

FLUIDIZED COMBUSTION OF LIQUID FUELS: PIONEERING WORKS, PAST APPLICATIONS, TODAY'S KNOWLEDGE AND OPPORTUNITIES

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Abstract: The use of liquid fuels for fluidized bed (FB) combustion is gaining importance for co-firing, waste incineration, switch to renewable energy sources or during plant start-up.

The design of a suitable liquid injection system is a key requirement to ensure that all of heat is released within the bed of a bubbling fluidized combustor or the riser of a circulating system.

The scientific literature has revealed around 100 papers dealing with FB combustion of liquid fuels since the pioneering work in 1975. This paper conveys an effort to review the relevant aspects of FB combustion of liquid fuels, with the exclusion of mixtures of solid fuels in liquids, which were left out of this work. Following a logical path that goes from early investigations toward a more sound knowledge, it is organized in four sections: Fuels, Fuel Feeding, Combustion Results and Emissions. The Conclusions summarize the main aspects and draw prospective for future research and application of liquid fuel FB combustion.

Keywords: bubbling fluidized bed, circulating fluidized bed, liquid fuel, fuel injection, combustion efficiency, sulfur oxides, NO_x, carbon monoxide

INTRODUCTION

The use of liquid fuels for fluidized bed combustion (FBC) is gaining importance for application during co-firing and waste incineration or for plant start-up. In parallel, increasing interest in biomass- and waste-derived fuels, as a consequence of the Kyoto protocol and the need of optimal energy-source share, calls for innovative combustion solutions. Since the fluidized bed technology is effective for burning high-volatile fuels like biomass and solid opportunity fuels, the extension to liquid fuels is rather straightforward, in particular if benefits are obtained, for instance burning liquid wastes with medium heating value and raw vegetable oils without any preventive chemical treatment. These fuels can be reliably processed using fluidized bed combustion thanks to FBC robustness, flexibility and effectiveness.

The literature on FB combustion of liquid fuels is still sparse. A part of studies have a fundamental character for understanding the mechanism of liquid fuel FB combustion; a number of papers are available on different aspects as well as on different technical options. So far, both options of bubbling fluidized bed (BFB) and circulating fluidized bed (CFB) have been used for liquid fuel combustion.

The search of the scientific literature revealed around 100 papers dealing with FB combustion of liquid fuels, after the exclusion of mixtures or suspensions of solid fuels in liquids, which were left out of this work. Nevertheless, no dedicated reviews are available on this matter. Therefore, this paper represents a first effort in this direction by addressing relevant practical aspects and scientific issues in FB combustion of liquid fuels.

FUELS

Table 1 reports the list of the liquid fuels used in the research activities reviewed by the present paper.

Concerning nature and origin, the majority of the fuels is originated upon petroleum refining processes as valuable products (diesel fuel, kerosene, gasoline, fuel oil), by-products (pitch, heavy oil, mazut) and liquid wastes to be disposed (acid tar waste, waste oil). Orimulsion® is a bitumen-based water suspension that is very similar to a heavy fuel oil in its appearance. It is produced from Venezuelan bitumen deposits in the Orinoco region by direct extraction with steam from the underground reservoirs and a further addition of surfactants for its stabilization (Zlatar, 1989).

Concerning renewable fuels, pyrolysis oils are generated by dedicated processes of thermo-chemical conversion of biomass/wastes into liquid fractions. Sunflower oil, commonly used for cooking, is produced by milling, pressing and separating the oil fraction of sunflower seeds. Biodiesel is obtained via trans-esterification of rape oil for generating a fuel with rheological properties similar to those of a common diesel fuel.

Table 1 Petroleum-derived liquid fuels for FB combustion (in alphabetical order)

Fuel name	Brief description	Origin	Nature	LHV MJ kg ⁻¹
Acid tar waste	By-products of oil-refining industry	Refinery	Fossil	20.0-30.0
Biodiesel	Bio fuel for automotive application	Chemical processing	Renewable	37.0
Diesel fuel	Standard fuel for automotive application	Refinery	Fossil	42.6
Fuel oil	Petroleum derived oil for heating	Refinery	Fossil	40.0-42.0
Gasoline	Standard fuel for automotive application	Refinery	Fossil	43.3
Heavy oil, mazut	Heavy oil from petroleum distillation	Refinery	Fossil	40.7
Kerosene	Standard fuel for aircraft application	Refinery	Fossil	43.1
Oil sludge	Residual oil from petroleum storage	Refinery, oil deposits	Fossil	30.0-40.0
Orimulsion®	Emulsion of natural bitumen in water	Steam assisted extraction	Fossil	39.7
Pitch	Petroleum pitch	Refinery	Fossil	30.0-40.0
Pyrolysis oil	Oil generated by pyrolysis of biomass/wastes	Chemical processing	Fossil/renewable	20.0-30.0
Sunflower oil	Vegetable oil for food appliance	Agro-industry	Renewable	37.1
Waste oil	Waste oil from mechanical processes	Industry	Fossil	30.0-40.0

FUEL FEEDING

Fuel viscosity. One of first FBC tests with petroleum liquid fuels in a fluidized bed (Pillai and Elliot, 1976) showed besides the low combustion efficiency the problems of blockage of the feeding nozzle and agglomeration of the bed material. Among fuel properties, the viscosity is very important. In many papers related to liquid fuel combustion in fluidized beds, authors reported that several first trials failed, on account of problems in the feeding system. Very often the high fuel viscosity was the cause of feeding problems.

For improving feeding system and enabling appropriate pumping of viscous liquid fuels, the tanks of liquid fuels are usually heated up to a certain temperature. In that case the whole transport line from the tank till the fluidized bed furnace must be heated. The level of temperature for heating up of tanks and transportation lines depends on liquid fuel viscosity and thermal stability.

Barker and Beacham (1980) estimated that very viscous liquid fuels can be satisfactorily transported and dispersed through appropriate nozzles if their kinematic viscosity is around 150 – 350 mm²/s. While for typical oil fuel in conventional burners it is 15 – 30 mm²/s. Taking into account viscosity of different petroleum-based liquid fuel, it was necessary for acceptable feeding to heat up the whole feeding system at temperatures usually not above 150°C (Brereton et al., 1995; Kerr and Probert, 1990; Anthony and Lu, 2001; Barczus et al., 2001). One of rare examples with higher heating temperature is reported by Legros et al. (1989 and 1991). They used a pitch obtained from refinery hydrocracking unit and they had to heat up this fuel to 190°C. While Anthony and Lu (2001) reported that for three different petroleum-based liquid fuels (fuel oil, pitch and bitumen) the feeding system was heated up to 120°C only. At this temperature only for one of the investigated fuels, that is for bitumen, its viscosity was over the proposed value of 350 mm²/s. Therefore the reported unsatisfactory combustion performance just for bitumen could be the too high viscosity for good dispersion in FB. In contrast, Orimulsion®, the bitumen-based emulsion, was rather successfully burnt in a fluidized bed furnace (Miccio et al., 1999) by carrying out its feeding at room temperature with a viscosity in the order of 500 mm²/s.

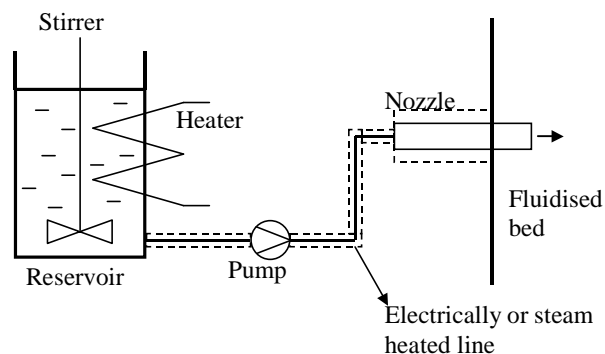


Fig. 1 Typical system for feeding viscous petroleum-based liquid fuels to FBC plants

Some refinery by-products, which were investigated for combustion in fluidized bed as liquid fuels, are actually in solid phase at room temperature. An example of that kind of material is asphalt. Wu et al. (2001) made experiments burning asphalt in CFB. The viscosity of this material at 170°C was reported to be 59650 mm²/s. This value is by three orders of magnitude greater than viscosity of typical oil fuels for conventional boiler. Nevertheless this kind of hydrocarbons also can find application as a liquid fuel for fluidized bed combustion. The authors reported that the tank and transportation line had to be maintained at temperatures between 200 and 340°C. Acid tar wastes of petroleum origin were investigated for combustion in a FB facility by Kerr and Probert (1990). This fuel contained a relatively large amount of water and did not show tendency of depositing tarry material as a result of long standing. Based on some pumping tests, the authors recommended that these acid tar wastes should be heated up to 30°C at least.

Feeding system. A typical feeding system for viscous petroleum-based liquid fuels is shown in Fig. 1. It consists of a tank containing fuel, an agitator for stirring fuel, a heater for maintaining fuel in good flow conditions, a transportation line till the pump, and after that till the injection point and the nozzle. The transportation line is usually heated and heat insulated. The heating of the tanks and the transportation lines, reported mainly from research activities with relatively small fluidized units, was provided by electric heaters or by steam. If the required temperature for heating up was higher, then the preferable solution was by steam. In industrial applications the heating of fuel with steam may be the only reasonable solution.

Nozzles. The nozzle is a critical point of feeding system, since its inappropriate design usually cannot be overcome by adjustment of other operational parameters. In first attempts of research activities on FBC of liquid fuels, these were fed through nozzles without cooling. Consequently, the nozzles were heated up to high temperature, and then petroleum-based liquid usually cracked forming deposits on the inside nozzle wall. Finally, after a relatively short time, the nozzle became blocked (Pillai and Elliott, 1976). In general, it is enough to cool the nozzle with air stream. The air stream used for nozzle cooling also served as a medium for dispersing or atomization of liquid fuel. By this way the air stream was being heated up, and at the exit of the nozzle it dispersed the liquid fuel without decrease of the fuel temperature, which accelerated the subsequent fuel evaporation (Anthony and Lu, 2001; Legros et al., 1991).

As an easier design solution, in pilot or industrial facilities, the nozzles are usually horizontally inserted into the fluidized bed. Since nozzles have to give a relatively even distribution of liquid fuel across the fluidized bed, it is necessary that parts of nozzles that are inside the furnace are relatively long. It means that these relatively long parts of nozzles are exposed to high heat flux coming from the surrounding hot fluidized bed. Experiences show that in these cases it is necessary to cool the nozzles by water, since the air cooling rate was not high enough to prevent overheating and cracking of liquid fuel within the nozzles, and finally blockage of the nozzle (North et al., 1999; Barczus et al., 2001). In some research investigation, vertical injectors directly inserted in the air distributor were preferred.

Since agglomeration of fluidized bed particles was experienced, some attempts for avoiding it, like increasing the excess air, variation of the bed height and using support gas combustion did not bring remarkable success (Pillai and Elliott, 1976). The experimental research of Miccio et al. (1999) with a bitumen-based emulsion showed that in inert atmosphere this fuel practically does not have tendency to form deposits on inert particles which could cause agglomeration of the fluidized bed. The experiments were done at 850°C, and they practically excluded the onset of reducing/sub-stoichiometric conditions in the bed as one of reasons for agglomeration during combustion of liquid fuels. The main reasons for agglomeration of inert particles of fluidized bed during combustion of liquid fuel are insufficiently high bed temperature and weak mixing at the location where the fuel is introduced. A first measure for avoiding FB agglomeration was introducing liquid fuels into fluidized beds only if the bed temperature was over 750°C (Brereton et al., 1995; Legros et al., 1991). Moreover, enhancing the mixing of the fluidized bed at least in the region of the liquid fuel injection and dispersing viscous fuels in relatively fine droplets are also effective (Legros et al., 1991; Barker and Beacham, 1980). Apart from inadequate nozzle designs or operating parameters, the agglomeration of fluidized bed particles might be caused if the nozzle is positioned too low in the bed. In the lowest part of the fluidized bed there is a great temperature gradient, starting from the inlet temperature of fluidizing air to the nominal bed temperature. This temperature gradient exists in a relatively narrow zone of fluidized bed, but if the exit of the nozzle is located just close to this zone, temperature of that zone will be even lower. Since the temperature in the zone is lowered, the gas velocity decreases, while the mixing becomes weak. These conditions could provoke agglomeration of fluidized bed particles. Legros et al. (1991) suggested a narrowed bottom part of fluidized beds as a measure for improving mixing in the zone of fuel injection.

Nozzle position. In available literature there is some data about the height where the fuel is injected into fluidized beds. Concerning CFB, in one case it was at 39 cm above primary air distributor (Brereton et al., 1995), while in another paper the nozzle was only 12 cm above the bubble caps (Anthony and Lu, 2001).

Regarding BFB, the height of the nozzle location in the fluidized bed was given only by Miccio et al. (1999), that is 6.5 cm above the distributor level. All these examples are from research activities, and in all the cases the feeding was regarded as a successful one.

Location of fuel nozzles is a matter of optimization between the need to avoid agglomeration (shallow nozzle) and that of increasing the residence time of liquid fuel and its vapor (deep nozzle). In both early and recent research works, it was determined that for good feeding and dispersion of liquid fuel in a fluidized bed it is favorable to assist the liquid fuel injection with air or steam (Brereton et al., 1995; Anthony and Lu, 2001; Wu et al., 2001; Miccio et al., 1999). However, in the case of larger pilot facilities or industrial plants, according to the published papers, there was no need for air assisting dispersion of liquid fuel (North et al., 1999; Barczus et al., 2001).

Miccio et al. (1999) made tests with and without air assistance to dispersion of liquid fuel (bitumen-based emulsion). During the liquid fuel feeding without air assistance no operation problems were experienced and the authors found that the combustion efficiency and the emissions were not largely affected by air assisting. However, they concluded that higher ratio of air to fuel flow rate gave more regular operation of nozzle feeding. Anthony and Lu (2001) provided similar comments: air assistance is necessary for good atomization and most importantly for improving the mixing in the immediate vicinity of the nozzle. They also did not recommend high flow rate of assisting air, since they did not notice better operation performance with a remarkably increased air flow rate through the nozzle.

Nozzle number. Finally, the design approach for the number of nozzles per unit cross section of the fluidized bed for liquid fuel feeding could be the same as that for high volatile solid fuels (e.g., lignite or biomass). For small-scale units used in research activity, with a cross section up to 0.15 m², a single injector was always used. Hence, from these investigations an appropriate conclusion could be hardly drawn about the optimum number of injectors per square meter of the furnace cross-section. The paper by North et al. (1999) reported that in an industrial plant of about 20 MWth there were 6 injectors per 21 m² of bubbling fluidized bed cross section. On another side there are some recommendations that number of nozzles for liquid fuels should be similar to the number of feeding points for coal, i.e., one feeding point per square meter of furnace cross section (Stubington and Davidson, 1981). Since there are very few published papers about fluidized bed industrial plants fired with liquid fuel, the optimum number of feeding points still remains a questionable design parameter.

COMBUSTION RESULTS

Petroleum-derived fuels. One of first published investigations with combustion tests on liquid fuels in a fluidized bed combustor was done by Pillai and Elliot in 1976. They used commercial liquid fuels, i.e., diesel fuel and heavy fuel-oil and tested four different positions for introducing liquid fuels into the furnace; one of ports was overbed, more exactly 0.25 m above the bed surface. In spite of suitable variations of excess air, fluidization velocity and temperature, this overbed trial was treated as unsuccessful. The main disadvantage was a very low burn off in the bed, which was made evident by a luminous and sooty flame above the bed. The authors highlighted that only few percentages of the heat introduced with fuel were developed in the fluidized bed. But the change of nozzle position did not give much better results. Other positions of the nozzle were just at the level of fluidized bed surface and in the bed. The combustion efficiency with reference to the fluidized bed was slightly higher after the changes in nozzle position, but not yet satisfactory, being only 20% at maximum. The main reason was the shallow bed, only 150 mm high. As an attempt for increasing the combustion efficiency, their idea was to enable long enough residence time of fuel vapors within the bed and to improve mixing between fuel and air within the bed. They tried a two-stage combustion process in a single fluidized bed. The leading idea was to create two zones in one fluidized bed: the bottom zone with greater and heavier particles for liquid fuel gasification at lower temperature, and the upper zone with lighter particles for combustion at higher temperature. For that purpose the inert solids consisted of two different materials, with different density and particle size.

Almost the same idea of two-zone fluidized bed was applied by a group of pioneering Russian investigators (Keler and Berg, 1979; Berg et al., 1983). In the first experimental set-up they installed heat exchanger tubes in the upper zone of the bed, 100 mm above the fuel nozzle and 200 mm above the distributor plate. The main purpose of the embedded tubes was to prevent formation of great gas bubbles and to improve mass exchange between fuel vapor bubbles and emulsion. At a bed temperature of 930°C and 25% excess air the heat loss in unburned gases was 1.5%, whereas at 1050°C and 10% excess air a negligible heat loss was found. This temperature, however, was too high for efficient sulfur retention. For that reason the authors decided to use coarser solid particles in the lower part of the bed, with the idea that different temperatures could be obtained in the lower and upper part of the fluidized bed. The lower temperature is favorable for sulfur

retention, while the higher temperature for large combustion efficiency. As the next step, the same authors built a two-stage fluidized bed, by separating it along its height with a distributor plate. In the lower part of the bed the liquid fuel was vaporized and partly burnt, whereas the intermediate distributor plate allowed much better mixing between the fuel vapors and air entering the upper fluidized bed. This segmented fluidized bed was suitable for much quicker heat up of the equipment. The authors observed that above 600°C the liquid fuels burned without any external support.

In parallel, a pioneering experimental work was satisfactorily carried out on pressurized fluidized bed combustion of liquid fuel by Roberts et al. (1975). The experiments were carried out on a combustor with a plan area up to 0.7 m², operating at pressures up to 600 kPa. Combustion of heavy oil was surprisingly successful even at the lowest tested temperature, i.e., 800°C, the combustion efficiency being always greater than 99.8%. On the contrary, the combustion efficiency of parallel coal-fired tests dropped down to 97.5% when decreasing the bed temperature to 800°C. It is worth noting that a baffle system was used in the freeboard to reduce the extent of splashing zone and hence to improve the combustion efficiency in the bed. An important authors' recommendation was that of ensuring exceptionally uniform fuel and air distribution in the bed. In turn, this will reduce undesirable freeboard combustion and consequent drawbacks like difficult control of heat exchange duties, excessive freeboard temperature resulting in possible ash softening, alkali volatilization, etc., and hence fouling of surfaces downstream.

Beacham and Marshall (1979) reported a successful experience and combustion results of heavy fuel oil in an industrial fluidized bed boiler, that was reconstructed from a spreader stoker fired boiler. The heavy fuel oil was injected through several specially designed injectors, the so-called "climbing film" oil nozzles. In the same boiler they tested different types of coal, too. The same nominal steam output obtained with coal was also reached by burning the heavy fuel oil with 40% excess air. Combustion efficiency was 99.5%, whereas CO concentration in flue gases was below 100 ppm.

On the basis of accumulated experience from several different fluidized bed combustors and boilers, Barker and Beacham (1980) gave some kind of overview of petroleum-derived liquid fuel combustion results in UK. Liquid fuels, especially the more volatile ones, are very quickly transformed into vapors as a result of heating, but pass through the fluidized bed without being adequately mixed with air. This leads to poor in-bed combustion and high temperatures above the bed and along the freeboard. Even worse, fuels can leave the combustion system without being completely burnt. They reported about the attempts to improve the combustion process performance. For instance, the tests performed in a 300 mm ID combustor showed that generally the increase in the bed solids inventory was beneficial, but not beyond a bed height of 50 cm. For other fluidized boilers Barker and Beacham discussed about satisfactory liquid fuel combustion with a bed height in the range 0.5-0.7 m and fluidizing velocities in the range 1.5-3 m/s. As a successful example, they reported results from a fluidized bed boiler where the combustion efficiency was 99.9%, the unburned carbon in fly ash was 0.23%, the freeboard temperature was lower than the bed temperature (760 versus 840°C), with an excess air of 20%. In this case high combustion efficiency was accomplished at the optimal bed temperature for sulfur retention (about 850°C).

Enyakin et al. (1980) made combustion tests with heavy fuel oil in a pilot bubbling fluidized bed boiler, with the cross section of 0.5 m². The bed was relatively deep, 0.9 m, and as a consequence 90% of the fuel was able to burn within the bed, 6% in the splash zone and the rest in the convective sections of the freeboard. They were able of achieving a specific power output as high as 2.9 MW/m² (with ref. to the combustor cross section). In order to further decrease the extent of combustion above the bed with this heavy fuel oil they recommended a bed depth till to 1.5 m. They also reported visual and acoustic observations; in particular, they noticed appearance and explosion of fuel bubbles at the bed surface.

Along the same path, Borodulya et al. (1992) challenged the issue of estimating the optimum height of a bubbling fluidized bed burning conventional liquid fuels. They concluded that the optimum bed height linearly depends on the liquid fuel feed rate; further, they provided reference values about the optimal height, which should be from 0.55 till 0.85 m for a fuel feed rate per single nozzle from 1.2 to 1.8 kg/h.

Combustion and desulfurization tests of a high sulfur liquid fuel (Egyptian mazut) have been successfully carried out by Okasha et al. (2003) in a bubbling fluidized bed combustor with 300 mm ID and 3.3 m height, equipped with a purposely designed fuel injector in the bed region. Among operating variables, the focus was on the role played by the bed height, the injection air flow rate and the Ca/S ratio, in order to minimize the influence of segregation phenomena in the bed on combustion efficiency and sulfur retention. In particular, the rate of dispersion gas used for the fuel injection had the largest effect on bed mixing and higher values boosted both fuel conversion and desulfurization.

Fluidized combustion of Orimulsion® was investigated in a joint project by ENEL (I) and National Research Council of Italy. Combustion tests were performed by Miccio et al. (1999) in a bubbling fluidized bed

experimental facility with 370 mm ID and 4.6 m height. The bed temperature was constant at 850°C. The combustion efficiency of the Orimulsion® was always greater than 98.5%. A part of the fuel burnt in the freeboard and, therefore, a temperature over 1000°C was measured there. This finding was interpreted as the consequence of insufficient mixing between the fuel and air within the bed. As a confirmation of intensive combustion in the splash zone, the oxygen concentration profile showed a very sharp drop of about 4% just above the bed. The bed height was in the range 30-71 cm, and it was noticed that the increase of the bed height led to the decrease of temperature in the freeboard, on account of a greater residence time of the fuel in the bed. For the bed height of about 70 cm, the temperature in the freeboard exceeded the bed one by 100°C. The measurements by Miccio et al. (1999) showed very uneven gas concentration profile in radial direction in the splash zone. The gas probe was positioned above the bed surface and oxygen concentration ranged from 2% above the injection point till 10% at the opposite side. This was the proof that even a bed as tall as 70 cm did not enable satisfactory mixing and residence time of fuel within the bed. This implies that lateral mixing could be a limitation for realizing efficient combustion of liquid fuel within large scale fluidized bed. In spite of this uneven gas concentration profile, the authors calculated that 80-95% of the liquid fuel conversion occurred in the fluidized bed.

Miccio et al. (1999) carried out some injection tests under inert atmosphere and found that only less than 10% of carbon originally contained in Orimulsion® was converted into a solid carbon phase. This evidence implies that combustion of Orimulsion®, after evaporation of fuel droplets, can be treated as homogeneous combustion only.

Non-commercial liquid fuels. Kerr and Probert (1990) attempted co-combustion of acid tar, a by-product of oil-refining industry, with coal. They run a bubbling fluidized bed combustor of 1.2m x 1.2m cross section, with a total heat input of about 2 MW_{th}, the share of acid tar being about a half. The bed height was 0.75 m, the bed temperature constant and equal to 855°C, the primary to secondary air ratio around 2:1. Several tests were made ending in very successful results: a combustion efficiency as high as 99% was attained. The authors reported that, however, about 2/3 of the heat was developed in the fluidized bed and 1/3 above the bed during co-combustion. Since they did not present combustion results of sole coal, it is hard to estimate how much the acid tar burnt in the fluidized bed and how much above the bed.

Very extensive testing of pitch combustion has been carried out at the University of British Columbia (CDN). Combustion tests were performed in a 152 mm square cross-section circulating fluidized combustor with a height of 7.3 m. Different values of primary to secondary air ratio were used in order to obtain good mixing characteristics in the bottom part and in the upper part with appropriate temperature distribution along the riser. Typical temperatures in the riser were 850-900°C. The pitch material was fed into the riser through a nozzle at the same level of the solids return valve, only after the combustor temperature had reached the value of 750°C. The measured values of operating temperature at several places along the riser were in a relatively narrow range, i.e., only 20°C. In all tests the combustion efficiency was very high, always over 99%. It is worth mentioning that a temperature in the riser of about 760°C was enough high to enable high combustion efficiency of over 99.9% (Legros et al., 1991). Even at this temperature the emissions of hydrocarbons and CO were not larger than 30 ppm and 160 ppm at 3% O₂ in flue gases. The authors did not notice any effect of the air flow ratio on the combustion efficiency.

In combustion tests performed afterwards, with the main aim of obtaining high sulfur retention efficiency by limestone, Brereton et al. (1995) changed the operational parameters a little. The primary to secondary air ratio was increased to 2.5, the pitch feed rate was decreased with a consequence of higher excess air and oxygen concentration of 7% in flue gases. Again the combustion efficiency was very high, i.e., 99.7%. Since very high temperature was measured in the secondary cyclone, almost the same value as in the riser, it was concluded that cyclones played an important role in final stage of homogeneous combustion of CO and hydrocarbons. Also Lafanechere et al. (2001) considered pitch for co-combustion with two coals at an industrial CFB boiler of 60 MW_{th} in Marseille (F). They were mainly concerned with the furnace temperature profile and the boiler heat transfer coefficients, with some benefits provided by pitch addition.

In a similar way, Wu et al. (2001) successfully tested asphalt in a pilot CFB combustor obtaining high combustion efficiency between 99 and 99.5%, while the temperature difference between the bottom bed and the top of the riser did not exceed 50°C. Differently from coal combustion in a circulating fluidized bed where there is a relatively sharp drop of oxygen concentration in the riser wall region rich in char and inert particles, during combustion of liquid fuel they measured relatively close values of oxygen concentrations near the wall and at the center of the riser cross section. This implies that in the case of liquid fuel combustion a more homogeneous gas concentration field establishes in the riser cross section.

At the same time, Barczus et al. (2001) tested a heavy oil in another pre-pilot CFB combustor. They concluded that temperature is not a critical parameter for highly efficient combustion. At a riser temperature of

850°C combustion efficiency was reported to be acceptably high and concentrations of CO and hydrocarbons in flue gases were very low, i.e., less than 30 ppm; at 915°C, unburned gaseous components were almost non-detectable.

Anthony and Lu (2001) equipped a pilot bubbling fluidized bed facility to burn three different petroleum-based liquid fuels: heavy oil, pitch and bitumen. Once a nozzle for good atomization of the liquid fuels was designed, an extensive program of experiments was carried out. The bed height ranged from 0.4 till 1 m. They found that the increase of bed height did not have effect on the temperature distributions along the furnace height and on the combustion efficiency. Secondary air was used, but there were no comments regarding the effect of the secondary air. The authors varied the fluidizing velocity from 1.3 till 2.8 m/s. They observed that fluidizing velocity affected the temperature in the freeboard. During combustion of the heavy oil with a lower fluidizing velocity, they measured lower temperatures in the freeboard, and it was explained by a longer residence time of fuel in the fluidized bed, and a greater part of the fuel burnt in the bed. However, during combustion of pitch, the opposite happened, i.e., the greater fluidizing velocity led to lower temperatures in the freeboard. This phenomenon was explained by an enhanced mixing in the bed. Comparing the measured values during combustion of different liquid fuels, they concluded that the type of liquid fuel did not significantly affect the temperature distributions along the height of the furnace. Much more influence on the temperature distributions had the nozzle type. Generally, the combustion efficiency was always higher than 98.5%.

One of very rare examples of industrial applications of bubbling fluidized bed for burning liquid fuel residues was given by North et al. (1999). In a boiler furnace of 21 m² cross section and 6 m height a high sulfur pitch was burnt with the addition of wastewater containing organic compounds. The authors reported an increase in the freeboard temperature up to 1200°C, which was 170°C over the bed temperature; therefore, they estimated that about 40% of the pitch burnt above the bed surface.

Recently, Miccio et al. (2008) burned two liquid biofuels, i.e., biodiesel and sunflower oil, in a lab-scale internal circulating fluidized bed reactor (ICFB) for co-gasification of biomass/waste fuels or incineration of liquid wastes. The fuel was fed to the inner column (riser), so the combustion of fuel vapors took place with a rather limited residence time. The study has been aimed at checking the occurrence of the micro-explosive behavior already observed in BFB combustion. The efficiency of combustion and the CO emissions slightly differ between biodiesel and sunflower oil, the biodiesel giving rise to a better combustion performance.

EMISSIONS

Sulfur oxides. Light petroleum-based liquid fuels have usually low content of sulfur and can be burnt in conventional burners with low emission. With combustion of heavy petroleum-based liquid fuels, one of main problems is the emission of sulfur oxides.

Roberts et al. (1975) carried out experiments on sulfur retention using dolomite and limestone at combustion pressures of 350-600 kPa and temperature of 800°C. The obtained results indicated that the sulfur retention efficiencies, both of heavy oil and coal, are similar. As expected, the sulfur retention was enhanced with Ca/S molar ratio, in particular, when using dolomite. For instance, sulfur retention increased from 72 % to 92% raising Ca/S ratio from 0.8 to 1.8 in the case of dolomite. On the other side, it increased from 65% to 77% raising Ca/S ratio from 1.8 to 2.8. They always found a modest improvement in sulfur retention with increase in bed temperature. The behavior is quite different from that at atmospheric pressure where sulfur retention falls sharply with a temperature increase above 800-850°C.

Beacham and Marshall (1979) reported a high sulfur retention in a FB boiler burning a heavy fuel oil containing 3% sulfur. About 95% SO₂ retention was achieved at the expense of a Ca/S ratio as high as 5.3.

Enjakin et al. (1980, 1985) performed combustion tests with commercial heavy fuel oil (mazut) containing 2.1% sulfur in a pilot plant with the fluidized bed cross section of 0.5 m². They made three trials, the first with dolomite, the second with limestone, and the third without adding any sorbent. In the latter case, the concentrations were 35 ppm SO₃ and 700 ppm SO₂. After adding sorbents the concentrations decreased to 6 ppm SO₃ and 210 ppm SO₂, at Ca/S ratio equal to 3. Further increase of the Ca/S ratio was not effective on further decreasing of the sulfur oxides concentrations. One of conclusions of the authors was that the measured concentration of SO₃ (6 ppm) was low enough and would not lead to dew-point corrosion of heat exchange surfaces. In fact, the major problem with SO₃ is related to lowering the acid dew-point of wet flue gases, which effects more rapid metal corrosion of heat exchangers. For instance, at 1 ppm SO₃ the acid dew-point is 110°C, while at 80 ppm SO₃ the acid dew-point is 150°C (Brereton et al., 1995).

In a further paper on petroleum-based liquid fuel combustion in fluidized bed, Barker and Beacham (1980) reported about concentrations of SO₃. The authors measured 6 ppm of SO₃ and 2640 ppm of SO₂ in combustion

tests without addition of limestone, while they did not detect any SO_3 in tests with limestone. In these combustion tests, similarly to findings of Enjakin et al. (1985), SO_2 did not show a remarkable tendency to SO_3 conversion at standard FBC temperature and with excess air of 20%.

Barker and Beacham (1980) noticed that the inert bed material of fluidized bed during combustion of petroleum based liquid fuel retained "a large proportion of the ash from liquid fuel". In their liquid fuel the main ash constituents were sodium and vanadium compounds. These metals created a surface layer on bed particles of relatively inert compounds. The authors reported that more than 90% of vanadium from the ash was retained on bed particles. The advantage of the layer is avoiding catalytic effects of vanadium in the stream of flue gases, in combination with SO_3 , with extreme corrosion of the heat exchange surfaces. Furthermore, it was noticed by Barker and Beacham (1980), Enjakin et al. (1985), and Brereton et al. (1995) that the presence of limestone has positive effects and significantly lowers the SO_3 concentrations.

Typical molar ratio Ca/S for limestone added in FB combustors during combustion of liquid fuels was in a similar range as for coal combustion. That means the ratio was usually around 3, but some combustion tests were carried out with the molar ratio from 2 till 6.9 (Anthony and Lu, 2001).

Arthursson and Ostenberg (1979) reported about a demonstration bubbling fluidized bed boiler of 25 MWth for district heating. Since the fuel was high-sulfur residual oil, for accomplishing the high sulfur retention they used dolomite as the inert bed material. Using this bed material the Ca/S molar ratio could be as low as 1.5, while the emission of SO_2 was below the environmental requirements.

There is some difference in emission between combustion in bubbling and circulating fluidized beds. Generally liquid fuels leave very quickly the bubbling bed in BFBC or the dense bottom bed in CFBC, and tend to burn above the bed. For bubbling fluidized beds, this means that the formation of sulfur-oxides can occur to a great extent above the bed, and practically without contacts with particles of limestone in the bed. As a result the concentration of SO_2 can be very high. In circulating fluidized bed boilers, conditions for capturing SO_2 are better, since limestone particles circulate together with inert material, passing the whole riser height and having improved contact with gaseous sulfur oxides.

However, for optimal sulfur retention it is necessary that the liquid fuel burn off mainly occurs, if it cannot be completed at all, just in the dense fluidized bed. That means the emission of sulfur-oxides is affected by the quality of fuel distribution and dispersion, and also by positions of nozzles in the fluidized bed furnace. If design solutions of nozzles and fluidized bed boilers enable combustion mainly in the bed, sulfur oxides will be formed within the bed and, under controlled temperature conditions favorable to SO_2 capture, sulfur retention by limestone or dolomite particles will result much higher.

Wu et al. (2001) conducted tests with asphalt in a CFBC pilot plant. They found that, for the same other operating parameters, the use of steam instead of air for assistance to fuel injection led to higher SO_2 emission. They achieved a maximum sulfur capture efficiency of 94% with SO_2 emission of 110 ppm.

The sulfur retention in CFB units burning liquid fuel was less effective if compared with coal, while maintaining Ca/S ratio and other parameters the same. At a CFB plant of 60 MWth (Lafanechere et al., 2001) the emission of SO_2 was almost quadrupled when half of the heat input was switched from coal to petroleum pitch, while the sulfur content expressed per MJ of fuel heating value was about twice less in the petroleum pitch than in the coal. Similar relatively low sulfur capturing efficiencies were measured during combustion of petroleum liquid fuel in other CFB units (Zhang et al., 1991, Barczus et al., 2001). Zhang et al. (1991) carried out combustion tests also in bubbling fluidized bed units, using petroleum fuels and coal; their conclusion was that concerning liquid fuel the circulating fluidized bed gives a higher sulfur capturing efficiency than the bubbling one.

In an industrial bubbling fluidized bed of 20MWth burning high sulfur pitch the sulfur capture efficiency was 85%, with SO_2 emission of 400 ppm. In a very extensive investigation of Anthony and Lu (2001) three different petroleum liquid fuels were tested in a bubbling FB combustor. Although the sulfur retention was in the range 71–93%, the SO_2 emission was till 1600 ppm due to very high sulfur content.

Nitrogen oxides. Petroleum-based liquid fuels contain usually less nitrogen than coal on mass basis. If the nitrogen content in liquid fuels is recalculated on the basis of heating value, it becomes even less compared to coal. Therefore it seems that for reaching allowable emissions of nitrogen oxides it would not be necessary to apply any special measures.

Roberts et al. (1975) reported that the NO_x emissions from heavy oil (typically 130 ppm) are much lower than from coal (300-600 ppm) in the case of atmospheric combustion. However, in the case of pressurized combustion NO_x emissions become comparable (around 110 ppm), as a large part of the NO_x formed during coal combustion is reduced inside the bed thanks to the high residence time and contact with char. NO_x was found to increase with excess air as usual, but no consistent effect of temperature was observed.

Beacham and Marshall (1979) confirmed the low NO_x emissions of FBC burning heavy liquid fuels. NO_x

levels were typically below 140 ppm, but above 300 ppm when burning coal.

Keler and Berg (1979) reported that during mazut combustion in a laboratory bubbling fluidized bed the NO_x emission were in the range 150-400 mg/m^3 at excess air 1.25. Comparing this value with the EU regulations of that time (650 mg/m^3) it was below the limit. But comparing with the present regulation these emissions are somewhere across the limits (200-400 mg/m^3 , depending on thermal capacity).

Enjakin et al. (1980, 1985) favorably compared the NO_x emissions during combustion of mazut in a pilot bubbling fluidized bed boiler with those from industrial plants with conventional burners. The emissions of NO_x from the industrial plants were between 135 and 155 ppm, whereas from the FB pilot boiler ranged between 90 and 110 ppm at the same value of excess air.

These good results obtained from the first research activities showed possibility for the fluidized bed technology to achieve low emission of nitrogen oxides during combustion of liquid fuels. Since the temperatures in combustion chamber of circulating or bubbling FB facilities are relatively low, the main part of NO_x originated from the nitrogen contained in the fuel. However, only a minor part of the fuel nitrogen is converted to NO_x . Barczus et al. (2001) found for a CFB unit that only 7% of the nitrogen from the used fuel was converted to NO_x . Anthony and Lu (2001) calculated that during experiments in their BFB combustor the conversion of nitrogen to NO_x was between 14 and 52%, whose range includes the value (19%) reported by North et al. (1999) for another industrial BFB facility.

More recent data were obtained in a pilot CFB unit by Barczus et al. (2001) with NO_x level very close to 100 ppm for two different operational temperatures (850 and 915°C). During these experiments N_2O was not detected, this result being attributed to presence of hydrogen radicals, formed during the hydrocarbon decomposition and active for reduction of N_2O .

At the previously mentioned CFB plant of 60 MWth (Lafanechere et al., 2001) replacing a half of the coal heat input by a petroleum pitch led to an increase of NO_x up to 25%, in spite of the fact that the petroleum pitch had a 4 times lower content of nitrogen. No information was reported on changes of temperature profiles in the combustor, but it was reported that during co-combustion the oxygen concentration was higher (39% expressed in relative number). Taking into account that in the case of co-combustion the content of char particles in the riser was smaller and the oxygen concentration was higher, it is likely that these factors led to higher concentrations of NO_x .

Investigating the effects of different types of assisting fluid in feeding of heavy petroleum residues, Wu et al. (2001) detected that for the same total excess air the use of steam as assisting medium for fuel injection, instead of air, led to considerably decreasing NO_x emission (260 ppm with air, 200 ppm with steam).

At bubbling fluidized bed facilities different values of NO_x emissions were measured. At an industrial unit of about 20 MWth (North et al., 1999), NO_x emissions in two tests were 200 and 140 ppm.

The influence of oxygen concentration changes on NO_x was presented in the work by Miccio et al. (1999) on Orimulsion®. The measured NO_x emissions ranged from 60 till 80 ppm at O_2 concentrations in flue gases below 3% and reached about 140 ppm at 5% O_2 .

Carbon monoxide. The emission of CO is a consequence of the inefficiency of combustion process. In general, high concentrations of CO have been measured in the flue gases from some lab-scale or pilot experimental facilities burning petroleum-based liquid fuel. However, those findings cannot be considered representative of a general assessment of combustion process. A liquid fuel very quickly vaporizes and runs out the fluidized bed, burning above the fluidized bed as well. Therefore small height of experimental FB unit can give rise to great concentrations of CO because of a too short residence time.

With reference to bubbling fluidized beds, Miccio et al. (1999) reported CO emissions around 200 ppm (in some trials as low as 50 ppm) in a 370 mm ID, 4 m tall experimental BFB facility. In contrast, Anthony and Lu (2001) reported measured values of much higher CO emissions from their pilot combustor, ranging from 150 to more than 3000 ppm.

In CFB facilities the emissions of CO varied, but in general were lower than in bubbling fluidized bed. In the industrial plant Somedith (Lafanechere et al., 2001) the CO concentration was halved during co-combustion of pitch and coal compared to solely coal. In other pilot CFB units, at approximately the same conditions of temperature and excess air, the CO concentrations varied from 24 ppm (Barczus et al., 2001), over 150 ppm (Wu et al., 2001), till 270 ppm (Brereton et al., 1995).

Ash. Since the liquid fuels - even the heaviest of them like bitumen and asphalt - have mineral components not over 2% and very often below 1%, ash problems are generally not reported. It was noticed that some of heavy liquid fuels have very high concentrations of heavy metals. Therefore, there is necessity of taking care about this material: for instance Wu et al. (2001) reported the chemical analysis of asphalt ash leachate after a 24-hour treatment in an acetic acid solution, showing that the concentrations of heavy metals were a few orders of magnitude less than the permitted values.

Since the content of vanadium can be high in ash of liquid fuels (in some petroleum pitch V_2O_5 rates up to 25%), and it exerts a very strong catalytic effect, vanadium was separately analyzed in a few papers. Besides its role in creating aggressive species, it is important that vanadium and generally heavy metals are not emitted as vapor with flue gases. Legros et al. (1991) checked the mass balance on vanadium during FB combustion of liquid fuels; it was closed to 95% in one case and 129% in another case, confirming that all vanadium remained in solid phase.

Barker and Beacham (1980) commented on the fate of liquid fuel ash and fluidized bed material. Contrary to coal combustion where coal ash usually replaces the initial bed material, during combustion of liquid fuel the initial bed material practically does not change. Since they detected that the bed material retained some components from the liquid fuel ash, they emphasized that an appropriate bed material should be chosen during combustion of liquid fuel to retain the main and the most harmful ash components.

CONCLUSIONS

A general picture of phenomena occurring during the liquid fuel combustion process in a bubbling fluidized bed or in the bottom bed of a CBFC riser is available nowadays. They are fuel injection with air-assisted atomization or without it, fuel vaporization, fuel vapor bubble formation, fuel vapor pyrolysis and homogeneous oxidation, mixing of the fuel (and its products) by coalescence with the exogenous (air) bubbles, mass transfer between the fuel bubbles and the dense phase by convection and diffusion.

Combustion results of different liquid fuels obtained at different pilot and industrial fluidized bed facilities imply that, in order to achieve an efficient combustion process, the main operating variables, such as bed temperature, fluidizing velocity, bed height, excess air factor, primary-to-secondary air ratio, etc., must have practically the same values as those adopted for coal combustion. The most important issues for efficient combustion of liquid fuels are in relation to design and operation of the fuel feeding system.

A reasonable choice of fuel injection design and operation parameters is more critical in BFBC than in CFBC because it is just the bubbling bed and not the freeboard the place where mixing actions and mass transfer phenomena, which are required for efficient contacting and burning, are carried out.

Many investigators (Pillai and Elliot, 1976; Enyakin et al., 1980; Stubington and Davidson, 1981; Deguchi et al., 1984; Kerr et al., 1990; Miccio et al., 1999; Frassoldati et al., 2007) reported a temperature increase in the freeboard with respect to the bed (e.g., up to 200°C) and intense above-bed combustion. This was due to incomplete burn off of fuel vapors or pyrolysis products within the bed and/or their partial bypass as bubbles. In general, the extent of post-combustion was reduced by increasing bed temperature, bed height and fuel feed nozzle size; it was less sensitive to dispersing air velocity, whereas it was enhanced by use of secondary air.

As long as the operating bed temperature moves downward from the typical value for FBC of solid fuels, i.e., 850°C, more and more of fuel burn off is deferred from the bed to the freeboard. More importantly, the general combustion pattern becomes less smooth and predictable, with proven evidence of sudden light flashes in the splash zone, pressure spikes in the freeboard and detectable acoustic waves (Ferrante et al., 2008). The ensemble of these events was referred to as micro-explosion (Miccio et al., 2003), was typical of the liquid fuel combustion at low-temperature, i.e., 650-750°C, and made the fluidized combustion of liquid fuels quite similar to that of premixed gaseous fuels (Pre et al., 1998).

Taking into account the possibilities of adding sorbent particles, with the consequent *in situ* capture of SO_2 , and of using catalytic particles as bed solids to retain or convert other harmful compounds, we can conclude that the fluidized bed technology is favorable compared to other conventional liquid fuel burning technologies, when the concept of *in situ* emissions control is preferred to that of post-processing of gaseous exhausts. This is especially true in the cases of high sulfur liquid fuels or dirty wastes.

A serious concern remains about the emissions of heavy metals and alkali species in the cases of heavy fuels or refinery wastes. Anyway, Barker and Beacham (1980) reported capture of Na (>75% of input) and Va (>90% of input) by bed particles.

Of course, the recently raised issue of nano-particulate emission remains open to questions and for sure deserves suitable investigations.

Combustion of petroleum-based liquid fuels in fluidized beds showed also that emission of nitrogen oxides can be lower than in conventional boilers. Since the earlier works low NO_x emissions were demonstrated in FBC of heavy liquid fuels. In bubbling FBC NO_x levels were typically below 140 ppm, whereas the levels were above 300 ppm when burning coal (Beacham and Marshall, 1979). The main part of NO_x originates from the nitrogen contained in the fuel, although only a minor part of the fuel nitrogen is converted to NO_x (e.g., between 14 and 52% according to Anthony and Lu, 2001).

Concerning N_2O , it was not detected in a reference set of experiments (Barczus et al., 2001).

Additional research work directed at improving liquid fuel distribution and dispersion will have a firm

fallout on the front of emissions. The resulting enhancement in contacting and mixing patterns will be reflected in diminishing emissions of CO and increasing SO₂ retention.

From the operation viewpoint, we may conclude that FB combustion of conventional liquid fuels (i.e., commercial products of oil refining) was demonstrated to be technically and environmentally feasible since the early works (Barker and Beacham, 1980). The most important aspects relevant to plant design, operation and performance refer to the fuel feeding system:

- number of nozzles or nozzle density per bed square cross section in large plants
- vertical location and arrangement of nozzles in the bed
- use of a secondary gaseous stream (e.g., air) for assistance to liquid fuel dispersion or atomization
- choice of an optimal dispersion velocity (referred to the nozzle exit section) for a suitable jet penetration inside the bed and a proper droplet size distribution of the dispersed liquid fuel
- choice of an optimal Air-to-Liquid fuel mass feed ratio for an appropriate fuel droplet size distribution

In general, bed design and operating conditions are to be preferred, under which the residence time of fuel-containing bubbles is prevailing on other characteristic times such as fuel vaporization. From an application point of view this can be achieved by deep underbed fuel feeding and air-assisted injection.

The above aspects have been studied at the lab scale and generally tested with success at the pilot scale. However, scale-up to industrial size application requires further consideration.

From the application viewpoint, we may conclude that FB combustion of conventional liquid fuels (i.e., commercial products of oil refining) is not competitive in the sector of utility or for process heat generation. It is not appealing from the viewpoint of fuel utilization and is not economically convenient from the viewpoint of investment and operation costs.

The situation changes when FB combustion is considered for non-commercial liquid fuels like high sulfur oil-derived fractions or dirty wastes or renewable liquid fuels. In the past, the FB combustion of high sulfur fuel oil was applied in some instances with the goal of attaining an effective desulfurization and a successful combustion at the same time (Barker and Beacham, 1980; Arthursson and Ostenberg, 1979). Renewable liquid fuels (e.g., vegetable oils) might be burned in FBC systems at small to medium scale for district heating or decentralized heat and power generation in developed countries or third-world regions where oily biomass is easily grown and processable. This option does not exclude the co-combustion with solid fuels or a dual fuel plant configuration with a switch between solid and liquid fuels, opening perspectives for both new investigations and applications.

Finally, a new possibility is envisaged for applications in which the released heat is directed at producing high temperature, high pressure fluid streams (e.g., for use in an external engine) taking advantage of the extremely high heat transfer coefficients in fluidized bed.

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