Identification of Operating Parameters Critical to the Reduction of Particulate Emissions from Oil Refineries

J.M. Whitcombe, R.D. Braddock and I.E. Agranovski

Faculty of Environmental Sciences, Griffith University, Nathan Qld 4111, Australia
(josh.whitcombe@mailbox.gu.edu.au)

Abstract: Catalyst emissions from Fluidizing Catalytic Cracking Units have the potential to impact significantly on the environmental compliance of oil refineries. Traditionally it has been assumed that gas velocity and fine particles significantly impact on emission levels. Through the use of a simple iterative fluidized bed model, sensitivity analysis was conducted to identify the key operating parameters that influence emission rates. It was found that as bed velocity increases, emission rates actually decrease, and that the coarse size fractions and particle characteristics are the most influential factors for emission rates. Further work is needed to identify how operating parameters can be altered during normal operations to reduce catalyst emissions.

Keywords: Sensitivity analysis; FCCU; Air pollution; Modelling

1. INTRODUCTION

The petroleum industry currently employs Fluidizing Catalytic Cracking Units (FCCU's) as the major tool in producing gasoline from crude oil (Figure 1). FCCU's typically consist of a rising main where the chemical reactions between catalyst and hydrocarbons occur, a reactor to separate the product and catalyst, and a regenerator to re-charge the used catalyst. The regenerator is a fluidized bed used to combust coke from the used catalyst, with cyclones to remove particles from the flue gas stream before venting to the atmosphere. The recharged catalyst then re-circulates through the rising main and the process is repeated [Kunii and Levenspiel, 1991].

In recent years, fine particle emissions from industry have been identified as important contributors to poor environmental and health standards across the United States [Johnson, 2001]. With increasing demands for cleaner air, catalyst emissions from FCCU's have the potential to impact significantly on the environmental efficiency of the overall refining operation [Rucker and Strieter, 1992]. Currently, FCCU's are designed and operated in such a way as to maximise output and profitability of the refinery [Lin, 1993]. Thus there is a need for the relationships between current operational strategies and air pollution to be better understood.

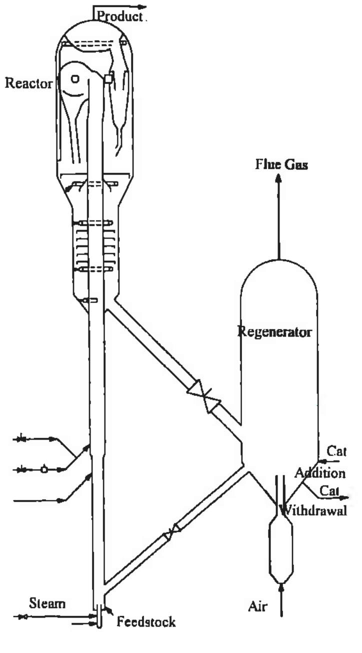

Figure 1. Stylised FCCU System.

2. METHODOLOGY

Matlab was used to develop a model to predict catalyst emissions from the fluidized bed, through the use of operating parameters of the system. The objective of the model was to produce qualitative trends, rather than accurate emission estimates.

Once trends could be identified, a sensitivity analysis was conducted to identify key operating parameters important for air pollution control.

2.1 Model Background

There are a number of different approximations and models used to predict all aspects of a fluidized system. However, even with such models fluidization is still to a large extent not fully understood [Geldart, 1986]. The complexity and accuracy of each model is dependent on the conditions and underlying assumptions used to develop and construct each model. Often models or equations found in the literature are too specific to be used in situations other than those for which they were designed.

To overcome this, a detailed literature review was completed to identify the key areas important to fluidization.

As there are a wide range of very detailed models for all aspects of fluidization, the aim of the literature review was to identify key equations that could be coupled to form a model of the entire fluidized bed operation. A simple iterative model with no feed back was developed to couple the large number of individual equations, dealing with such phenomena as entrainment, elutriation, cyclone efficiency, and bed effects, in order to develop a basic emission model for an FCCU fluidized bed. An illustrative outline of the model's main steps and major subroutines can be seen below in Figure 2.

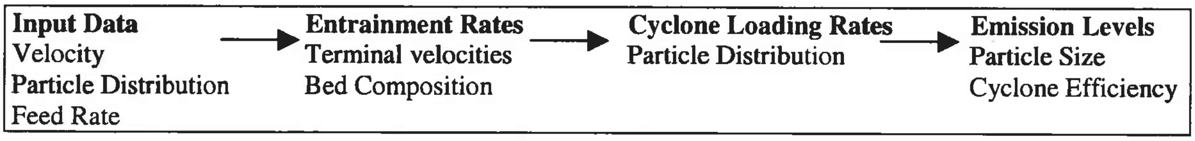

Figure 2. Illustrative outline of the model's main processes and selected subroutines.

The model is designed to have 12 input variables (operating parameters) and one output variable (emission rates). The input factors, consisting of operating parameters are listed in Table 1. The output variable is a matrix of 64 elements, with each element representing the emission rate for one of 8 particle sizes at a specific bed velocity. Refer to Figures 3 to 5 for examples of output.

The model is a function of the form of $x^* = f(x)$, where x is a vector of 12 input elements. The solution, x^* is found, and the sensitivity of x^* to the 12 input variables is determined. The model, using the initial operating parameters, steps through a series of sub-routines, each comprising one non-linear equation, to calculate a specific process in the fluidized bed (25 in total). As independent equations, each subroutine uses a combination of operating parameters and/or the solution to a previous subroutine to calculate a solution. Thus, the sub-routines are coupled to enable the exchange of data in such a way that the output of one subroutine will become the input of another. The model steps though the fluidizing process, from start to finish until the final emission rates are determined. During this process, data is collected to allow corrections and calibrations to be made.

Currently, the model is based on a linear structure, stepping though the fluidizing process from start to finish, without a feed back loop to account for catalyst material returned to the FCCU from the cyclones. This limits the accuracy of the model for prediction purposes, as a feedback loop will alter the particle composition, thus altering the results of all other processes. With out a feedback loop the model deals with a simplified bed composition and can not determine emission rates in real life situations where the bed composition fluctuates over time. As the objective of the modeling exercise is to determine the sensitivity of air emissions to the input parameters, removing the feedback loop simplifies the calculations without altering the way the actual system operates.

Finally, worked examples from the literature were used to validate the model and test the accuracy of the output. Once the model was operating correctly, real-life FCCU operating conditions were used to track emission trends.

2.2 Sensitivity Analysis

The New Morris Method, as developed by Campolongo and Braddock [1999], was used to test the model's input parameters for sensitivity. The New Morris Method is an extension of the original Morris method, extended to identify second order interactions between input parameters. The software developed by Campolongo and Braddock [1999] allows a mean (μ) and standard deviation (δ) from the Morris Method, as well as a new parameter, lambda (λ), to be determined for the input factors of the model.

The mean allows the overall influence of the factors to be determined, while the standard deviation identifies factors with possible interactive effects. The new term, lambda provides a global sensitivity measurement for 2-factor interactions [Campolongo and Braddock, 1999].

The software requires the identification of the input factor, and the range of values to be set for these factors (Table 1), number of sample runs, and the discretisation of the parameter space.

Table 1. List of Factors and their ranges in values used in the Sensitivity Analysis.

Factor	Parameter	Lower bound	Upper bound
1	Bed velocity (m/s)	0.1	1.5
2	300μm size fraction (% mass)	0.001	0.20
3	200μm size fraction (% mass)	0.001	0.40
4	100μm size fraction (% mass)	0.05	0.60
5	80μm size fraction (% mass)	0.1	0.90
6	60μm size fraction (% mass)	0.1	0.90
7	40μm size fraction (% mass)	0.05	0.60
8	20μm size fraction (% mass)	0.001	0.40
9	1μm size fraction (% mass)	0.001	0.20
10	Feed rate (kg/s)	1	350
11	Catalyst density (kg/m^3)	1197	1323
12	Shape factor (perfect sphere = 1)	0.70	1

3. RESULTS

The following results were obtained from the model and from the sensitivity analysis of the output.

3.1 Model Results

Refer to Figure 3 for the variation in entrainment rates (amount of solids lifted off the bed surface) for various bed velocities (velocity of gas moving through the bed) and particle size.

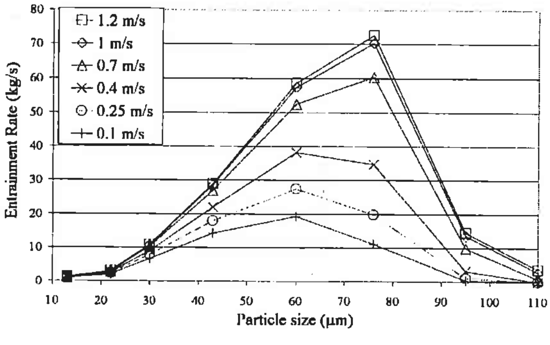

Figure 3. Entrainment rate (kg/s) vs particle size (μm) for bed velocities ranging from 0.1m/s to 1.2m/s.

From the graph it can be seen that even at very low bed velocities smaller particles are completely entrained.

As an increase in bed velocity only inceases the entrainment rates for the larger particles, it can be concluded that the maximum entranment rate for smaller size particles has already been reached under low velocty conditions.

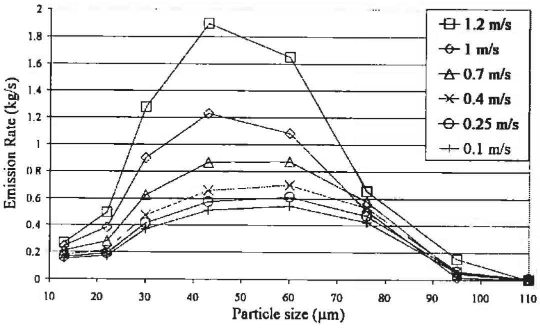

Figure 4. Emission rates (kg/s) vs particle size (μm), from the Primary Cyclone for bed velocities ranging from 0.1m/s to 1.2 m/s.

Emission rates for the primary cyclone for a number of bed velocities can be seen in Figure 4. With an increase in bed velocity, higher emission rates are generated, except at 1m/s, where emission rates are less than the 0.7m/s bed velocity for particles in the 80μm size fraction.

Emissions for the Primary Cyclone flow into the Secondary Cyclone for further treatment before being emitted into the atmosphere.

Emissions from the Secondary Cyclone can be seen in Figure 5. The higher the bed velocity the larger the emission rates, with a dramatic increase in emission rates being seen above the 1m/s bed velocity.

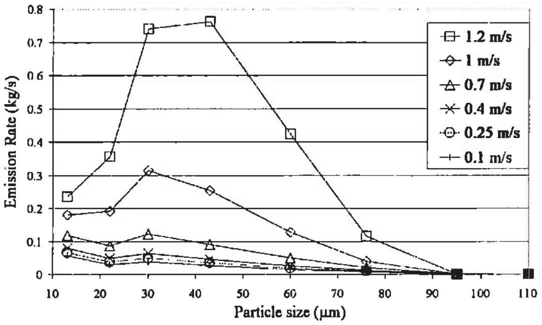

Figure 5. Emission rates (kg/s) vs particle size (μm) from the Secondary Cyclone , for bed velocities varing from 0.1m/s to 1.2 m/s.

The model was also run using specific operating data from an Australian oil refinery. The results of this run were used to calculate a total predicted emission rate from the fluidized bed under standard operating conditions.

Emission samples taken from the refinery during a previous and unrelated project were used for comparison [Agranovski and Whitcombe, 2001].

Although accurate in terms of trends in the FCCU, the model over estimates the actual emissions levels by a factor of ten to twenty.

3.2 Sensitivity Results

As seen in Figure 6 there appears to be a a wide spread in sensitivity between all parameters. Factors 12 and 10 appear to be the most sensitive with factors 3, 5, 1, and 2 having some sensitvity towards emission rates.

The lambda values seen in Table 2 are obtained from the New Morris method [Campolongo and Braddock, 1999]. Pairs of factors are altered (others remain constant) and their influence on emission levels are calculated, producing lambda values. The higher the lambda value the more influence those factor pairs have on emission levels. The lambda values appear to be very high for all factor pairs. However, several pairs are much higher than the others (in bold), and are the most sensitive in terms of influencing air emissions.

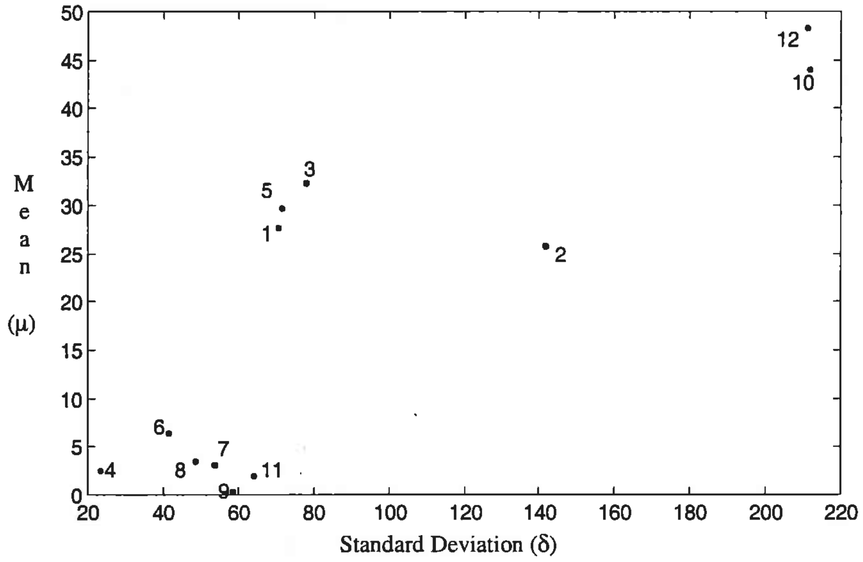

Figure 6. Plot of the Standard Deviation vs Mean Using the Morris Method.

Table 2. Output from the New Morris Method.

Pair	Lambda	Pair	Lambda	Pair	Lambda	Pair	Lambda	Pair	Lambda
1,2	3428	2,6	2508	3,11	**28414**	5,10	**20246**	8,9	6884
1,3	15794	2,7	2841	3,12	9499	5,11	12833	8,10	**20028**
1,4	14366	2,8	**23382**	4,5	4689	5,12	5416	8,11	16037
1,5	1863	2,9	**24240**	4,6	**21862**	6,7	4723	8,12	7820
1,6	16381	2,10	10933	4,7	**22257**	6,8	**23529**	9,10	17066
1,7	8253	2,11	12479	4,8	2676	6,9	**22324**	9,11	12652
1,8	3479	2,12	**31550**	4,9	2991	6,10	3902	9,12	9184
1,9	**28207**	3,4	4981	4,10	**23353**	6,11	4147	10,11	8888
1,10	9222	3,5	2702	4,11	**24453**	6,12	17377	10,12	**31257**
1,11	14631	3,6	2741	4,12	11766	7,8	**21941**	11,12	3452
1,12	12132	3,7	**27127**	5,6	**20570**	7,9	3917		
2,3	13429	3,8	**19996**	5,7	2804	7,10	3971		
2,4	**20545**	3,9	11418	5,8	2855	7,11	**23312**		
2,5	8163	3,10	3725	5,9	**28919**	7,12	12887		

4. DISCUSSION

The overall sensitivity analysis (Morris Method) indicates that the shape factor of the particle and feed rate of catalyst into the fluidized bed are the most sensitive parameters for air emissions. Surprisingly, coarse particles (300 and 200μm), which are not very prevalent in catalyst make up, appear to have a relatively high sensitivity - higher than that of the smallest fines.

Conventional wisdom states that larger particles do not influence emissions rates, as they are captured by the cyclones and returned to the bed. From the sensitivity analysis it appears that coarse particles do influence emission rates dramatically.

The New Morris Method indicates that the coarse particles also have several key interactions in the bed. In general, the larger particles interact largely with the finest particle sizes and particle density. The presence of coarse particles may alter the availability of fines, which in turn would alter emission rates. Due to their size, it is reasonable to assume that density would impact on their interactions in the bed, yet how this occurs is unknown. It is possible that using catalyst with a larger percentage of coarse material may help to control emission levels. Further work is needed to study coarse particle interactions.

The majority of the catalyst particles are in the 60 to 100μm range, therefore interactions in this size range can be seen as very important. These size fractions appear to have a generally high value for most 2-factor interactions. In particular, their interactions with the finer fractions, feed rate and density are the most significant. These interactions can in part be explained by the sheer volume of this fraction in the bed - a slight change in density of this fraction would lead to an overall shift in the bed composition. Flow patterns and other phenomena will also be changed by a small change in the characteristics of this, the most dominant species, in the bed. Density can also affect the efficiency of centrifugal devices such as cyclones. Changes in the density of the catalyst will therefore alter the forces acting on the particles in the cyclone. These changes will subsequently alter the collection efficiency of the cyclone and over all emission rates.

Interestingly, the fines appear to only interact with the 80 and 60μm size fraction, with very low interactions with the 100 and 40μm fraction. As yet no explanation can be given for this behaviour.

The calculated emission rates from the model are much higher than actual samples taken during operation of an FCCU. It is assumed that the main reasons for this are two-fold: errors in the model and errors in confirmation data. The main sources of errors in the model are believed to be the lack of a feedback loop for collected material, the use of 8 discrete particle classes and the lack of an accurate way of determining the shape factor for the catalyst in the system.

As predicted results were compared with emission levels determined from a non-related project, the exact operating parameters used by the FCCU during sampling are not known. Therefore general operating procedures have been assumed for that period. More detailed emission samples, taking into account operating parameters are required for calibration of the model.

The spike in emission rates for particles in the 40 - 60µm size fraction (Figures 4 & 5) is believed to be caused not by a decrease in cyclone efficiency but through an increased amount of that size fraction in the cyclone. The 40-60µm size faction is the first size fraction that is significantly increased by an increase in bed velocity. This leads to a larger increase in the entrainment rate for a smaller increase in the bed velocity (Figure 3). This increase in entrainment causes more of these particles to enter the cyclone, and thus a larger number to exit.

The entrainment and emission rates obtained using various bed velocities indicates that increasing the bed velocity may not lead to the largest emission rates. It can be seen from Figure 4, that an increase in bed velocity to around 1m/s will actually decrease emission levels in the primary cyclone. This may be due to the relationship between cyclone removal rates and inlet velocity. As velocity in the bed increases, more particles are carried up into the gas stream, leading to high loading rates in the cyclone, and high velocities, which in turn increase the removal efficiencies, causing less emissions to occur [Fassani and Leonardo Jr, 2000]. This theory, that increased loading rates actually decreases emissions, is supported by the fact that only the primary cyclone, with its larger loading rates, and not the secondary cyclone, experience reduced emissions for larger velocities.

However, beyond the 1m/s bed velocity, emission levels again increase as the shear volume of material flowing into the cyclone exceeds the increase in cyclone efficiency.

This is supported by the sensitivity analysis, which indicates that emission levels are not overly sensitive to velocity (Figure 6). The relatively low lambda values for all 2-factor interactions, except the smallest size fraction, with velocity further supports this idea (Table 1).

As expected with a fluidized bed, the finer size fractions (<1µm) interacts with other parameters. However, these interactions are not as prevalent as commonly believed. As expected, velocity and fines interact significantly, but this is due in part to the low removal efficiencies of cyclones for such small particles.

5. CONCLUSION

The common belief that only fines and velocity affect emission rates from FCCUs is not supported by this work.

The model has shown that by increasing bed velocity, emission rates can actually be lowered through a gain in cyclone efficiencies. The interactions of other parameters such as catalyst shape and density along with the concentration of large coarse particles are significant. Further work is needed to identify exactly how and why these parameters are so influential. It is hoped that oil refineries can use this information to alter operational conditions in such a way as to lower particle emissions without expensive end of pipe control measures being utilized.

6. ACKNOWLEDGEMENT

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