Pure & Appl. Chem., Vol. 66, No. 6, pp. 1231-1238, 1994.
Printed in Great Britain.

Plasma fluidized and spouted bed reactors: an overview

G. FLAMANT

Institut de Science et de Génie des Matériaux et Procédés
CNRS, B.P. N°5, ODEILLO, 66125 FONT-ROMEU Cédex, FRANCE

ABSTRACT : The characteristic particle mixing, high rate of heat and mass transfer and continuity of solid processing are the main advantages of fluidized systems for ultra high temperature operations with dense particulates. The association of plasma generators with such systems is examined in this paper from various points of view : applications, hydrodynamics, heat and mass transfer, chemical engineering. Fluidized and spouted beds reactors are presented as well as the original properties of these systems with respect to classical one.

INTRODUCTION :

The association of the main advantages of both fluidized bed and plasma is an exciting challenge for the development of a new generation of chemical reactors. On the one hand, fluidized and spouted beds are characterized by perfect mixing of the particles (i.e., low temperature gradient, large thermal diffusivities), high rate of heat and mass transfer, continuous operation with solid, high apparent density of solid; on the other hand, plasma flows are composed of very reactive chemical species and can provide ultra high temperature sources for solid heating. Thus the coupling of these two systems gives a lot of opportunities for :

- Gas phase reactions (in plasma) combined with quenching (in fluidized bed),
- High temperature solid processing in small size reactors (large power density in the plasma and large particle density in the bed),
- Particles coating and surface treatment by fluid-solid reaction,
- New processes based on multisteps multifunction reactors using the temperature (and chemical reactivity) differences between plasma and bed and (or) the possibility of particles injection in the immersed plasma.

All these developments are now limited by the poor knowledge of basic properties of plasma fluidized and spouted beds (PFB and PSB) and by some technical problems such as particles agglomeration observed by pioneers. This paper tries to propose an overview of previous PFB and PSB processes and to point out the main hydrodynamic and transport properties of PSB. Finally the main research and development needs are presented in the view of new processes design.

LITERATURE SURVEY :

The first applications of PFB have been proposed thirty years ago by Goldberger and oxley [1] for quenching plasma reaction species in fluidized bed. The D.C. plasma torch was located vertically at the center of the fluidized bed column, and additional fluidizing gas was provided in order to ensure a uniform fluidization. Quenching rate larger than 10^6 K/s was determined on the basis of temperature distribution measurement. Pyrolysis of methane was then studied by Amouroux and Talbot [2] using a R.F. plasma generator located below the fluidization distributor of beds composed of sand, zirconia and graphite. Quenching rates of about $0.4 10^6$ K/s were measured and maximum acetylene conversion yields of 50% were obtained with pure methane and graphite particles fluidized bed. Results were explained on the basis of radicals mechanisms.

Plasma spouted beds (PSB) were used more recently. In 1971, Bal et al. [3] reported experimental results about coal pyrolysis in PSB using a DC argon-hydrogen plasma.

A condensed presentation of previous PFB and PSB developments is proposed in Table 1. Three main application fields have been selected :

(1) Hydrocarbons pyrolysis
(2) Minerals processing
(3) Materials processing.

These last applications (3) were developed very recently in the early nineties.

Concerning plasma generators, DC arc torch, inductive plasma torch and microwaves systems were used. But in the main cases, DC generators were associated with minerals processing in which high temperature treatments are concerned, and RF generators were used for gas and materials synthesis.

TABLE 1 : Fields of application of plasma fluidized beds (PFB) and plasma spouted beds (PSB)

TYPE OF APPLICATIONS	PLASMA SOURCE	REACTOR	INPUT/OUTPUT	REFERENCE
HYDROCARBONS PYROLYSIS	RF, Argon	PFB	CH_4/C_2H_2	Amouroux, Talbot (1968) [2]
	DC, Ar/H_2	PSB	Coal/C_nH_m	Bal et al.(1968)[3]
	RF, Ar/H_2	PFB	$C_{16}H_{34}/C_nH_m$	Nikravech et al. (1990) [4]
			nHexadecane/C_nH_m	Pernin et al. (1992) [5]
MINERALS PROCESSING	DC, Ar	PFB	$Ca_3(PO_4)_2/P_4$	Goldberger (1965)[6]
	3 AC,N_2/O_2	PFB	ZrO_2/ZrO_2 spheres	Bonet et al. (1973) [7]
	RF, Ar,N_2,N_2/H_2	PFB	$CaCO_3/CaO$	Arnould, Amouroux (1987) [8]
	DC, Ar/N_2	PSB	$V_2O_3+Na_2CO_3/Na_2VO_3$	Munz, Mersereau (1990) [9]
	DC, Ar	PSB	$CaCO_3/CaO$	Flamant et al. (1990) [10]
			Pb dust processing	Flamant et al. (1992) [11]
MATERIALS PROCESSING	RF, Ar/O_2	PFB	Surface treatment of carbon fiber	Kawamura et al. (1990) [12]
	RF, N_2	PFB	Nitriding of Ti	Okubo et al. (1990) [13]
	DC, Ar	PSB	C coating from CH_4	Kojima et al. (1991) [14]
	microwaves, air	PFB	Pharmaceutical granulations drying	Doelling, Nash (1992) [15]

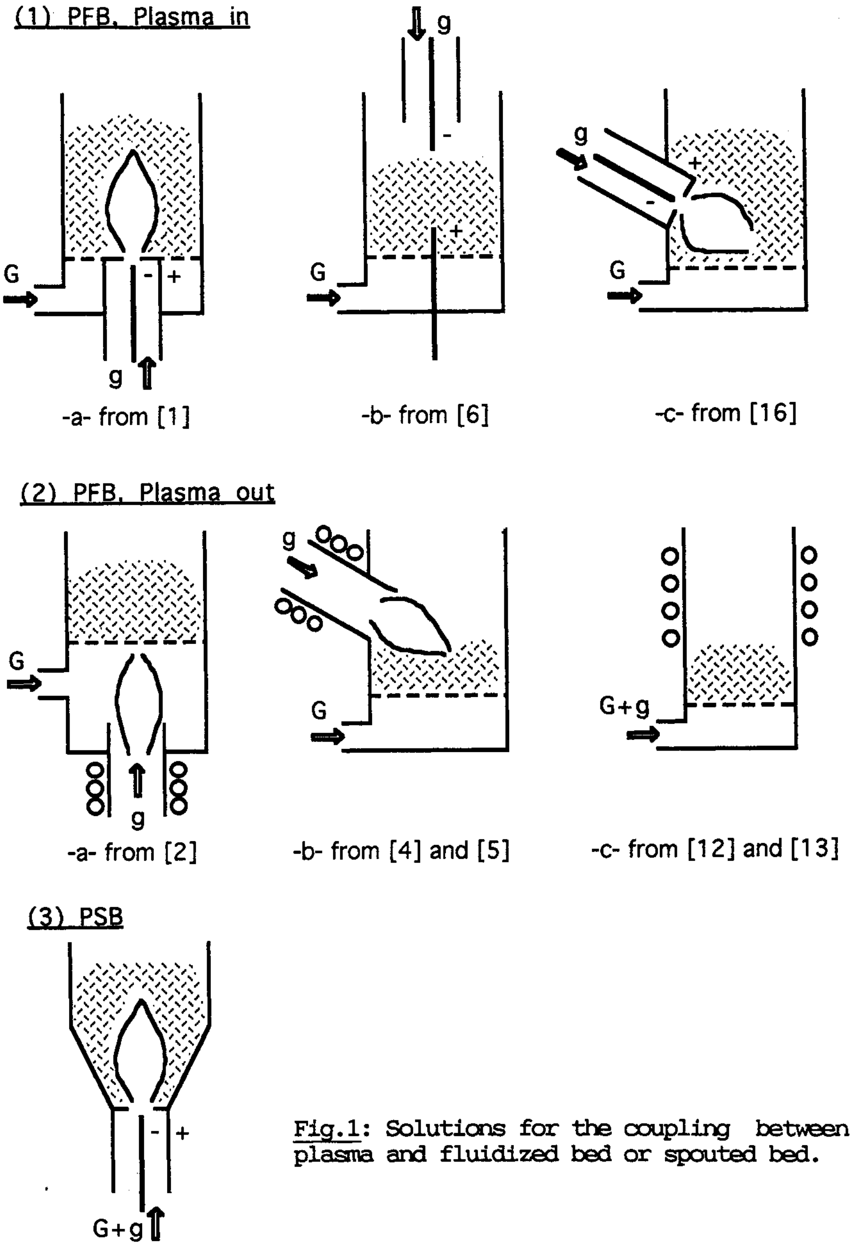


Fig.1: Solutions for the coupling between plasma and fluidized bed or spouted bed.

The PFB concept was chosen more frequently than the PSB one because the possible use of fluidizing gas is an additional degree of freedom in PFB. The various reactor geometries using PFB and PSB are presented next.

FLUIDIZED AND SPOUTED BED REACTORS

The coupling between a plasma generator and a fluidized bed of particles can be realized by different ways. Basic situations are schemed in figure 1. Two main groups can be considered :

(1) the plasma jet is immersed inside of the bed,
(2) the plasma jet is located outside of the bed.

The former can produce very rapid reaction rate (quenching rate) because of the direct contact between the plasma and the particles, but it can induce instabilities and local agglomeration.

The PSB reactor (situation (3)) appears as a particular case of design 1-a in which additional fluidizing gas in introduced in the bed.

Reactor 1-b was proposed by [6] as "Fluidized electrode plasma reactor" in order to increase the plasma torch efficiency. This design looks like a transferred arc system and it was found to be very stable. Unfortunately, some agglomeration was observed. This observation points out one of the main difficulties encountered when using PFB and PSB : the hydrodynamics of such reactors is complex and so far it is not understood well enough.

HYDRODYNAMICS OF PLASMA SPOUTED BED AND PLASMA FLUIDIZED BED

In PSB the plasma jet transfers momentum and energy to the particles; therefore, the hydrodynamics of this system is more critical than that of PFB because agglomeration depends on a very fragile equilibrium between the particles mean residence time in the spout and the plasma-particle heat transfer rate. In PFB this equilibrium may be modified by injecting some additional gas.

Main characteristics of fluid and solid circulation in standard spouted bed

A multi-dimensional model of spouted bed was proposed recently by [17], they propose velocities distribution for both the gas and the particles as shown in figure 2. The gas flows upward in the spout and in the annulus (fig.2.a) but the velocity in the former zone is one order of magnitude larger than that in the latter. Gas recirculation exists in the lower part of the annulus.The particles move upward in the spout and downward in the annulus (fig.2.b). The velocity reverses at the interface between the spout and the annulus, and inside the fountain. Particles velocity distribution measured by [18] in the axial direction is shown in figure 3. A parabolic-like profile is observed in the spout. Concerning solid concentration distribution, relative data have been obtained using optical fibers mounted for measuring the variation of transmitted light by [19]. The map is plotted in figure 4. Three main regions have been identified :at the axis, the gas is enriched with particles from the bottom to the top. On the contrary in the annulus, the porosity is low and constant (packed bed). An intermediate region is detected between the spout and the annulus in which the voidage is larger than in the annulus and smaller than in the spout. The variation of spout voidage along the axis was predicted by [17]; in agreement with our experiments, it varies from 1 at the injection orifice to about 0.6 at the bed surface.

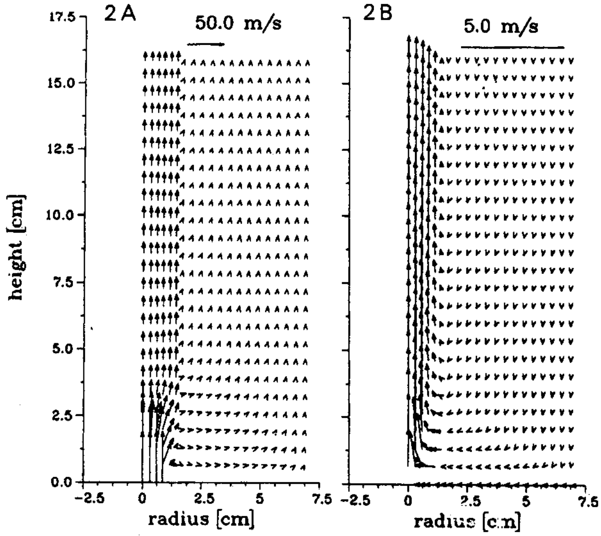
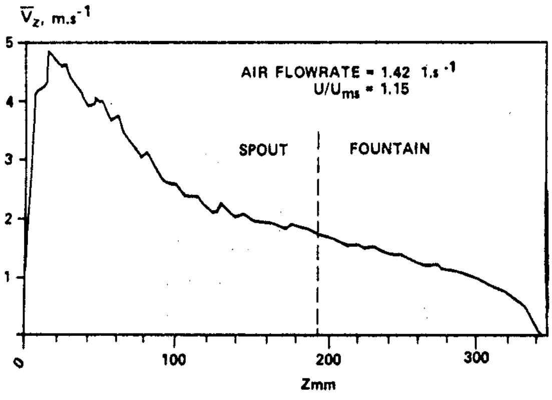
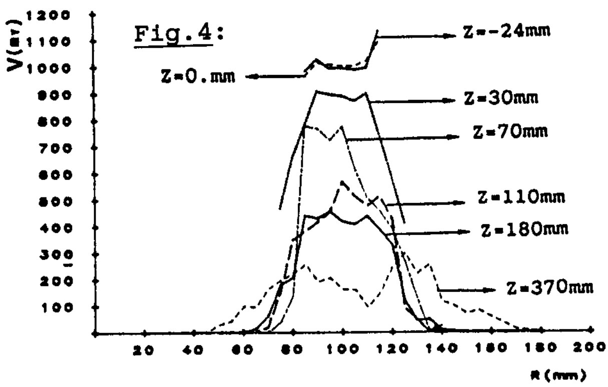
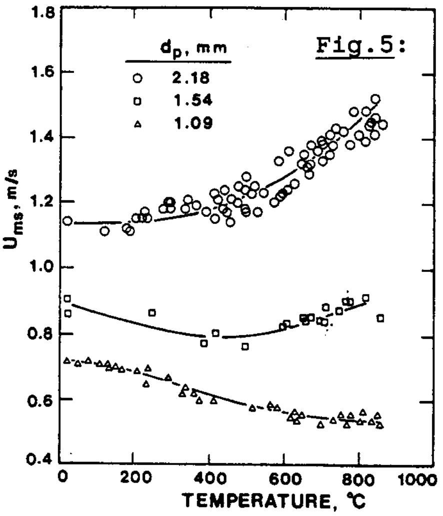


Fig.2: Velocity distribution in a standard spouted bed (SSB) after [17]
$D_c = 0.152$m, H= 0.165m, $D_i = 9.5\ 10^{-3}$m,
glass beads, 2a : gas velocity
2b : particle velocity.

Fig.3: Measured axial mean vertical velocity of particle in a SSB after [18]







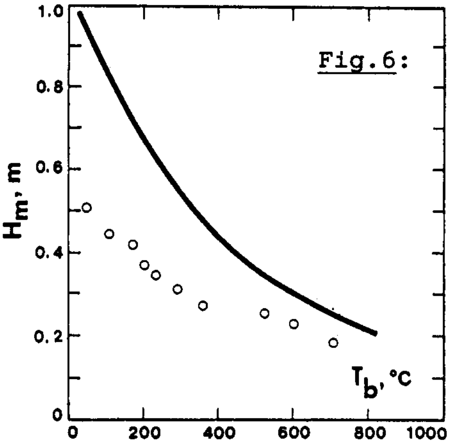


Fig.4: Relative voidage distribution in a cold spouted bed as a function of height (2). (square section 0.20 x 0.20m) after [19].

Fig.5: Minimum spouting velocity versus bed temperature in a SSB after [20].

Fig.6: Maximum spoutable depth versus bed temperature in a SSB after [20].
Solid line : correlation from [22].

Temperature and plasma effect on hydrodynamics

The effect of temperature on spouted bed hydrodynamics was studied up to 880°C by [20]. The authors point out the poor agreement between literature equations and their results about minimum spouting velocities (U_{ms}). As observed for minimum fluidization velocity [21], they measured (fig.5) an increase of U_{ms} with temperature for large particles (dp ~ 2mm) while for small particles U_{ms} decreases (dp ~ 1mm). As a rule, a temperature increase narrows the stable spouting range, i.e. the maximum spoutable bed height H_m decreases with temperature. Experimental and theoretical data are plotted in figure 6.

For PSB our measurements with D.C. jet do not reveal large influence of temperature on minimum spouting velocity because the plasma jet properties are dominant. The dimensionless pertinent parameter for describing this transition is the Stokes number [23]:

$$St = \frac{\rho_p U(T)\, d_p^2}{\mu(T)\, D_i} \qquad (1)$$

ρ_p, d_p are the particle density and diameter, μ the fluid viscosity, D_i the injection orifice diameter, U the plasma velocity. μ and U are calculated at the film temperature : $T = T_F = T_\infty + T_b/2$, where T_∞ is the mean plasma temperature at the orifice, and T_b is the mean bed temperature. With this assumption, the minimum spouting velocity is well predicted by the following equation:

$$St_{ms} = \frac{\rho_p U_{ms} d_p^2}{\mu D_i} = 4.48\ 10^{-4} Ar^{0.53} \left[\frac{D_i}{D_c}\right]^{0.09} \left[\frac{H}{D_c}\right]^{0.22} \left[\frac{\rho_p d_p}{\rho_f D_i}\right]^{0.9} \left[\frac{\rho_F}{\rho_\infty}\right] \left[\frac{V_\infty}{V_F}\right]^{0.15} \qquad (2)$$

$$Ar = \frac{g\,\varrho_f\ (\varrho_p - \varrho_f)d_p^{\,2}}{\mu^2}$$

D_c: column diameter, H: bed height, v: cinematic viscosity.

Experimental results are plotted in figure 7, they were obtained in the following range : $10^6 < St_{ms} < 10^7$, $0.8mm < d_p < 2.36mm$, $2600 < \varrho_p < 3500$ kgm^{-3}, $5mm < D_i < 7mm$, $80mm < H < 100mm$ ($D_c = 90mm$). Corresponding velocities range between 200 and 600 ms^{-1}.

Concerning PFB, the minimum fluidization velocity of a microwawe-assisted low pressure (266-2660Pa) fluidized bed was studied by [24]. Experimental data reveal non conventional behavior since minimum fluidization velocities increase with temperature for small particles, which can be explained by inter-particles forces.

The maximum spoutable height variation with the mean bed temperature was reported by [25], it is plotted in figure 8. The comparison between figure 6 and figure 8 shows a complete contradiction of the results with standard spouted beds. It is because, as shown previously, the bed temperature is not a pertinent parameter for hydrodynamics in PSB.

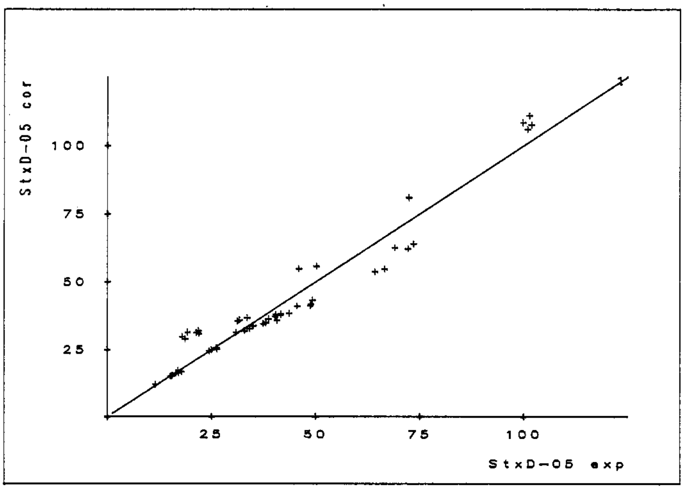


Fig.7: Comparison of calculated and measured transition Stokes numbers for a DC Plasma spouted bed after [23].

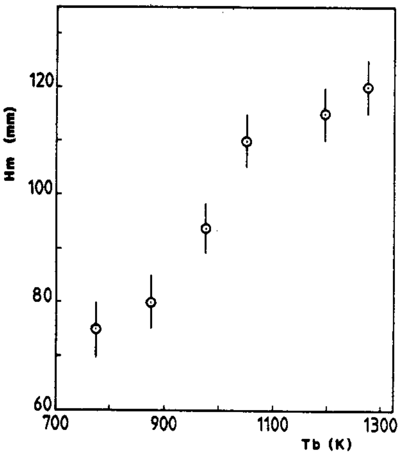


Fig.8: Maximum spoutable depth as a function of mean bed temperature, after [25].

HEAT TRANSFER IN PLASMA SPOUTED BED AND PLASMA FLUIDIZED BED

Heat transfer in PSB and PFB was studied by [1],[2] and [25]. Quenching rates by particles obtained with immersed plasma system [1] are much larger than when the plasma jet is located outside of the bed [2]; in the former case, rates as large as $50\ 10^6$ K/s are reported whereas $0.4 10^6$ K/s are obtained in the latter situation. On the basis of transient experiments, plasma/particle heat transfer efficiency and bed effective axial and radial conductivities (λ_z, λ_r) were determined by [25]. Even for bed height lower than H_m, more than 90% of plasma energy is transferred to particles with nitrogen and about 70% with argon. Effective thermal properties λ_z and λ_r were identified by numerical fitting between experimental temperature distributions and calculated ones as plotted in figure 9. An intensive axial mixing was shown, because λ_z is three orders of magnitude larger than in packed bed ($\lambda_z \sim 10^3$ $W.m^{-1}K^{-1}$) and a rather poor radial diffusion was measured ($\lambda_r \sim$ 10 $W.m^{-1}K^{-1}$).

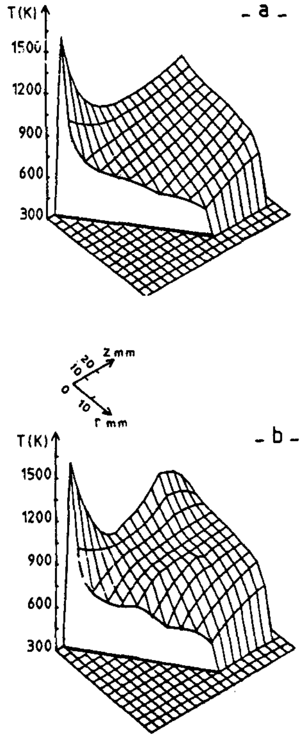


Fig.9: Calculated (a) and measured (b) temperatures distribution in a PSB after [25].

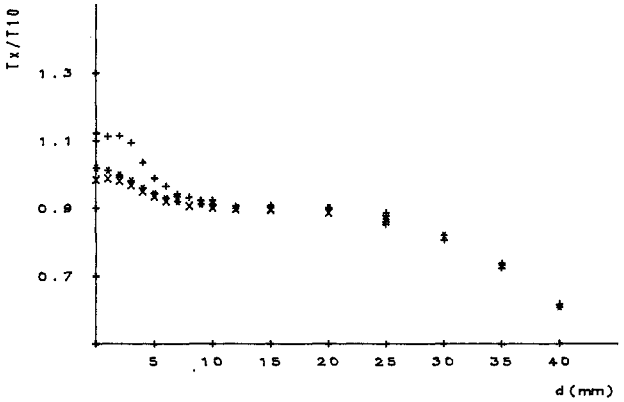


Fig.10: Radial temperature profile in a PSB. Argon, Al_2O_3, dp= 1mm, H= 0.120m, D_c = 0.09m.

+ : U= 31, I= 100A, Q_f = 511/mn, T_b = 520°C

* : U= 29.6V, I= 100A, Q_f = 491/mn, T_b = 650°C.

X : U= 26.5V, I= 200A, Q_f = 381/mn, T_b = 960°C.

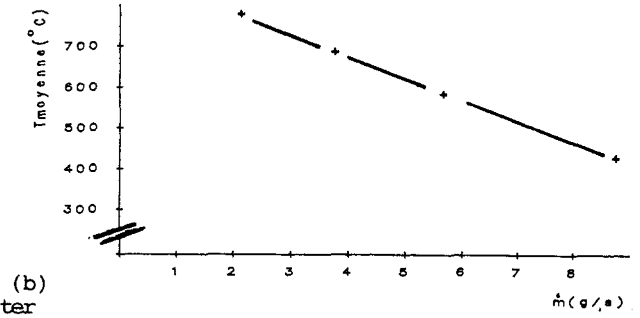


Fig.11: Mean bed temperature variation as a function of particle mass flow rate in a PSB. P_e = 11,5 kW, SiC, dp= 1.14 mm.

Typical radial temperature distribution obtained with a moving thermocouple at level Z = 20mm is plotted in figure 11. Four regions are well identified from the spout axis to the column wall in agreement with fig.4.

(1) The core of the spout where temperature is maximum (its size is about the injector diameter),
(2) The transition zone (included in the so-called "spout") affected by a large thermal gradient,
(3) The annulus where some significant temperature variation is obtained,
(4) The vicinity of the wall concerned with temperature decrease due to heat losses.

The distribution shape is not affected by operating conditions, the temperature difference only changes with mean bed temperature.

DISCUSSION AND CONCLUSION

The coupling of plasma with a fluidized bed of particles offers a large range of original properties for the development of new chemical reactors such as :

- Quenching of highly reactive species and out of equilibrium gas phase reactions. In particular, the influence of H and CH_3 radicals in the pyrolysis of hydrocarbons was demonstrated by [3].

- Ultra high temperature minerals or wastes processing in small size reactors. Continuous operation can easily be obtained by solid circulation as shown in fig. 11. Bed temperature is regulated by a change of particle mass flowrate for a constant plasma power or reverse.
- Material elaboration such as particles coating.

The main difficulties pointed out by investigators are agglomeration and particle attrition [10], [26]. The former can be solved by a better understanding of complex hydrodynamics of PFB and PSB. the latter can be limited by using a cold plasma which provides reactive species without a strong thermal effect.

REFERENCES :

1- GOLDBERGER W.M., OXLEY J.H., A.I.Ch.E Journal, Vol 9, N°6, pp 778-782, (1963)
2- AMOUROUX J., TALBOT J., Ann. Chim. (Masson, Paris), t.3, N°3, pp 219-233, (1968)
3- BAL S., MUSIALSKI A., SWIERCZEK R., Koks, Smola, Gaz, 16, p 320, (1965)
4- NIKRAVECH N., OUTIFA L., AMOUROUX J., Sup. Journal de Physique, Colloque C5 , Sup. N°18, t.51, pp 91-99, (1990)
5- PERNIN J.F., MOTALLEBI C., LEUENBERGER J.L., CAVADIAS S., AMOUROUX J., Journal of High Temperature Chemical Processes, Colloque, Sup.N°3, Vol 1, p 87-93, (1992).
6- GOLDBERGER W.M., Chemical Engineering Progress Symp. Series, 62, N°62, pp 42-46, (1965).
7- BONET C., VALLBONA G., FOEX M., DAGUENET M., DUMARGUE P., Rev. Int. Htes. Temp. et Refract., t.11, pp 11-24, (1974).
8- ARNOULD P., AMOUROUX J., Bull Soc. Chim. Fr., N°6, pp 985-995, (1987).
9- MUNZ R.J., MERSEREAU O.S., Chemical Engineering Science, Vol 45, N°8, pp 2489-2495, (1990).
10- FLAMANT G., CHRAIBI M.A., VALLBONA G., BERTRAND C., Sup. Journal de Physique, Colloque C5, Sup.N°18, t.51, pp 27-34, (1990).
11- FLAMANT G., BAMRIM A., BADIE J.M., LECADET J., Journal of High Temperature Chemical Processes, Col., Sup.N°3, Vol 1, pp 239-246, (1992).
12- KAWAMURA H., OKUBO T., KUSAKABE K., MOROOKA S., Journal of Materials Science Letters, 9, pp 1033-1035, (1990).
13- OKUBO T., KAWAMURA H., KUSAKABE K., MOROOKA S., J. Am. Ceram. Soc., 73, (5), pp 1150-1152, (1990).
14- KOJIMA T., MATSUKATA M., ARAO M., NAKAMURA N., MITSUYOSHI Y., Sup. Journal de Physique II, Col. C2, Vol 1, pp 429-436, (1991).
15- DOELLING M.K., NASH R.A., Pharmaceutical Research, Vol 9, N°11, pp 1493-1501, (1992).
16- FAUCHAIS P., Private communication.
17- KRZYWANSKI R.S., EPSTEIN N., BOWEN B.D., The Canadian Journal of Chemical Engineering, Vol 70, pp 858-872, (1992).
18- BOULOS M.J., WALDIE., The Canadian Journal of Chemical Engineering, Vol 64, pp 939-943, (1986).
19- FATAH N., FLAMANT G., HERNANDEZ D., OLALDE G., SEIMPERE P., KONIUTA A., Récents progrès en Génie des Procédés. "La fluidisation". ED. Lavoisier, Paris, Vol 5, N°11, pp 138-145, (1991).
20- YE B., LIM C.J., GRACE J.R., The Canadian Journal of Chemical Engineering, Vol 70, pp 840-847, (1992).
21- FLAMANT G., FATAH N., STEINMETZ D., MURACHMAN B., LAGUERIE C., International Chemical Engineering, Vol 31, N°4, pp 673-684, (1991).
22- Mc NAB G.S., BRIDGWATER J., Proc. European Congress on Particle technology, Nuremberg, (1977).
23- BAMRIM A., FLAMANT G., VALLBONA G., Journal of High Temperature Chemical Processes, Colloque, Sup. N°3, Vol 1, pp 27-34, (1992).
24- WIERENGA C.R., MORIN T.J., A.I.Ch.E Journal, Vol 35, N°9, pp 1555-1559, (1989).
25- FLAMANT G., Plasma Chemistry and Plasma Processing, Vol 10, N°1, pp 71-85, (1990).
26- JUREWIEZ J., PAROULX P., BOULOS M.I., ISPC-7, Eindhoven, paper N°B-2-4, pp 243-248, (1985).