize does not specifically refer to coal liquefaction, but emphasizes the technical aspects of managing reactions under high pressure. It must be recalled that ammonia synthesis, which was the first industrial process involving hydrogenation under high pressure, required a major effort in the development of materials and devices. Particularly dramatic were the decarburization of steel and the consecutive deterioration of mechanical properties of reactors which probably caused major disasters before being identified. The complexity and multiplicity of technical issues that had to be solved in order to achieve a safe function of commercial plants during this historical period can be appreciated through a look at the numerous technical reports published by DOE or US Bureau of Mines: until the nineteen sixties they still were a concern and they occupy a significant part of the content. Thus, the talent of Bergius was multi-faceted: chemist, but also engineer, mechanical, metallurgist. As a businessman, his success was more mitigated. After his patents rights concerning coal liquefaction were transferred to major industrial partners, he devoted to the hydrolysis of wood to produce sugar for industrial use, and he invested most of his own funds. Complex technical problems and elevated costs led him to economic failure, and he could not get the totality of the money from his Nobel Prize.

1.2. Documental aspects

The cumulated number of articles, patents and technical reports published since 1913 up to 2012, including coal hydrogenation or liquefaction in the title is about 7000. Historical references mainly consist of patents. It is only after World War II that experts from the US and UK inspected German coal liquefaction plants and studied technical documents from research laboratories. This intelligence effort was materialized in the form of exhaustively documented reports [2] which constituted the basis for the political decision to support the development of large scale production of synthetic liquid fuels from coal, the US Bureau of Mines being the leading arm of this strategic objective. After an intensive period dedicated to acquiring basic knowledge and designing pilot plants, it was concluded that: "The existence of giant petroleum refining facilities, the high construction cost of coal-hydrogenation plant and the continuous discovery of petroleum reserves make gasoline from hydrogenation of coal and tar unable to compete with gasoline from petroleum in the United States at the present time" [3].

Any research activity dealing with coal conversion was suspended, in the USA as well as in European coal producing countries, until the first oil shock in 1974. The possibility of shortage in oil supply prompted western governments to support coal liquefaction R&D. Part of the previously acquired knowledge had already been forgotten and university courses did not include coal

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