TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Multiphase reactions using solid foams

Citation for published version (APA):
Stemmet, C. P., Kuster, B. F. M., Schaaf, van der, J., & Schouten, J. C. (2006). Multiphase reactions using solid foams. (Patent No. *WO20006065127-A1*).

Document status and date:
Published: 22/06/2006

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 05. Oct. 2023

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 June 2006 (22.06.2006)

PCT

(10) International Publication Number
WO 2006/065127 A1

(51) International Patent Classification:
B01J 35/04 (2006.01) *B01J 35/10* (2006.01)
B01J 19/32 (2006.01)

(21) International Application Number:
PCT/NL2005/050016

(22) International Filing Date: 19 October 2005 (19.10.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
04077882.1 19 October 2004 (19.10.2004) EP

(71) Applicant *(for all designated States except US)*: **STICHTING VOOR DE TECHNISCHE WETENSCHAPPEN** [NL/NL]; Van Vollenhovenlaan 661, NL-3527 JP Utrecht (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **STEMMET, Charl, Philip** [NL/NL]; Tramstraat 60, NL-5611 CR Eindhoven (NL). **KUSTER, Bernardus, Franciscus, Martinus** [NL/NL]; De Vroente 107, NL-5672 TV Nuenen (NL). **VAN DER SCHAAF, John** [NL/NL]; Vossermeer 8, NL-2993 PN Barendrecht (NL). **SCHOUTEN, Jacob, Cornelis** [NL/NL]; Copernicuslaan 22, NL-5251 ZC Vlijmen (NL).

(74) Agent: **VAN WESTENBRUGGE, Andries**; Nederlandsch Octrooibureau, Postbus 29720, NL-2502 LS Den Haag (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/065127 A1

(54) Title: MULTIPHASE REACTIONS USING SOLID FOAMS

(57) Abstract: The present invention relates to a gas-liquid-solid (GLS) process comprising contacting reactants on a solid foam material, wherein the solid foam material has a surface to volume ratio of at least 250 m^2/m^3. This foam material may include a catalyst composition or a catalyst material may be supported on the foam material. The foam material proyides improved mass transfer and favourable hydrodynamic parameters when compared to conventional packings so that an enhanced contact between reactants and an improved reactor performance is achieved.

MULTIPLE REATIONS USING SOLID FOAMS

Field of the invention

The present invention relates to multiphase reacting processes wherein solid foam material is used as a contacting material or used as a catalyst or as a catalyst support. In particular, the present invention relates to a gas-liquid-solid (GLS) process comprising contacting reactants on a solid foam material. This foam material may include a catalyst composition or a catalyst material may be supported on the foam material.

Background of the invention

The chemical industry is continuously striving at reduced capital and operating costs of plants by optimising chemical processes. In these optimisations, reactor design plays an essential role since in the reactor chemical conversion of reactants occur. In these (GLS) chemical processes catalyst compositions are commonly used that are included in the reactor as fixed or fluidized beds. The fixed beds include packing materials such as spheres, Raschig rings, monoliths and structured packing alternatives. The fluid beds include all systems where the solid material moves around in the reactor volume, e.g. slurry bubble columns, (circulating) fluidized beds etc. These solid supports and catalyst compositions, mentioned previously, need to have suitable properties with respect to pressure drop, specific geometric surface area to volume ratio, activity and selectivity etc. to obtain a reactor design that is economically feasible. This is in particular important in three-phase catalytic reactors such as gas-liquid-solid (GLS) reactors. In slurry bubble columns, a typical example of GLS-reactors, gas bubbles flow upwards through the liquid phase that contains the finely divided solid catalyst particles, the liquid is considered to be in a batch. The bubbles draw liquid and catalyst in their wakes and induce thereby back-mixing in the liquid. Slurry bubble columns are usually employed where high interfacial areas between the various phases is necessary (cf. Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 20, 4th Ed., pages 1007 – 1059, **1996**). Slurry bubble columns are widely used in industry, because of the simplicity of construction, the high liquid hold-up, and the excellent heat transfer characteristics. However, these reactors are not always the most

appropriate for a reactor design due to the back-mixing behaviour, and require solids handling.

The most common GLS-reactor systems found in industry employ a catalyst slurry (typical particle diameter 1-100 μm, typical concentration range 1 to 10 vol.%) or a packed bed catalyst (typical particle diameter 1 to 4 mm, typical volume fraction 65%). The batch wise operated, stirred GLS-reactor is the workhorse of the fine-chemicals industry. The slurry bubble column is preferably used for the somewhat larger scale operations. The trickle-bed reactor, where gas and liquid are in co-current down flow over a packed bed of solid catalyst particles or pellets, is often used in the petrochemicals industry. In between the slurry and packed bed configurations, three-phase fluidisation can be discerned, applying intermediate particle sizes and solids loading.

Catalyst compositions comprising random packings and structured packings are commonly employed in GLS-reactors. These packing materials, apart from their catalytic action for some reaction, also provides a surface for the fluid flow and thus enable reactors to be operated in a number of flow configurations. Co- and counter current are the most common flow configurations. These packed columns are operated in different regimes depending on the relative flow rates of the fluid phases moving through the packing material: bubbly or pulse flow in co-current up-flow or trickle flow in counter current flow are common examples of these regimes. In many instances the operating range for gas and liquid flow is limited to boundaries between regime transitions, where transition to an undesired regime occurs, or where multiphase flow cannot be realized, e.g. flooding in counter current flow. These operating limits are determined under hydrodynamically similar conditions for two phase flow and are dependent on factors such as the physical properties of the fluids (density, viscosity), the physical properties of the packings (hydraulic diameter, voidage, surface area to volume ratio, hydrophobicity), etc. Important factors affecting the use of particular packings for reacting systems are the hold-up of each of the respective phases in the reacting volume, the frictional pressure drop per unit length over the packing material, the back-mixing behaviour of the fluids flowing through the packings and the mass transfer between the respective phases. Structured packings have the advantage of a low pressure drop and high void space thereby enabling intimate contact between catalytic sites and reactants. However, structured packings suffer from the disadvantage

that they have low surface area to volume ratios so that only relatively low amounts of catalytic material can be deposited on the support. Also known in the art are solid foam packings which not only have the beneficial features of structured packings, but also have the desired high surface area to volume ratio.

Processes wherein catalyst compositions are used which comprise catalytic material supported on solid foam packings are known in the art, although these processes are basically limited to gas phase reactions, separation processes and the like.

US 4.810.685 discloses a catalyst composition for in particular steam reforming, but also e.g. Fischer-Tropsch reactions and hydrodesulfurisation reactions, wherein the catalyst composition comprises a ceramic foam support having a total porosity of 40% to 85% and an apparent density of at least 1 g/cm^3. The ceramic foam support is manufactured by impregnating organic plastic foam, e.g. polyurethane foam, with aqueous slurry of e.g. alumina so that the pores of the organic plastic foam are filled with the slurry. Upon drying, the aqueous alumina slurry remains in the pores and after calcination a "negative" structure of the organic plastic foam in the form of a ceramic foam is obtained. Subsequently, the ceramic foam support may be impregnated with a catalytically active material or a precursor for a catalytically active material, e.g. a nickel or a cobalt compound. The ceramic foam supports loaded with catalytically active material are said to be suitable for use in gas-solid phase reactions, e.g. methanation, hydrodesulphurisation, ethylene oxidation, xylene oxidation, sulphur dioxide oxidation, and liquid-solid reactions, e.g. hypochlorite decomposition.

US 2003/0162649 discloses a catalyst composition that may be used for chemical reactions in a gaseous phase or a liquid phase including cracking, acylation, alkylation and isomerisation reactions of hydrocarbons, wherein the catalyst composition comprises a zeolite that is deposited on a rigid support that preferably has a specific surface area of at least 5 m^2/g so that large quantities of zeolite can be deposited on the rigid support. According to US 2003/0162649, the rigid support is preferably a β-SiC support having a high BET surface area of about 10 to about 100 m^2/g. Most preferably, the rigid support is a SiC foam.

US 6.750.258 discloses a catalyst composition for a Fischer-Tropsch process wherein the catalyst composition comprises a ceramic or metal foam and optionally a catalyst layer.

GB 1.484.461 discloses a packing material for gas-liquid distillation or absorption, wherein the packing material comprises a ceramic foam through which the gas and liquid components can flow.

US 4.208.284 discloses a process for separating at least a liquid component from at least one solid or liquid component in which process a highly porous material with a open pore structure and low pressure drop is employed. An example of this material is given to be a polyurethane foam.

US 6.238.464 discloses a process for separating gas streams containing liquid or solid particles substantially smaller than 1 μm wherein a separator is used that comprises a foam made of either polyurethane, carbon or metal of some sort.

US 2004/0112794 discloses a process for gas-liquid counter current processing wherein a liquid reactant and a gaseous reactant are contacted in counter current flow through a fixed bed of catalyst material, wherein the fixed bed comprises at least two catalyst layers. The voidage of mentioned catalyst layers may be increasing or decreasing in the direction of the direction of the liquid flow for an increased range of gas-liquid ratio, and an improvement in stability and flexibility of the overall reactor design. The catalysts may have different sizes and shapes in a preferred voidage range of 0.45 to 0.8.

DE-A-102 08 711 describes packing material of a ceramic material with monolithic type channels diagonally down its structure, and its use for thermal separation of a fluid mixture. The channels as described are similar to a porous inclined monolith, which has been cut and stacked on top of one another. These pores are not required to be completely open structures. All channels seem to run along the same path, parallelly arranged within one packing element, thus disadvantageously keeping turbulence low. It is also not clear how the redistribution of the phases would proceed at the ends of the channels, whereas redistribution and high gas-liquid mass transfer are essential in a multiphase reaction process. Further, DE-A-102 08 711 is silent on the pore size of the ceramic material.

US 2003/0116503 discloses the preparation of a catalyst structure comprising carbon nanotubes over a porous support, such as a foam, felt, mesh or membrane. These supports are considered to be "large pore" supports, but pore sizes are disclosed mostly in the range of several hundreds of nanometers. Examples are given for gas phase Fischer-Tropsch processes. Herein, the catalyst is described to have a higher

activity towards the conversion of CO, which is also mentioned by Wang et al. (Chinese Chemical Letters, Vol 13, No 12, pp1217, 2002) where carbon nanotubes are shown to increase the activity for the conversion of CO to methanol.

Whereas the pore sizes taught in US2003/0116503 may be suitable for gas-phase reactions as shown in the examples given therein, these relatively small sized pores are disadvantageous in a multiphase reactor. Due to capillary forces, but also to the initial distribution of the fluids to the reaction volume, the effective contact between liquid and gas phases are limited dramatically. At these small pore sizes effects like high pressure drop may occur, and the flooding point, i.e. the point where gas flux from the bottom is large enough to reverse the flow direction of the liquid flowing down in counter-current operation, would be reached at lower gas velocities, thus making the operation of counter-current reactor unit impossible.

US 4.251.239 teaches the use of a solid foam as a catalyst support for a gas-phase reaction or as a gas filter.

Summary of the invention

The present invention relates to catalytic gas-liquid-solid (GLS) processes comprising contacting at least two fluid reactants (gas or liquid) with solid foam for the intention of reaction of the contacting phases. This solid foam with a surface area to volume ratio of at least 250 m^2/m^3 may comprise of a supported catalyst composition or be used as a support for a catalyst composition or the precursor of a catalytically active material. This invention also relates to using solid foam materials as a gas/liquid interfacial area enhancer for slurry reactor systems. The invention also relates to the improved mass transfer and favourable hydrodynamic parameters when compared to other packings i.e. extending the operating ranges of uniformly distributed two-phase flow in either co-current or counter-current flow configurations.

The surface area can be calculated straightforwardly with the equations given in example 1 attached hereto. It could be referred to as the specific geometric surface area, in order not to confuse the surface area with the BET surface area as often reported in literature. Hence, where it is mentioned surface area in the context of the invention, it is meant the "specific geometric surface area", unless specified otherwise. The BET surface area is a measure of the total surface per unit volume, including small pores and

rough surfaces. It expresses the surface area available for catalyst deposition. However, pores and surface roughness typically do not provide gas liquid mass transfer area for multiphase flow. Therefore, a better indication of this behaviour of importance to multiphase reactions is the above-reported specific geometric surface area, which accounts for the fact that the surfaces are not smooth and contain meso- and macropores. A large discrepancy between both values is thus unavoidable.

In the context of the invention the solid foam of the invention is "open celled", where most cells are of a uniform size. With "open celled" it is understood that a predominant fraction of the pores is connected to one another; preferably at least 70%, more preferably at least 90%, most preferably at least 95% of the pores form a interconnected, continuous structure inherent to a foam, and which tortuous passages allow for continuous distribution of gas and liquid flows. The open celled solid foam has an open reticulated structure with interconnected tortuous pores, which results in enhanced flow and turbulence and optimises contact between fluids.

Description of the drawings

Figure 1 shows the surface area for aluminium metal foams as a comparison with commercial packings: 1. Foam 40 ppi [http://www.ErgAerospace.com]; 2. Foam 20 ppi [http://www.ErgAerospace.com]; 3. Foam 10 ppi [http://www.ErgAerospace.com]; 4. Rashig rings, 6 mm [Perry's Chemical Engineering Handbook, 1997]; 5. Sulzer CY [Perry's Chemical Engineering Handbook, 1997]; 6. Monolith 200 cpsi [Chemical Engineering Science *56*, p. 805 – 812]; 7. Monolith 600 cpsi [Chemical Engineering Science *56*, p. 805 – 812]; 8. Monolith 25 cpsi [Chemical Engineering Science *54*, p. 2381 – 2389].

Figure 2 shows the gas hold-up for batch liquid configuration compared with bubble column, air/water system: ■ 5 ppi foam; ▲ 40 ppi foam; ◆ bubble column 2D.

Figure 3 shows the liquid hold-up for counter-current flow, 5 ppi aluminium foam, water and air system: □ High hold-up, liquid velocity 0.028 m/s; ○ High hold-up, liquid velocity 0.02 m/s; ■ Low hold-up, liquid velocity 0.028 m/s; ● Low hold-up, liquid velocity 0.02 m/s.

Figure 4 shows a comparison of flooding points for foam packing in counter-current flow, air/water system: ■ 40 ppi foam; ▲ 5 ppi foam; ---- Katapak-S [Chemical engineering Science *54*, p. 1339 – 1345]; —— Monolith 25 cpsi [Catalysis Today *69*, p. 153 – 163].

Figure 5 shows the regime map for 1/3 inch Raschig rings for an air/water system, comparison with solid foam packings: ---- Raschig rings (BR-PR); —— Raschig rings (PR-SR); ● Foam 5 ppi (BR-PR); □ Foam 40 ppi (BR-PR).

Detailed description of the invention

Advantages of the present invention are that an improved reactor performance can be achieved due to an enhanced intimate contact between the reactants, in particular for mass transfer controlled processes. This holds in particular for the gaseous reactants of which mass transfer to the catalytic site is often rate-determining. Employing a solid foam material as support avoids internal diffusion resistances. Hence, the process according to the invention shows enhanced mass transfer when compared with traditional fixed bed processes due to the lower resistance to diffusion through the internal pores of such materials. Comparing the solid foam alternatives with fluidized bed alternatives avoids the problems of downstream filtering of the solid from fluid streams. Additionally in such processes, the catalyst is in slurry form and flowing with the liquid components. As a consequence, there is a low shear between solid and liquid whereas in the solid foam material the shear between solid and the fluid phases is enhanced which leads to higher local mixing of the fluids, the latter leading to an enhanced mass transfer between gaseous and liquid components.

Likewise, heat transfer is improved by the present invention. In conventional support materials, e.g. monoliths, observed temperature gradients result in loss of selectivity and/or catalyst deactivation. Additionally, in fixed bed reactors hot spots are known to occur which also affects selectivity. In the solid foam material according to the invention, however, hold-up of the liquid components is higher so that sufficient heat exchange may be achieved. Improved heat transfer is in particular observed where heat conducting metal foam is used. Consequently, it is preferred according to the present invention that the solid foam material is heat conducting metal foam when improved heat transfer is desired.

According to the invention, it is also preferred that the solid foam material is metal foam or carbon foam when in the process it is beneficial that the support has electrical conducting properties. For example, conductive supports enable monitoring and control of the oxidation state of a metal catalyst. Additionally, a conductive support enables that by forcing the potential of the catalyst to a particular level, surface coverings and redox properties of the catalyst can be influenced and controlled without the need of large electrical currents. Conductive supports also have an advantage in oxidation reactions where catalyst deactivation is overcome by the application of a redox cycle to the catalyst since this cycle can be applied directly by electrochemical means. Hence, according to the invention, the solid foam material is preferably an electrically conducting foam, in particular metal foam or carbon foam, when the process involves electrical monitoring and/or control of catalyst condition, electrochemical enhancement of catalyst activity and/or selectivity, or electrochemical prevention of catalyst deactivation.

For improving the hydrodynamics of slurry bubble columns, various types of internals are used, e.g. vertical plates and pipes, horizontal screens and perforated plates. The use of internals perpendicular to the direction of flow enhances bubble break-up and diminishes back-mixing. Back-mixing in the fluid phase is also reduced by the use of the solid foam material according to the invention.

A further advantage of the present invention is that the solid foam material can be manufactured with different size and shape. For example, disk forms are preferred in centrifugal reactors for intensified mass transfer. Sheets of solid foam material can be applied on supporting frames and stirrers and cylindrical forms can be applied in pipes and tubes. Also, the arrangement of the same or different forms can be adapted as required for a good gas-liquid contact, direction of flow and low pressure drop. The flow orientation of the fluid may be either in the co- or counter current directions through the solid foam. For some processes such as hydrodesulphurisation a counter current operation is beneficial.

The solid foam material may also be suitable for the reaction of fluids in biological processes where the reaction is enhanced by enzymes immobilized on the surface of the solid foam. Here a high enough solid surface area per unit volume is beneficial. According to the invention, it is preferred that the solid foam material has a surface area to volume ratio of at least 250 m^2/m^3, more preferably at least 500 m^2/m^3.

Although it is preferred that the surface area to volume ratio is as high as practically possible, according to the invention this ratio is not higher than a BET surface area of 100 m^2/g, preferably of 500 m^2/g without the addition of wash coats or the use of other surface modifications. These surface modifications may be used to increase the surface area to volume ratio of the solid foams up to 600 m^2/g, preferably up to 1000 m^2/g.

It is additionally preferred that the solid foam material has a void volume in the range of 60 to 99%, relative to the total volume of the solid foam material. It is even more preferred that the solid foam material has a void volume in the range of 85 to 98%.

According to the invention, the solid foam material has an average pore size of 250 μm to 5100 μm, more preferably 635 μm to 5100 μm. A pore size of 250 μm to 5100 μm corresponds approximately to pore sizes of 100 ppi (pores per inch) to pore sizes of 5 ppi respectively (1 ppi ≈ 0.0254 pores per m). It is preferred that the average pore size is at least 420 μm (corresponding to 60 ppi). Solid foam material having pore sizes of 420 μm or higher gives the advantage that high pressure drop is avoided and the flooding point in counter-current operations would not be reached at too low a gas velocity.

It is furthermore preferred that the solid foam material is selected from the group consisting of metal foam, ceramic foam, carbon foam and polymer foam. These materials are known in the art. For example, ceramic foams are used in filtration of molten metal, metal foam as light-weight construction material and carbon foam as electrode material in electrochemistry. Ceramic foams have also been used as catalyst support in e.g. exhaust gas catalytic converters as have monoliths. Metal foams have also been used as catalyst supports. However, the use of these foams is limited to single phase conversions. Suitable foams are commercially available, e.g. from ERG Material and Aerospace Corp. (carbon, ceramic and aluminium foam) and Porvair plc. (ceramic and metal foam).

According to a preferred embodiment of the process according to the invention, at least one reactant is in the gaseous phase and at least one reactant is in the liquid phase.

The process according to the invention may be performed co-currently or counter currently. That is, that the reactants are contacted co-currently or counter-currently.

The catalyst composition employed in the process according to the invention preferably comprises a metal, preferably a noble metal, preferably Pt or Pd, or a zeolite, wherein the zeolite may be a natural zeolite or a synthetic zeolite.

The present invention also provides a GLS-reactor comprising a supported catalyst composition, wherein the support comprises a solid foam material having a surface area to volume ratio of at least 250 m^2/m^3.

Examples

Example 1

The commercial foams available from the manufacturers mentioned above have a high surface area compared to other packing materials. This is described in Figure 1 where the surface area to volume ratio and void space for the solid foams and some commercial packings are plotted.

The information in Figure 1 of one of the manufacturers of solid foams (ERG Material and Aerospace Corp.) shows the increase in surface area for solid foams. This surface may be used for effective catalyst deposition and operate in counter current and co-current flow regimes not previously described for other packings. The most recent publication for calculating this specific surface area is described by Fourie and Du Plessis (Chemical Engineering Science, **57**, pg 2781-2789) where only geometrical considerations are taken into account assuming smooth solid surfaces. Here the foams are described by a representative unit cell: one of the corner edges of an array of tetrakaidecahedron. The following formulae were used to calculate the surface area, or the specific geometric surface area, for the foam:

$$a = 25.4\text{mm} / (\text{PPI number})$$

$$\text{Void fraction} = 1 - 3.87(d_m/a)^2 - 18.5(d_m/a)^3$$

wherein a is the average cell size, and d_m is a parameter solved for using the void fraction of the foam (cf. formula (15) in Chemical Engineering Science, **57**, pg 2781-2789). The specific geometric surface area may then be calculated:

(Specific geometric) surface area = 26.8 (d_m/a^2) - 14.9 (d_m^2/a^3)

Table 1 gives values calculated using the formulae above for solids foams of 5 to 40 ppi with void fractions 0.8 and 0.95.

Table 1: Calculated values for the specific surface area for solid foams 5 to 40ppi.

		Void fraction = 0.95		Void fraction = 0.8	
ppi	a	d_m	Specific Surface Area	d_m	Specific Surface Area
[-]	[mm]	[mm]	[m^2/m^3]	[mm]	[m^2/m^3]
5	5.1	0.50	487	0.77	723
10	2.55	0.25	974	0.38	1447
20	1.275	0.13	1948	0.19	2894
40	0.6375	0.06	3750	0.10	5787

As mentioned above, the specific geometric surface area differs from the BET surface area. The BET surface area measurements are almost 200 times these calculated values; described in Richardson and Remue (Applied Catalysis A: General, **204**, pg 19-32). They account for the discrepancy in surface area measured using BET-techniques and the geometric specific surface area because the surfaces are not smooth and contain meso- and macropores. The specific geometric surface area is a good indication of the available gas-liquid contact area for mass transfer; whereas the BET-surface area gives a measure of the available area for deposition of catalyst material, and is thus an indication of the available liquid-solid mass transfer.

Example 2

The gas and liquid may be contacted on the solid foam material where the liquid is in a batch mode and the gas is distributed from the bottom of the column. The gas has a certain hold-up in the volume as described by the following equation:

Gas hold-up = Volume Gas / (Volume Gas + Volume Liquid + Volume solid)

For these experiments metal foams made of aluminium were used (ERG Material and Aerospace Corp.) with an approximate solid volume of 6-8 %. The volume of the solid material is 6-8% of the total volume, thus a porosity of 92-94%. The materials tested were metal foams of 5 and 40 ppi. Figure 2 shows the variation of the gas hold-up and gas-liquid interfacial area with gas velocity:

One observes that in the example given above gas hold-up comparable to bubble columns may be achieved with the solid foam packing due to the high porosity of the foam.

Visual observation of the flow through the packing indicates a more stable uniform flow pattern. The gas-liquid interfacial area is compared with bubble columns. For solid foams the following was used:

(Gas-Liquid surface area) =(specific geometric surface area per volume) x(Gas Holdup)

It is expected that a thin film of liquid is on the surface of the solid foam packing, where the gas phase is passing in the form of a bubble and complete wetting is assumed. The surface area per unit volume for 40 and 5 ppi foams are 2560 and 250 m^2/m^3 respectively. Especially in mass transfer limited processes the 40ppi solid foam may be advantageous due to the high interfacial area. An added advantage over bubble column is that the catalyst may be fixed within the reactor volume on the solid foam support, thus no filtering is required to separate the liquid and solid phases.

Example 3

The solid foam may also be used to contact gas and liquid in a counter current flow configuration. A liquid hold-up may be described in a similar way as the gas hold-up:

Liquid hold-up = Volume Liquid / (Volume Gas + Volume Liquid + Volume solid)

Here the hold-up of liquid is described depending on the liquid and gas flow rate. This data may be found in Figure 3 for the 5 ppi foams.

Here, two flow operations in counter-current flow are possible with the foam packing: a high- and a low liquid hold-up. The low liquid hold-up (closed symbols) is described as counter current trickle flow and is the common countercurrent regime for other packings. In this regime the liquid hold-up is increased with increasing gas velocity as the gas flow opposes the liquid flow trickling down the solid foam. At a certain gas flow rate the gas velocity is high enough so that the liquid flow through the packing material is impossible. This is noted as the flooding point and is the highest gas flow rate on the graphs given above for the two different liquid flow rates. The high liquid hold-up regime (open symbols) is similar to a bubble column with liquid continually being removed from the bottom and distributed at the top of the column. As the gas velocity is increased the liquid hold-up is reduced. This regime has not been experimentally observed for other packing materials.

From Figure 4 it appears that the flooding point for solid foams is reached at lower liquid and gas velocities than for monoliths. The flooding points are similar to the Katapak-S packing, which has been considered for reactive distillation applications.

As the number of pores per inch of the solid foam is increased, the flooding point is reached at lower gas velocities, for a specific liquid velocity; hence, if the open celled solid foam material has too small pores, the operation of a counter current gas-liquid unit will become impossible.

Example 4

Packed bubble columns are packed bed systems where the liquid and gas move co-currently upwards through the column. The regimes identified for Raschig rings [AIChE, 1967, pg 1196-1202] is the bubble, pulse and spray regime. The bubble regime exists at relatively high liquid to gas ratios and low gas rates and resembles a bubble column. As the gas rate is increased pulses of liquid and gas are observed. At low liquid to gas rates a spray regime can be identified where the liquid travels through the void space of the packing in the form of a fine mist.

The foam packing extends the bubble regime to higher gas velocities. This is due largely to the high voidage of the solid foams compared with more conventional packings.

Claims

1. A catalytic GLS-process comprising contacting reactants with a solid foam material, wherein the solid foam material has a surface area to volume ratio of at least 250 m^2/m^3.
2. The catalytic GLS-process according to Claim 1, wherein the solid foam material is a support for a catalyst composition.
3. The catalytic GLS-process according to Claim 1 or Claim 2, wherein the solid foam material has a void volume in the range of 60 to 99%, relative to the total volume of the solid foam material.
4. The catalytic GLS-process according to any one of Claims 1 - 3, wherein the solid foam material has an average pore size of 420 to 5100 μm.
5. The catalytic GLS-process according to any one of Claims 1 – 4, wherein the solid foam material is selected from the group consisting of metal foam, ceramic foam, carbon foam and polymer foam.
6. The catalytic GLS-process according to any one of Claims 1 – 5, wherein at least one reactant is in the gaseous phase and wherein at least one reactant is in the liquid phase.
7. The catalytic GLS-process according to any one of Claims 1 – 6, wherein the reactants are contacted co-currently.
8. The catalytic GLS-process according to any one of Claims 1 – 7, wherein the reactants are contacted counter-currently.
9. The catalytic GLS-process according to any one of Claims 1 – 8, wherein the catalyst composition comprises a metal.
10. The catalytic GLS-process according to any one of Claims 1 – 9, wherein the catalyst composition comprises a zeolite.
11. A GLS-reactor comprising a supported catalyst composition, wherein the support comprises a solid foam material having a surface area to volume ratio of at least 250 m^2/m^3.

Fig 1

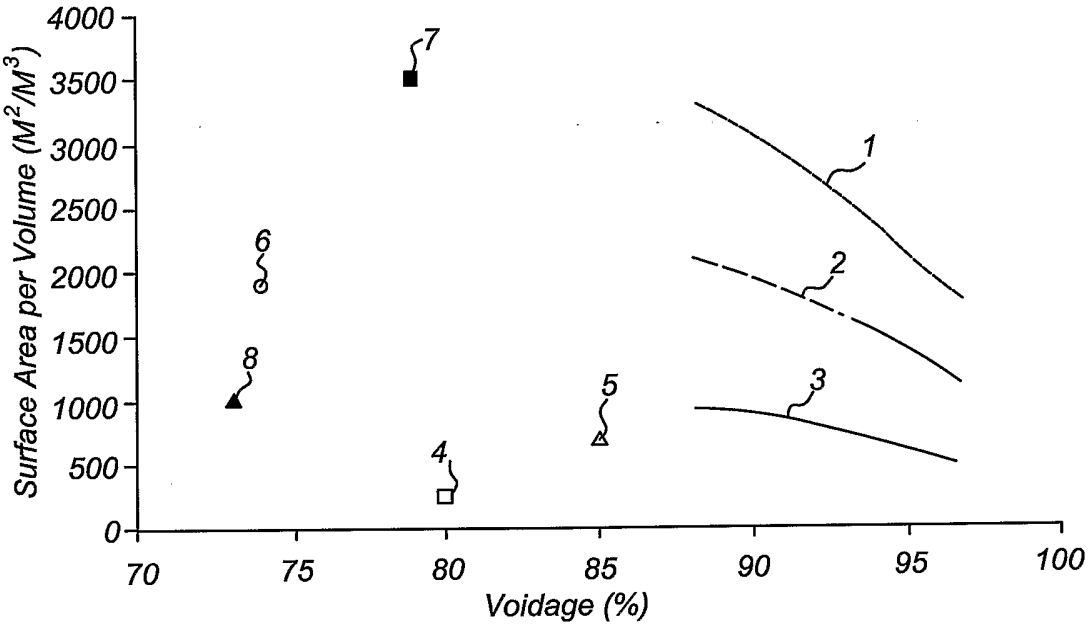

Surface Area per Volume (M^2/M^3)
4000
3500
3000
2500
2000
1500
1000
500
0
70
75
80
85
90
95
100
Voidage (%)
1
2
3
4
5
6
7
8

Fig 2a

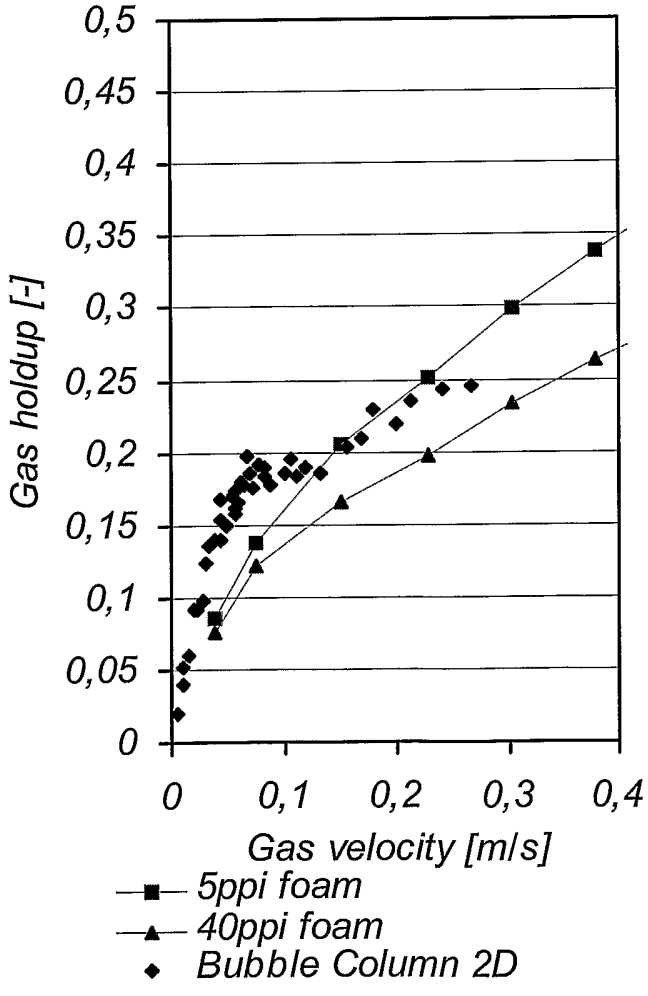

Gas holdup [-]
0,5
0,45
0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
0
0,1
0,2
0,3
0,4
Gas velocity [m/s]
5ppi foam
40ppi foam
Bubble Column 2D

Fig 2b

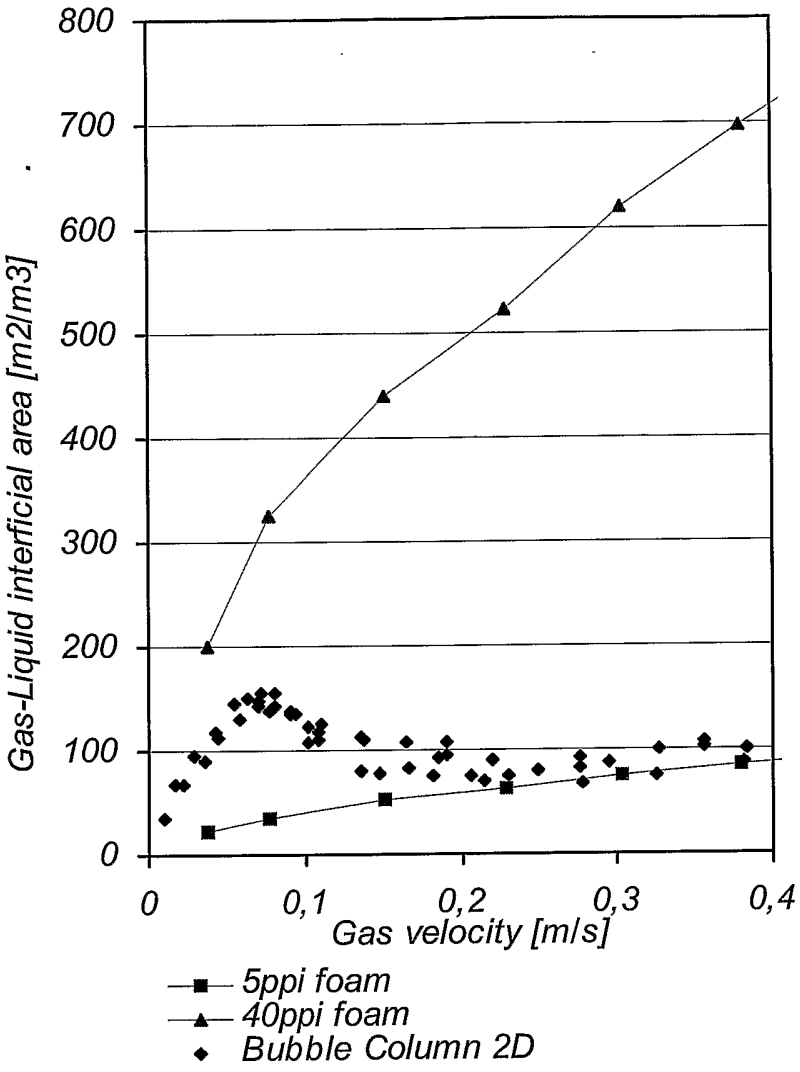

800
700
600
500
400
300
200
100
0
Gas-Liquid interficial area [m2/m3]
0
0,1
0,2
0,3
0,4
Gas velocity [m/s]
5ppi foam
40ppi foam
Bubble Column 2D

Fig 3

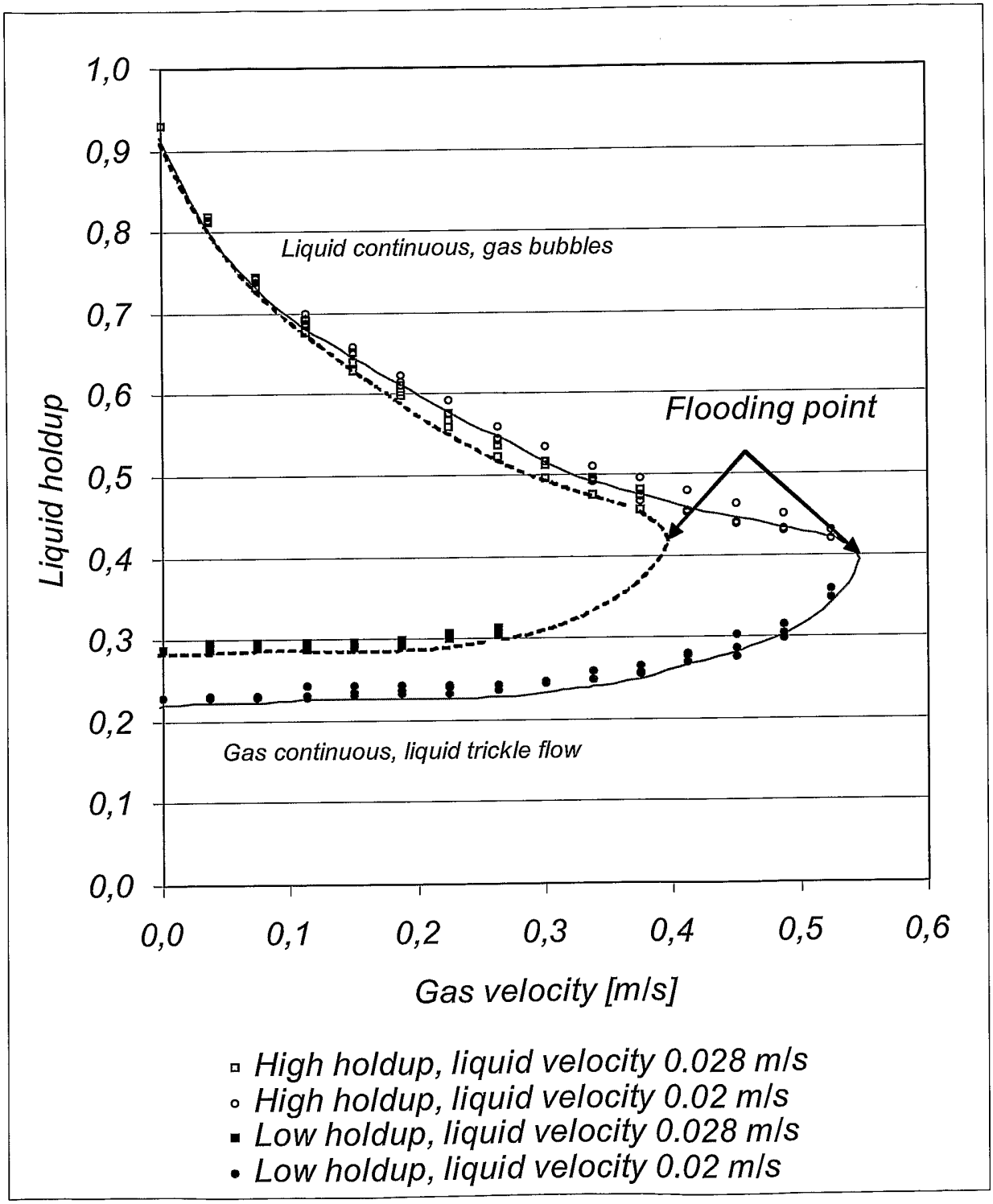

1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
Liquid holdup
Liquid continuous, gas bubbles
Flooding point
Gas continuous, liquid trickle flow
0,0
0,1
0,2
0,3
0,4
0,5
0,6
Gas velocity [m/s]
High holdup, liquid velocity 0.028 m/s
High holdup, liquid velocity 0.02 m/s
Low holdup, liquid velocity 0.028 m/s
Low holdup, liquid velocity 0.02 m/s

Fig 4

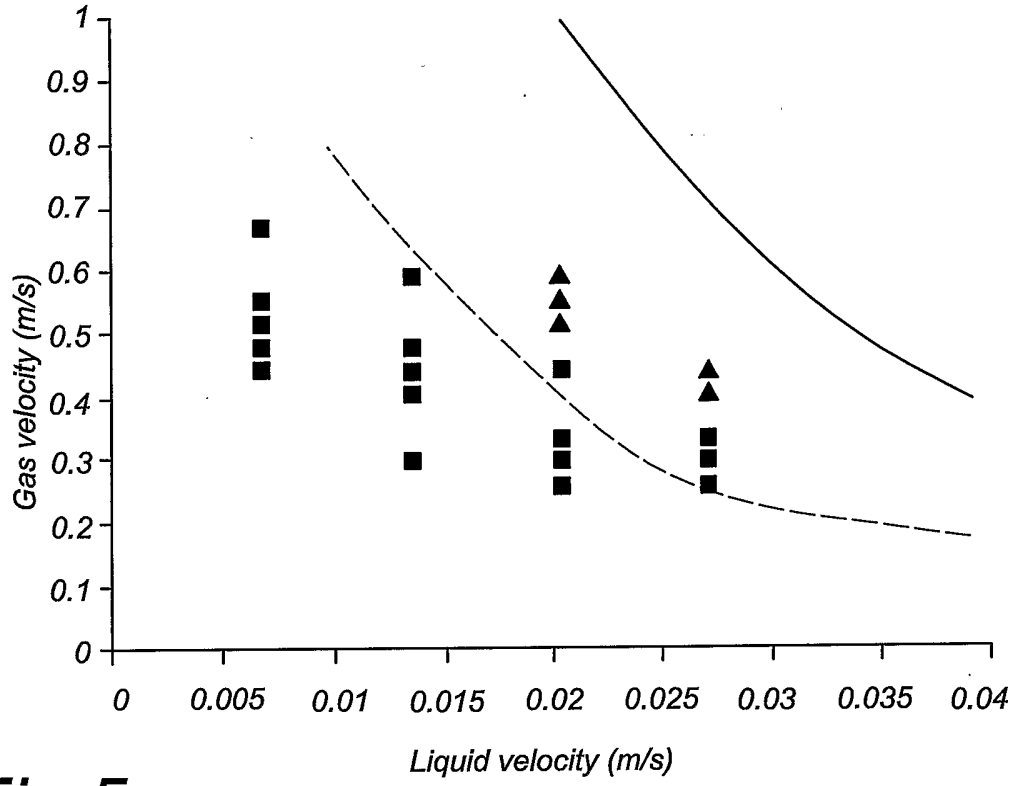
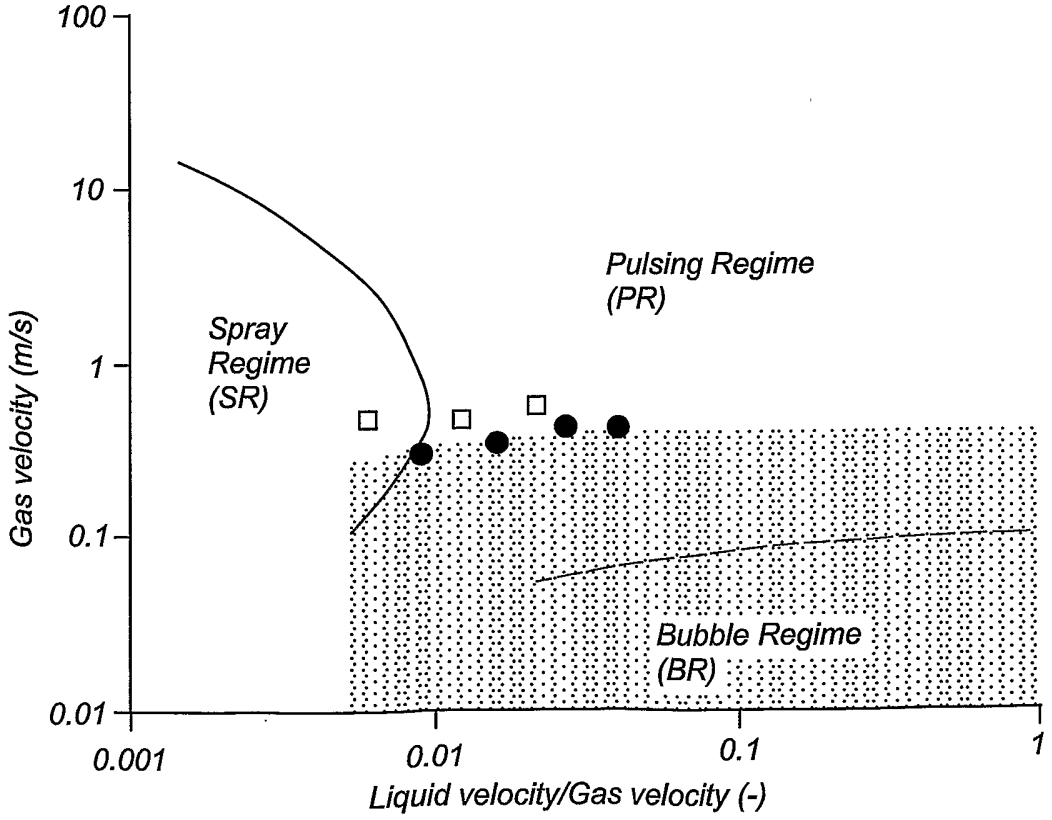

Gas velocity (m/s)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04
Liquid velocity (m/s)

Fig 5


Gas velocity (m/s)
100
10
1
0.1
0.01
0.001
0.01
0.1
1
Liquid velocity/Gas velocity (-)
Spray Regime (SR)
Pulsing Regime (PR)
Bubble Regime (BR)

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2005/050016

A. CLASSIFICATION OF SUBJECT MATTER
B01J35/04 B01J19/32 B01J35/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 102 08 711 A1 (BASF AG) 25 September 2003 (2003-09-25) cited in the application	1-11
Y	paragraphs [0002] - [0004], [0014] - [0017], [0023]	1-11
X	US 2003/116503 A1 (WANG YONG ET AL) 26 June 2003 (2003-06-26) cited in the application paragraphs [0044], [0062], [0064], [0067], [0074] - [0077]	1-11
Y	US 4 251 239 A (CLYDE ET AL) 17 February 1981 (1981-02-17) cited in the application column 5, line 19 - line 63	1-11

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 March 2006	29/03/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Besselmann, S

2

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2005/050016

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 1 097 473 A (BERNARD J. LERNER) 3 January 1968 (1968-01-03) page 1, left-hand column, line 10 - line 25 claims page 2, right-hand column, line 111 - line 116	1-11
P,Y	DE 103 27 986 A1 (M.PORE GMBH) 27 January 2005 (2005-01-27) paragraphs [0013], [0030] claims	1-11
P,X	STEMMET C P ET AL: "Hydrodynamics of gas-liquid counter-current flow in solid foam packings" CHEMICAL ENGINEERING SCIENCE, OXFORD, GB, vol. 60, no. 22, November 2005 (2005-11), pages 6422-6429, XP004993344 ISSN: 0009-2509 the whole document	1-11

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2005/050016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 10208711 A1	25-09-2003	NONE	
US 2003116503 A1	26-06-2003	US 2003119920 A1 US 2004147620 A1	26-06-2003 29-07-2004
US 4251239 A	17-02-1981	NONE	
GB 1097473 A	03-01-1968	DE 1544061 A1	12-03-1970
DE 10327986 A1	27-01-2005	NONE	