



Gas Splitting of SO₃-in-Air for Sulfonation

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In the detergent industry, it is often desirable to use one SO₃/Air generator to supply several Sulfonators. There is a loss of accuracy in the control system when the SO₃/Air mixture is split between multiple Sulfonators, and quantifying that loss is not simple. Even so, it remains a necessary piece of information when making an informed decision about the plant configuration. This paper describes and demonstrates a method to predict the accumulation of field instrument errors in control systems.

The field instruments in a standard Sulfonation plant contribute approximately $\pm 0.2\%$ error to the signal controlling the mole ratio of organic feed to SO₃. When the gas is split between two reactors, the error due to field instruments increases to $\pm 0.3\%$ if the reactors are the same size, and to a maximum of $\pm 0.4\%$ when the reactors are of different sizes or when there are more than two reactors. In any of these cases, the accuracy is better than the $\pm 1\%$ variance in mole ratio that is considered acceptable for the production of quality Sulfates. With proper design, gas splitting is a viable option and should be considered.

Introduction

The economics of scale and the need for precise control over gas/liquid contacting are important factors in the design of Sulfonation plants. Gas flow splitting enables the use of multiple reactors, while sharing a common gas plant and tail gas treatment system. A question, which often arises during discussions about flow splitting, is: "That's fine in theory, but does gas splitting really work?" It does. Splitting a gas stream is simple and is used in many processes from HVAC to Boilers to Sulfonation. Controlling the split and the process with the accuracy necessary to make a quality product is more difficult.

Chemithon has installed flow-splitting systems in several multi-train Sulfonation plants. These systems performed well when the field instrumentation is properly maintained. Conversely, flow-splitting systems will fail when field instruments are not maintained. The success of flow splitting mainly depends on two factors: the plant operator's commitment to maintaining the complete control system, including calibration of the field instruments, and on the designer developing good control logic and selecting field instruments with the required accuracies.

Mole Ratio Control

Chemithon has performed extensive research on reactor design and demonstrated the need for accurate mole ratio control. When we discuss "mole ratio", we mean the ratio of the moles of SO_3 in the gas mixture divided by the moles of the organic feed. In the specific case of Ethoxylates, a small excess of SO_3 results in a large increase in the production of Dioxane and color. Linear Alkyl Benzene (LAB), the most common material used in the detergent industry, is not as sensitive to a high mole ratio, yet for both Ethoxylates and LAB there is an economic penalty for under Sulfonating/Sulfating, i.e., loss of yield. A one percent loss in yield over the life of a plant is very expensive and will offset a considerable capital investment. Additionally, if a plant is designed to process only LAB, then its future is severely restricted since the industry trend favors naturally derived feedstocks and the need to Sulfate. The reactor and the entire plant should be designed with the goal of controlling the mole ratio to within $\pm 1\%$ in both the micro (point-to-point in the reactor) and macro (sulfur feed to the gas plant compared to the organic feed to the reactor).

Present day control systems use computers where mathematical algorithms generate control signals based on signals from field instruments, often using several signals to control a single valve. The devices that limit the accuracy of the mole ratio control are the field instruments, not the computer. The computer is capable of mathematically calculating the control signals to $\pm 0.01\%$, while the field instruments are capable of generating signals for the computer no better than $\pm 0.1\%$ of actual flow rates. In many cases, the results are worst as errors accumulate from multiple field instruments used in one loop to needlessly correct for temperature or pressure. The intent of this

paper is to provide the mathematical tools to evaluate the overall accuracy of a control system given the accuracy of the field instruments, thus allowing the purchaser of a plant to make an informed decision on the configuration of their plant.

The Case for Splitting

As implied by the name, continuous processes are designed to be operated for extended periods of time under stable operating conditions, but they produce “off-spec” product during start-ups, shutdowns and product changeovers. Sulfonation plants are continuous processes, but the market may require multiple products and sometimes, small quantities of many products. There are several schemes to improve the plant’s performance by reducing the percentage of time the plant is producing off-specification product by increasing the run time. For example, the use of additional product storage can lengthen runs, but there are additional costs of inventory and capital investment for tanks, as well as additional risk.

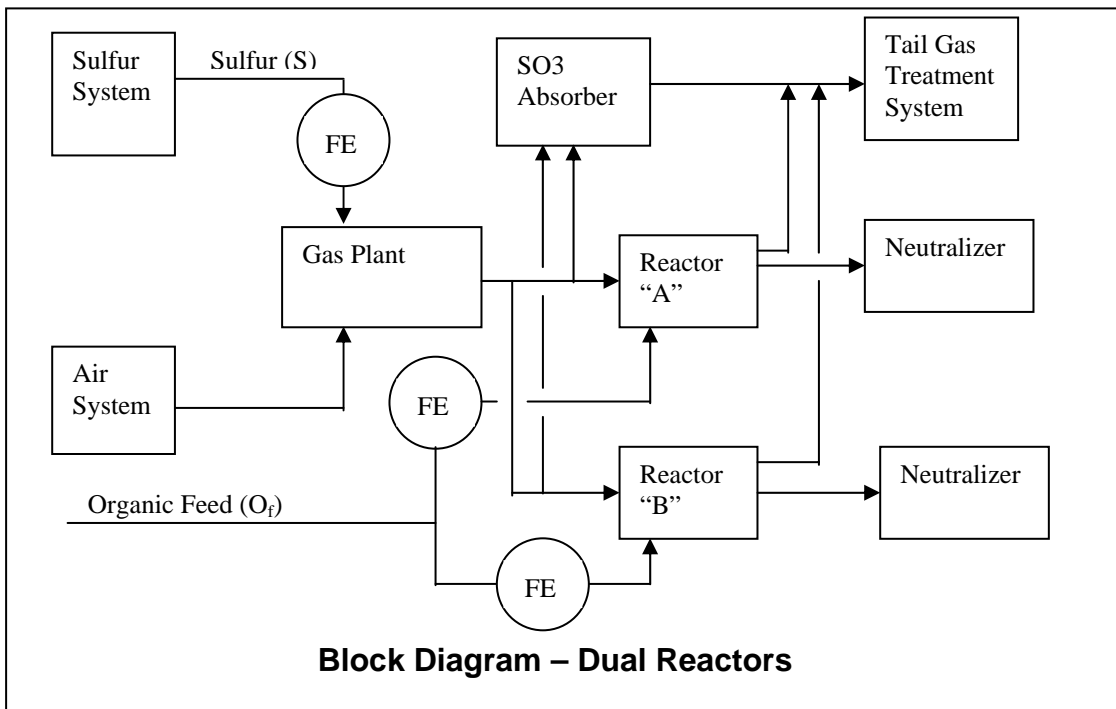
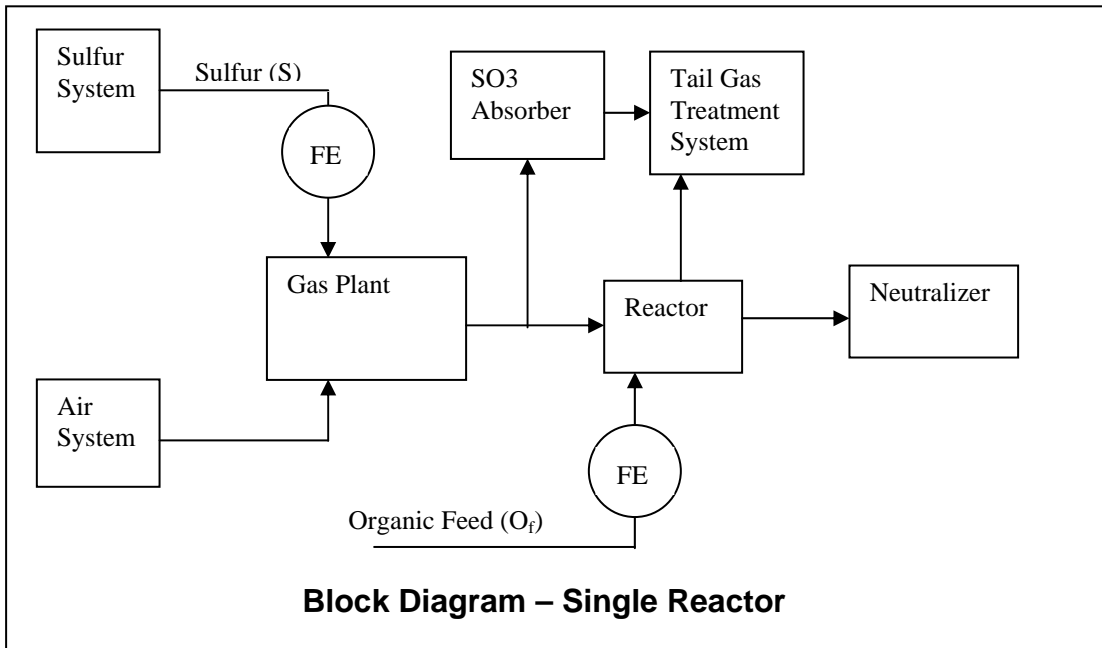
Generally speaking, the amount of time required for start-up, shutdown or a changeover is the same regardless of the plant’s size, so another solution is to use several smaller plants to extend the run time for each product and thereby reduce the quantity of off-spec material per quantity of on-spec material. This has capital and operating cost penalties. Larger plants are cheaper to purchase and cheaper to operate on a “per-unit-of-product” basis. A compromise solution is to use one large gas plant and tail gas treatment system with multiple Sulfonators and Neutralizers. Though the capital cost is greater than one large plant, it is less than using several small complete plants, but still has the advantage of extended run times.

Two half-size Sulfonation plants to meet a given capacity will increase the capital cost about 32% over a single plant with the same total capacity. A compromise design using multiple reactors with a single gas generator and tail gas treatment system reduces the capital cost by approximately 14% compared to two complete plants of the same total capacity. Of course, this requires that the SO₃/Air mixture be split between the reactors, hence the concern of increased error in the mole ratio inherent to this option.

Single Train Plants

Following are block diagrams of a single and dual reactor plants. Chemithon uses mass flow meters capable of maintaining a mole ratio of approximately $\pm 0.2\%$ to measure the Sulfur and Organic flows. This limit is due to the repeatability of the Sulfur and Organic mass flow meters. The mole ratio (M_r) is determined by multiplying the ratio of the Sulfur mass flow (S) by the Organic mass flow (O_f) and a constant (K). Appendix A demonstrates that the total error of an equation of the form $Y = K U/V$ is equal to the error in U plus the error in V or, in this case, the sum of the transmitter errors. The error in available mass flow meters is $\pm 0.1\%$: therefore, the system accuracy is $(\pm 0.1\%) + (\pm 0.1\%)$ or $\pm 0.2\%$. (Note that the concern is error in repeatability. Chemithon recommends that the mole ratio be verified by chemical analysis every four

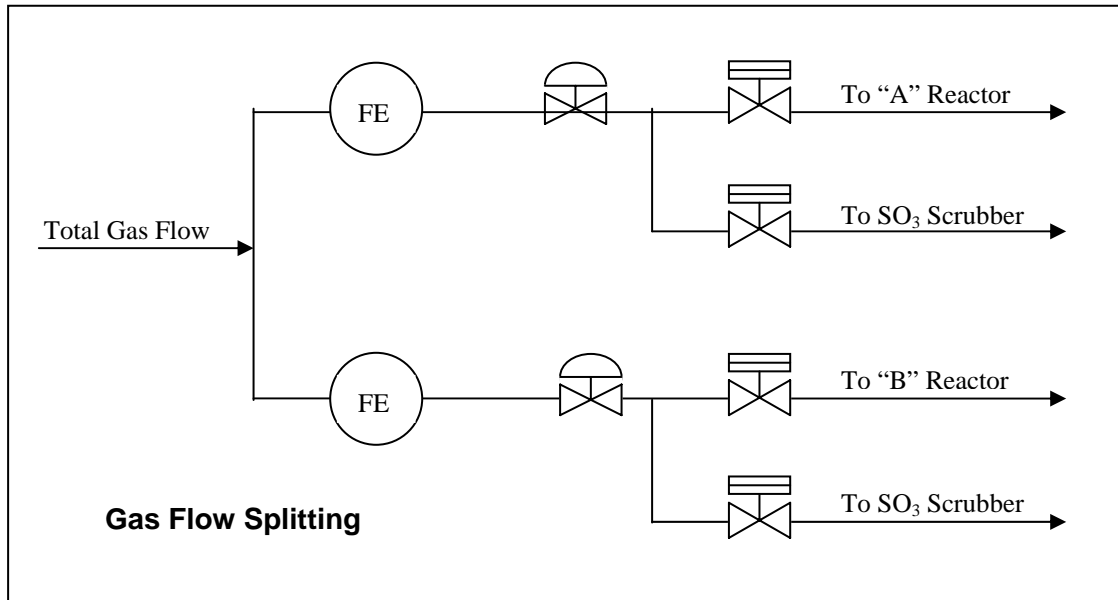
hours to reduce errors due to changes in molecular weight of the feed, percent conversion of sulfur to SO_3 , or the flow meter's absolute accuracy.)



Dual Train Plants

When flow splitting to two reactors as shown in the preceding diagram, the same mass transmitters for sulfur and organic are required with the inherent contribution to error for each, as well as instruments to measure the split between the reactors.

The following diagram shows the instruments required for splitting in more detail.



This scheme was chosen because it uses a minimum number of transmitters. The flow measuring devices can be orifice plates with dP transmitters, vortex shedding transmitters or thermal dispersion transmitters, but all meters in a given plant should be of the same type. The transmitters must be installed so that the process gas temperatures and pressures are the same. Under these conditions values for temperature and pressure are not required to determine the split of gas between the reactors. If the temperature and pressure are not equal at the flow transmitters, then additional transmitters are required, the total error of the system will increase, maintenance increases and reliability decreases.

While the type of meter may or may not be important from the mathematical viewpoint, it is significant from the reliability viewpoint. Based on transmitters available at this time, Chemithon would select transmitters for gas flow in this order: vortex shedding, dP and thermal dispersion. Another factor that should be considered is the ability of local technicians to maintain the instruments. In many parts of the world, dP transmitters would be a good choice since they are well understood and spares are available, while vortex shedding transmitters would be chosen in most parts of Europe, North America and Asia Pacific.

Since the sulfur flow is known, it is not necessary to know the SO₃ gas concentration: only what percentage of the total gas (and, therefore, the percentage of the total SO₃ derived from the known sulfur flow) goes to a specific reactor. The mole ratio for an individual reactor becomes a constant times the total sulfur molar flow to the gas plant, times the fraction of the total gas going to that reactor, divided by the molar flow of organic feed to the reactor.

Based on experience, the actual split of the gas stream between reactors should not be controlled with an automatic controller. Systems where the gas flows are automatically adjusted tend to become unstable. Chemithon recommends that the control valves be positioned by a hand signal and that the signal from the flow meters be used to determine the fraction of the gas going to each reactor. The fraction of the gas flow going to the reactor, the reactor mole ratio and the total sulfur flow are used to calculate a set point for an automatic controller that adjusts the organic feed to the reactor.

Three or More Reactor Trains

The equation for determining the accuracy of a three-way split is more interesting since it is simple to see how to modify the equation for different numbers of reactors. The equation is:

$$\epsilon_{MrA} = \epsilon_S + (1-f_A)(\epsilon_A) + f_B\epsilon_B + f_C\epsilon_C + \epsilon_{Of}$$

where

$$f_A \equiv A/(A + B + C), \quad f_B \equiv B/(A + B + C), \quad f_C \equiv C/(A + B + C)$$

and A \equiv Gas Flow to Reactor "A", B \equiv Gas Flow to Reactor "B", C \equiv Gas Flow to Reactor "C".

Let's test the boundaries of the equation. For case 1, assume that all meters have a repeatability of $\pm 0.1\%$ and that all three reactors are using the same fraction of the gas. Then the error in the accuracy of the mole ratio to reactor "A" is:

$$0.1\% + ((1-0.33) \times 0.1\%) + (0.33 \times 0.1\%) + (0.33 \times 0.1\%) + 0.1\% = 0.33\%$$

In a similar manner, case 2 is when only one reactor is running and case 3 is when the reactor of interest is using much less of the gas than the other two. The trend is that the fewer the number of splits (Reactors) and the more evenly the gas is split between the reactors, the nearer the total error approaches that of a single reactor plus the error of one gas flow meter. If more reactors are added or if the fraction of gas going to the reactor of interest is very small, then the error increases to that of a single reactor plus double the error of a gas flow transmitter.

Case	Percent Flow			Total % Error
	Reactor A	Reactor B	Reactor C	In Reactor A
1	33	33	33	0.33
2	100	0	0	0.2
3	2	49	49	0.396

Development of the Equation

For any given reactor (A), the mole ratio can be calculated by the following formula:

$$Mr_A = K \times S \times f_A / O_{fA}$$

where K is the ratio of the molecular weight of sulfur and the organic feed times the conversion rate of sulfur to SO₃, S is the Sulfur flow rate to the gas plant, O_{fA} is the organic feed to reactor "A" and f_A is as earlier defined.

The equations in Appendix "A" can be combined with algebra, using equations 2 and 3 in Appendix "A", so that the error is:

$$\epsilon_{MrA} = \epsilon_S + \epsilon_{fA} + \epsilon_{Of}$$

Next, the value of ϵ_{fA} needs to be evaluated. The equation for f_A as defined earlier is:

$$f_A \equiv A / (A + B + C)$$

An equation of this exact form is not listed in Appendix "A", but an equation of the form $Y = K (U / V)$ is listed, so we will set $U = A$ and $V = (A + B + C)$.

$$\epsilon_{fA} = (\epsilon_U + \epsilon_V).$$

The development of equation 3 needs to be considered at this point. While determining the function U / V the result is $(\epsilon_U - \epsilon_V)$, but the minus sign was eliminated by taking the absolute value of the results. In this case, "A" will appear in both the denominator and numerator, the sign must be maintained and the absolute value taken after the values are combined.

Evaluating ϵ_U is simple: it's ϵ_A , but ϵ_V must be evaluated by equation 1. Equation 1 is of the form

$$Y = K_1U + K_2V + K_3W, \text{ then}$$

$$\epsilon_Y = (K_1U/Y \times \epsilon_U) + (K_2V/Y \times \epsilon_V) + (K_3W/Y \times \epsilon_W)$$

The Y in this equation will be equated to (A + B + C). In a similar fashion, U will be equivalent to A, and U/Y is equal to A / (A + B + C) which we defined as f_A , and the same logic is applied to B and C. Additionally, in this case there are no constants (K_1 , K_2 or K_3) or, more accurately, they are all equal to one and the equation simplifies to:

$$\epsilon_{fA} = \epsilon_A - (f_A\epsilon_A + f_B\epsilon_B + f_C\epsilon_C)$$

Combined, the equation further simplifies to:

$$\epsilon_{fA} = (1-f_A)\epsilon_A - f_B\epsilon_B - f_C\epsilon_C$$

Taking the absolute values now that the values with A have been combined:

$$\epsilon_{fA} = (1-f_A)\epsilon_A + f_B\epsilon_B + f_C\epsilon_C$$

Finally, combining with $\epsilon_{MrA} = \epsilon_S + \epsilon_{fA} + \epsilon_{Of}$, we get:

$$\epsilon_{MrA} = \epsilon_S + (1-f_A)(\epsilon_A) + f_B\epsilon_B + f_C\epsilon_C + \epsilon_{Of}$$

Conclusions

The requirements for successful gas splitting are:

1. Instruments with repeatability of $\pm 0.3\%$ or better of indicated value in the operating range
2. The use of chemical analysis on a regular basis to verify the mole ratio
3. The resources to maintain the instruments
4. Operation of the reactors at or near full design capacity

There is a small penalty in completeness when splitting, as would be expected considering the reduced accuracy in mole ratio predicted by the equations. Asymmetrically splitting gas flow two-ways has been successfully demonstrated on commercial plants with one reactor producing cosmetic quality product.

APPENDIX "A" ERROR ANALYSIS

With the advent of digital controllers, it has become possible to implement complex control schemes using multiple field instruments that were virtually impossible, or impracticable with analog controllers. These complex control schemes have made it necessary to evaluate the total error for various functions using multiple variables. The following table summarizes various common functions and the total error. In the equations, Y, U, V, and W all represent variables and the K values represent constants. The remainder of this section reviews the math necessary to determine these relationships, and then demonstrates the implementation of a function.

No	Equation	Error
1	$Y = K_1U + K_2V + K_3W$	$\epsilon_Y = (K_1U/Y \times \epsilon_U) + (K_2V/Y \times \epsilon_V) + (K_3W/Y \times \epsilon_W)$
2	$Y = K (U \times V)$	$\epsilon_Y = \epsilon_U + \epsilon_V$
3	$Y = K U/V$	$\epsilon_Y = (\epsilon_U + \epsilon_V)$
4	$Y = K \sqrt{U}$	$\epsilon_Y = 1/2 \epsilon_U$
5	$Y = K U^n$	$\epsilon_Y = n \epsilon_U$
6	$Y = U/(U+V)$	$\epsilon_Y = (V/(U+V))(\epsilon_U + \epsilon_V)$
7	$Y = K (U/V - 1)$	$\epsilon_Y = U/(U-V)(\epsilon_U + \epsilon_V)$

Accuracy of field instrumentation is commonly reported as an error, $\pm X\%$ of the real value, which is noted as follows:

$$E_r \equiv \pm \frac{\Delta V_r}{V_r}$$

where E = error
 V_r = real value

To evaluate the total error of a function, the variables plus their change are substituted. As an example using the function $Y = (U \times V)$, the variables would be modified to:

$$(Y + \Delta Y) = (U + \Delta U) \times (V + \Delta V)$$

Then algebra is used to expand the function to:

$$Y + \Delta Y = UV + U\Delta V + \Delta UV + \Delta U\Delta V$$

We are interested in evaluating the total change in Y , or ΔY . By subtracting the original function, $Y = U \times V$, the value of ΔY remains:

$$\Delta Y = U\Delta V + \Delta UV + \Delta U\Delta V$$

To convert the equation to the form $E \equiv \pm \frac{\Delta Vr}{Vr}$, the equation is divided by the original function, $Y = U \times V$ with the result:

$$\Delta Y/Y = U\Delta V/(UV) + \Delta UV/(UV) + \Delta U\Delta V/(UV)$$

By canceling common terms the equation reduces to:

$$\Delta Y/Y = \Delta V/V + \Delta U/U + (\Delta U/U)(\Delta V/V)$$

The errors in the variable are defined as $E_Y \equiv \pm \Delta Y/Y$, $E_U \equiv \pm \Delta U/U$, $E_V \equiv \pm \Delta V/V$. These values are substituted to yield:

$$E_Y = E_V + E_U + E_U E_V$$

If it is assumed that an individual instrument error is small, the value, $E_U E_V$, can be ignored since it is much smaller than the other terms. This is the same assumption used to determine differential equations and it is now convenient to introduce the expression:

$$\mathcal{E} = \left| \frac{dVr}{Vr} \right|$$

The Greek symbol \mathcal{E} denotes that the equation was evaluated by differentials, and therefore, the error was assumed to approach zero. Also, the absolute symbol is used in place of the \pm sign. This was the method used to determine the table of common equations and the related total errors at the start of this section. Care needs to be taken when evaluating equations with the same variable in both the denominator and numerator. In that specific case, the sign is important and must be taken into account and the term in the denominator must be subtracted from the term in the numerator.

To demonstrate the validity of this method, assume that the value used in a control system is the result of two instruments multiplied:

$$Y = K(U \times V)$$

The differential of the equation is:

$$\partial Y = KV \partial U + KU \partial V$$

It is desired to substitute the errors, $\epsilon_Y = \left| \frac{\partial Y}{Y} \right|$, $\epsilon_U = \left| \frac{\partial U}{U} \right|$, $\epsilon_V = \left| \frac{\partial V}{V} \right|$ into the equation, so we divide the differential by the original equation and obtain:

$$\frac{\partial Y}{Y} = \frac{KV \partial U + KU \partial V}{KUV}$$

Then the common terms are canceled with the following results:

$$\frac{\partial Y}{Y} = \frac{KV \partial U}{KUV} + \frac{KU \partial V}{KUV}$$

$$\left| \frac{\partial Y}{Y} \right| = \left| \frac{\partial U}{U} \right| + \left| \frac{\partial V}{V} \right|$$

and then the equalities, $\epsilon_Y = \left| \frac{\partial Y}{Y} \right|$, $\epsilon_U = \left| \frac{\partial U}{U} \right|$, $\epsilon_V = \left| \frac{\partial V}{V} \right|$ are substituted to yield:

$$\epsilon_Y = \epsilon_U + \epsilon_V$$

The method can be tested by substituted values for the variables and evaluating the equations.

Assume	U = 100	$\epsilon_U = \pm 1\%$
	V = 0.1	$\epsilon_V = \pm 2\%$
	K = 2	

By substituting the values for U, V and K, the value of the function with no error is determined to be 20.

$$Y = 2 \times 100 \times 0.1 = 20$$

The differential equation predicted that the error would be the sum of the errors, or $\epsilon_Y = \epsilon_U + \epsilon_V$. By substituting the assumed errors, the total error, ϵ_Y , should be $\pm 3\%$.

To evaluate error by the algebraic method and assuming the worst case, values at the maximum range allowed by the error (U = 101, V = 0.102) are substituted into the original function:

$$Y = 2 \times 101 \times 0.102 = 20.604$$

The total error is the difference of the function evaluated using values at the maximum range, less the value of the function expressed as a percentage, or:

$$E_Y = (20.604 - 20) / 20 = 3.02\%$$

This demonstrates that the total error predicted by the differential is essentially the same as the total error determined by the algebraic method.

APPENDIX "B" Determining f_A using Orifice Plates

A traditional method to measure gas flow is by the pressure drop across a known restriction such as a venturi, a nozzle or an orifice plate. Using an orifice plate, the mass flow is:

$$W = (KB^2)AYFa \sqrt{2gc\Delta P\rho}$$

Where $W \equiv$ Gravimetric flow rate
 (KB^2) is a constant determined by the ratio of the orifice plate and pipe diameters
 $A \equiv$ Inside cross sectional area of pipe
 $Y \equiv$ Gas expansion factor
 $Fa \equiv$ Area factor for thermal expansion of orifice
 $g \equiv$ gravitational constant
 $\Delta P \equiv$ measured pressure differential
 $\rho \equiv$ gas density

By choosing the geometry when splitting between two users, so that temperature, pressure and gas concentration are the same at the orifice plates for both reactors, as in the diagram on page 5, then Y , Fa , $2gc$ and ρ are constant and the weight fraction of the total gas going to reactor A is:

$$f_A = \frac{(KB^2)_{AA} \sqrt{\Delta P_A}}{(KB^2)_{AA} \sqrt{\Delta P_A} + (KB^2)_{BA} \sqrt{\Delta P_B}}$$

To simplify the equation it is convenient to define $C \equiv \left[\frac{(KB^2)_{BA}}{(KB^2)_{AA}} \right]$ and the equation can be simplified to:

$$f_A = \frac{1}{1 + C \sqrt{\frac{\Delta P_B}{\Delta P_A}}}$$

(Note that $C \sqrt{\frac{\Delta P_B}{\Delta P_A}} = W_B / W_A$.)

Appendix C shows how the derivative of $f(U,V) = \frac{1}{1 + C\sqrt{U/V}}$ is determined. By substituting $U = \Delta P_B$ and $V = \Delta P_A$, the same method demonstrated in appendix A is used.

$$\partial_A f_A = \frac{C(U \partial V/V^2 - \partial U/V)}{2\sqrt{U/V}} \left(\frac{1}{1 + C\sqrt{U/V}} \right)^2$$

$$f_A = \frac{1}{1 + C\sqrt{U/V}}$$

$$\text{then } \frac{\mathcal{J}_A}{f_A} = \frac{C(U/V \mathcal{N}/V - U/V \mathcal{U}/U)f_A}{2\sqrt{U/V}}$$

$$\mathcal{E}_{f_A} = \left| \frac{\mathcal{J}_A}{f_A} \right|, \quad \mathcal{E}_V = \left| \frac{\mathcal{N}}{V} \right|, \quad \mathcal{E}_U = \left| \frac{\mathcal{U}}{U} \right|$$

$$\mathcal{E}_{f_A} = \frac{CU/V(\mathcal{E}_V + \mathcal{E}_U)f_A}{2\sqrt{U/V}}$$

Substituting back, $U = \Delta P_B$ and $V = \Delta P_A$

$$\mathcal{E}_{f_A} = 1/2 f_A C \sqrt{\Delta P_B / \Delta P_A} (\mathcal{E}_{\Delta P_A} + \mathcal{E}_{\Delta P_B})$$

From earlier $C\sqrt{\Delta P_B / \Delta P_A} = A/B$ and $f_A = \frac{A}{A+B}$

$$\mathcal{E}_{f_A} = 1/2 \left(1 - \frac{A}{A+B}\right) (\mathcal{E}_{\Delta P_A} + \mathcal{E}_{\Delta P_B})$$

and finally

$$\mathcal{E}_{f_A} = 1/2 (1 - f_A) (\mathcal{E}_{\Delta P_A} + \mathcal{E}_{\Delta P_B})$$

APPENDIX "C"

Determination of $f(U,V) = \frac{1}{1 + C\sqrt{U/V}}$

This section shows the determination of this function referenced in appendix "B".

$$f(U,V) = \frac{1}{1 + C\sqrt{U/V}}$$

Define $n \equiv U/V$ and $m \equiv 1 + C\sqrt{n}$

then $F(U,V) = 1/m$

$$\partial F(U,V) = -\frac{\partial n}{m^2}$$

$$\partial n = (1/2 C/\sqrt{n}) \partial n$$

$$\partial n = \partial U/V - U \partial V/V^2$$

$$\partial n = \frac{1/2 C \partial U/V - U \partial V/V^2}{\sqrt{U/V}}$$

$$\partial F(U,V) = \frac{-1/2 (\partial U/V - U \partial V/V^2)}{\sqrt{U/V} (1 + C\sqrt{U/V})^2}$$