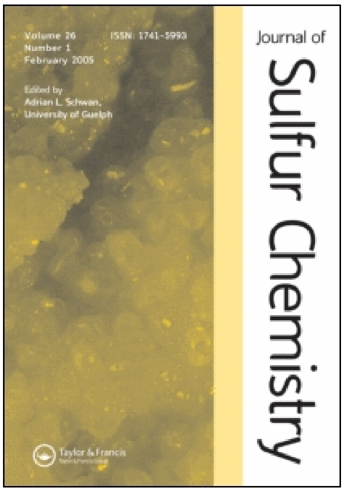

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Ethylene manufacture by partial oxidation with sulfur

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Ethylene manufacture by partial oxidation with sulfur

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The objective of this study was to examine the sulfur-mediated oxidation of ethane to ethylene. In summary, it has been found that ethylene can be produced in high yield (ca 75%) by the oxidation of ethane with excess sulfur in the 800–850 °C temperature range using a residence time of about 1 s. It is surmised that the high ethylene yield arises from the relatively weak C–S bond which precludes the formation of carbon–sulfur compounds so favoring pathways to ethylene. A process scheme is suggested which incorporates ethylene production into sulfur recovery, plants for which are found in essentially all refineries and in sour gas processing. A potential advantage of this chemistry over standard ethane steam cracking is that the sulfur process considerably increases carbon efficiency for ethylene production as most of the energy required for ethylene synthesis is supplied by the oxidation of H_2S.

Keywords: ethylene; sulfur; carbon and energy efficiency

1. Introduction

Most of the world's ethylene arises from steam cracking of ethane and more complex hydrocarbon mixtures, although it can also be recovered from off-gases from refinery catalytic cracking and coking units. State-of-the-art steam-cracking plants can achieve moderate ethylene yield (ca 65%) from ethane with by-product combustion supplying some of the heat needed to support the endothermic cracking processes (*1*). Nevertheless, over the last decade or so, new methods have been sought for selective and thermally efficient ethylene production. In particular, the research conducted by Schmidt and co-workers (*2–10*), among many studies, has investigated the chemistry and technology for production of ethylene by catalytic partial oxidation of ethane and other hydrocarbons.

The extensive research of Schmidt and co-workers has shown that yields of ethylene, equivalent or better than those obtained by conventional steam cracking, can be realized by passing O_2 and ethane over a Pt-based catalyst. Analysis of numerous data sets from the studies on this reaction suggest (*11*) that ethylene is formed, in the main, by catalytic oxidation of part of the ethane to CO_2, CO and H_2O at the Pt surface with the heat of reaction of these processes promoting the thermal conversion of the remaining ethane to ethylene and H_2 via gas-phase, radical-based

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chemistry. Direct conversion of ethane to ethylene via surface species also plays a role in the high selectivity to ethylene (*11*). To date, this type of process has not been commercialized, perhaps a consequence of the complexity of mixing ethane and pure oxygen safely on a large scale and because of the high cost of producing O_2 from air.

Research in our laboratories has examined the use of S_2 in place of O_2. Sulfur is a primary product of the thermal stage of the modified Claus sulfur recovery process, a standard unit found in all refineries processing sulfur-containing crude oils (*12*). In addition to being a vital technology in an oil refinery, the furnace of the Claus plant is equivalent to an air separation plant operating at 1200 °C because S_2, formed by the reaction of H_2S with O_2 in the furnace, is a chemical equivalent to O_2. A brief explanation of the Claus process will be helpful in explaining the relevance of the research described in the body of this paper.

In a refinery, H_2S, recovered from hydrotreater off-gases, is fed to a furnace where partial oxidation converts ca 65% of the H_2S to S_2, which on condensation yields liquid sulfur (S_8) at ca 140 °C. The combustion, in most cases, is supported by air resulting in a furnace temperature of approximately 1200 °C, the actual temperature being dependent on the partial pressure of the H_2S in the feed acid gas which may also contain CO_2 and H_2O. The other products of partial oxidation are H_2O and SO_2which pass from the waste heat boiler and furnace sulfur condenser, along with unreacted H_2S and N_2, to a series of catalytic converters which yield further elemental sulfur. The primary condensation of sulfur from the combustion stage then acts as the air separation equivalent. As is illustrated in Figure 1, the heat produced in the Claus furnace is recovered as steam, but in a sulfur-based process for ethylene, the heat produced in a parallel Claus-type furnace that is reprocessing the H_2S formed during ethylene formation would be harnessed to convert the condensed liquid sulfur to S_2 for reaction with ethane (Figure 1). The H_2S and SO_2 produced in the dedicated furnace would be combined with the gases entering the Claus catalytic converter train in order to maintain high S recovery.

Experimental studies reported here show that ethylene can be obtained in 75–79% yield by contacting ethane with S_2 at 800–850 °C with reformation of H_2S and co-production of a small amount of CS_2, a solvent used in Rayon production. If there is no outlet for CS_2, it would be recycled with the H_2S to the ethylene furnace for reconversion to sulfur (Figure 1). The scale of such an ethylene plant is coupled to the turnover of H_2S and CS_2 through the dedicated furnace as it provides the thermal energy to drive the conversion of ethane to ethylene. Importantly, it is

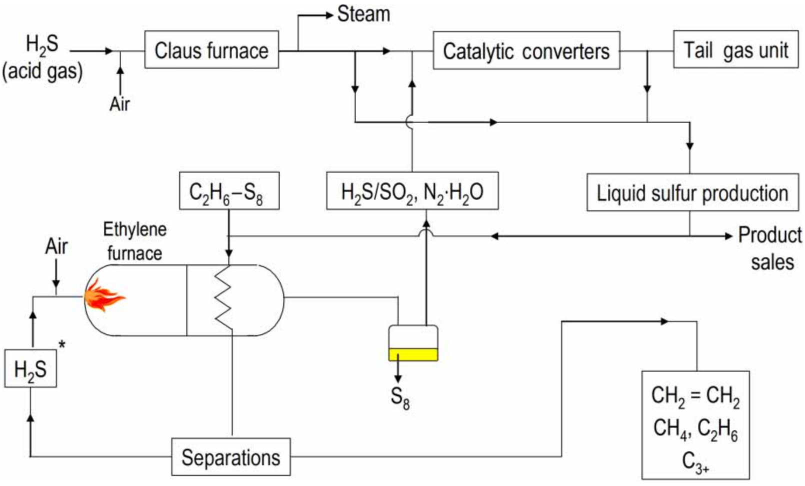


Figure 1. A conceptual process configuration for integration of ethylene production with Claus-based sulfur recovery. Note: *Fuel supply may be supplemented by product H_2, CH_4, CS_2 and by supplemental H_2S.

evident that ethylene production by this technology would be driven by partial oxidation of H_2S to sulfur essentially harnessing the free energy of O_2. The thermo-chemical data of the overall processes illustrate the favorable energy balance for an ethylene plant based on this chemistry.

$$H_2S + \frac{1}{2}O_2 \longrightarrow H_2O + \frac{1}{2}S_2(-157.0\,\text{kJ/mol})$$

$$\frac{1}{2}S_2 + C_2H_6 \longrightarrow H_2S + C_2H_4(52.1\,\text{kJ/mol})$$

Clearly, excess heat energy is produced from H_2S oxidation for the conversion, although it should also be noted that pre-heat of the ethane and sulfur feeds will also be required, with heat recovery from the product stream necessary to maintain heat balance for the overall process (heat exchangers are not shown in Figure 1). Important industrial aspects of the process are that there are no technical limitations in mixing sulfur vapor with ethane and the technology required for the reactors would be equivalent to those used in a Claus furnace. This paper presents data which underpin the ethylene process illustrated in Figure 1 and discusses the thermal efficiency and carbon balance associated with sulfur-assisted partial oxidation of ethane to ethylene.

2. Previous studies and background to the experimental design

Little work has been conducted on the conversion of ethane to ethylene by sulfur and only one study reports some success. Garwood *et al.* (*13*) reported that CS_2 was the major carbon-containing product when ethane was passed over a zeolite catalyst that had been impregnated with sulfur and they did not detect ethylene. In the 1950s, Morningstar reported ethylene formation in a study in which ethane was bubbled through a reactor-containing liquid sulfur at temperatures of 600–850 °C (*14*). These authors calculated the ethane/sulfur feed ratio based on the amount of H_2S that was formed in the reaction, although the actual ratio would have been a function of the mixing patterns occurring in the reactor. Ethylene yields of 50% were reported at 874 °C using an ethane/sulfur ratio of ca 7 and a residence time of 7 s. Morningstar also reported that acetylene became a major product as the ethane/sulfur feed ratio decreased.

In related work, Pasternak and co-workers at Imperial Oil laboratories in Sarnia, Ontario, passed ethane with H_2S and O_2 over a CdS catalyst demonstrating that high yields of ethylene (ca 70%) could be achieved with *in situ* formation of sulfur species (*15*, *16*). Despite these high yields, no attempts have been made to commercialize this type of process, possibly because water co-product of H_2S oxidation leads to formation of CO, COS and CO_2 which would complicate the separation and purification of ethylene. Most likely, at the time of the Pasternak (*15*, *16*) study, there was little incentive to implement a high efficiency, low carbon-emission ethylene process.

As an aid to the experimental design, equilibrium calculations were conducted allowing for the absence or presence of solid carbon as a product (Table 1). These calculations employed an inlet feed temperature of 600 °C and studied the effect of varying the inlet ethane/sulfur ratio. When carbon is allowed to form, ethylene is predicted in negligible quantities and carbon, H_2 and CH_4 are the only products of note. Data from these calculations will not be analyzed further as laboratory studies show that, although some carbon-based products are formed, the quantities produced are much less than predicted. The equilibrium calculations excluding carbon formation (Table 2) show that ethylene is predicted to form to almost 25% at an ethane–sulfur ratio of 8:1. CH_4, CS_2 and propylene were also formed in significant quantities with CH_4 predicted as, by far, the largest carbon-containing product. At lower ethane–sulfur ratios, less ethylene and propylene are expected at equilibrium with CS_2 becoming a major product. Overall, these calculations suggest that high ethane/sulfur ratios should favor ethylene production, although only in moderate equilibrium yield, with CH_4 as the dominant carbon-containing product.

Table 1. Equilibrium calculations for ethane/N_2/S_2 with formation of carbon, feed temperature: 600 °C.

	Moles/100 moles of reactant			
	2:1	4:1	6:1	8:1
N_2	40.00	50.00	53.33	55.00
C_2H_2	4.4E−09	1.8E−10	7.1E−11	4.4E−11
C_2H_4	9.6E−06	4.4E−06	3.3E−06	2.8E−06
C_2H_6	7.2E−05	2.1E−04	2.6E−04	2.8E−04
C_3H_6	1.1E−09	7.9E−10	6.4E−10	5.7E−10
C_3H_8	2.6E−09	9.7E−09	1.2E−08	1.4E−08
CH_4	8.40	22.21	27.44	30.12
H_2	63.21	55.58	51.79	49.76
CS_2	2.6E−03	8.3E−05	2.2E−05	9.6E-06
H_2S	39.99	20.00	13.33	10.00
S_2	2.9E−04	8.0E−06	2.0E−06	8.7E-07
C(S)	71.60	57.79	52.56	49.88
T(adb) (C)	627.4	543.8	522.8	512.9

Table 2. Equilibrium calculations for ethane/N_2/S_2 without formation of carbon, feed temperature: 600°C.

	Moles/100 moles of reactant			
	2:1	4:1	6:1	8:1
N_2	40.00	50.00	53.33	55.00
C_2H_2	0.20	0.36	0.24	0.18
C_2H_4	2.21	7.65	8.96	9.21
C_2H_6	0.16	0.49	0.68	0.79
C_3H_6	6.29E−02	1.13	2.45	3.39
C_3H_8	1.64E−03	2.12E−02	4.83E−02	7.06E−02
CH_4	55.11	49.56	46.09	44.27
H_2	3.62	0.25	7.83E−02	4.37E−02
CS_2	19.56	9.98	6.66	5.00
H_2S	0.87	3.18E−02	8.86E−03	4.58E−03
S_2	4.37E−04	4.86E−06	7.20E−07	2.57E−07
T(adb) (C)	734.7	603.1	547.9	521.4

3. Results and discussion

3.1. *Ethane–sulfur reactions*

Table 3 summarizes the data obtained from the reaction of ethane with sulfur at 800 °C and 850 °C over selected residence times and a ethane–sulfur feed ratio of approximately 4:1 (note that it was difficult to control the sulfur feed rate precisely with the liquid sulfur delivery system (LSDS) so the feed ratios were not exactly the same for each experiment). C and S_2 product quantities were calculated from mass balance equations with [C] representing any non-gaseous carbon-containing species reported in the tables. Despite attempts to detect other carbon-containing species, the only volatile products that were observed were propylene and thiophene albeit in only very small quantities (<0.01 mole%). The isolation of dark-colored sulfur, in experiments which gave high yields of [C], suggests that carbon was present in the liquid sulfur, most likely as complex C–S polymeric species, usually referred to as carsul. The sulfur referred to here is unconsumed reagent sulfur (Table 3).

The first point to note from the data sets shown in Table 3 is that the ethane–sulfur system operates under kinetic control at the limited residence times used in this study as very high

Table 3. Sulfur-promoted conversion of ethane.

		Products (moles/100 moles of feed)									Conversion (%)		Selectivity (%)				Yield (%)
t(res) (s)/T °C	Feed/product	N_2	C_2H_6	S_2	C_2H_4	CH_4	CS_2	[C]	H_2S	H_2	C_2H_6	S_2	C_2H_4	CH_4	CS_2	[C]	C_2H_4
3/800	Feed	54.7	37.2	8.1													
	Product	54.7	3.5	0.8	25.0	8	2.2	7.1	10.2	26.1	90.6	90.1	74.2	11.9	3.3	10.5	67.2
2.4/800	Feed	54.5	37.1	8.4													
	Product	54.5	3.7	0.0	26.3	7.8	2.9	3.7	11.6	27.6	90.3	100	78.7	11.7	5.5	5.5	70.9
1.2/800	Feed	54.7	38.1	7.2													
	Product	54.7	5.9	0.7	29.5	3.3	1.6	0.5	9.9	25.3	84.5	90.3	91.6	5.1	2.5	0.8	77.4
1.2/850	Feed	55.2	37.7	7.1													
	Product	55.2	3.7	3.2	26.7	9.2	1.1	5.4	5.5	33.7	91.5	54.9	77.4	13.3	1.6	7.8	70.8

ethylene yields (77.3–79.6%) could be obtained at 800 °C and 850 °C. In addition, as can be seen by comparison with the reference experiments without sulfur, ethylene yields significantly exceeded those obtained for thermal and O_2-promoted conditions (Table 4).

For experiments at 800 °C, it was observed that selectivity to and yield of ethylene increased as the residence time was reduced from 3.0 to 1.2 s at a feed ethane/sulfur ratio of 4.59, 4.41 and 5.29, respectively. The highest yield of ethylene obtained at 800 °C (77.3%) was observed using a 1.2 s residence time which, in terms of carbon efficiency, can be explained by the lower production of CH_4, CS_2 and [C]. Indeed, based on these observations, it is concluded that ethylene formation occurs rapidly with further reaction of the product ethylene yielding methane, more complex carbon products [C] and CS_2 at longer contact times. H_2 and H_2S were the other major products formed in an approximate 1:0.5 molar ratio with respect to the amount of ethylene produced. At 850 °C, a significantly lower yield of ethylene was obtained using a 1.2 s residence time (70.8% compared with 77.4% at 800 °C), the lower yield resulting from, most probably, the decomposition of hydrocarbon species to carsul-type products (Table 3).

As was the case for the experiments at 800 °C, reference experiments at 850 °C which examined either thermal cracking of ethane or the O_2-assisted partial oxidation resulted in lower ethylene yields (66.7% and 62.5%, respectively, Table 4) in comparison to when sulfur was present (70.8%, Table 3). Note, however, that the reference experiments were conducted using a 0.5 s residence time compared with 1.2 s for the sulfur-promoted reaction. Although not presented in detail here, reference experiments using 1.2 s resulted in very low ethylene yields ($<$50%) and large amounts of carbon-based products which made running such experiments very difficult because of plugging of the reactor. Clearly, the use of sulfur, at either temperature, inhibited the formation of polymeric products [C], thus enhancing the conversion of ethane to ethylene. An observation of significant mechanistic interest is that while sulfur was essentially reacted to extinction at 800 °C with the formation of H_2S and CS_2, at 850 °C, lesser amounts of these products were observed along with some residual sulfur with considerably more H_2 per mole of ethane. This result prompted investigation of higher ethane–sulfur ratio conditions.

3.2. *Effect of ethane–sulfur ratio*

In an attempt to probe the mechanism of sulfur-assisted ethylene production from ethane, a series of experiments was conducted in which the temperature and residence time were held constant (850 °C and 0.6 s) and in which the ethane/sulfur ratio was varied from 8.4, 12.6 to 17.1 (Table 5). Because of difficulties in easily changing the liquid sulfur delivery via the LSDS, these ratio changes were accomplished by changing the ethane flow and decreasing the inert nitrogen flow. One interesting observation from these experiments was that a very high ethylene yield (79.6%) and high selectivity (90.3%) to ethylene was observed at the 8.4 ethane/sulfur feed ratio together with low selectivity to carbon-based products (0.9%). Ethylene yields decreased progressively at the higher feed ratios (73.3% and 69.7% at 12.5 and 17.1, respectively) with higher conversions to methane and [C]. Thus, it can be concluded that sulfur species and, possibly, H_2S play a significant role in curtailing cracking-type reactions. Two experiments that included H_2S in the feed (Table 5, at ethane–sulfur feed ratios of 8.5 and 12.8) resulted in ethylene yields of 74.3% and 74.7%, respectively, and low selectivity to [C] products (1.1%).

Overall, it can be concluded that adjustment of the balance of ethane/sulfur feed ratio, residence time and reaction temperature would allow engineering of a process yielding around 75% of ethylene with minimal conversion to solid carbon products. The hydrogen and methane by-products could be used in generating heat and utilities for the plant or burnt within the ethylene furnace to maintain heat balance.

Table 4. Thermal and O_2-promoted conversion of ethane.

		Products (moles/100 moles of feed)											Conversion (%)		Selectivity (%)				
t(res) (s)/*T* °C	Feed/product	N_2	C_2H_6	O_2	C_2H_4	C_2H_2	CH_4	CO	CO_2	H_2	H_2O^a	$[C]^a$	C_2H_6	O^b	C_2H_4	CH_4^b	CO_x^b	$[CO]^b$	Yield (%)
0.5/800	Feed	59.2	40.8	–															
	Product	59.2	16.8	–	20.8		0.3			19.3		6.8	58.8	–	86.7	0.6	–	14.1	51.0
0.5/800	Feed	54.2	40.3	6.7															
	Product	54.2	10.0	0.0	22.8		4.0	3.3	0.6	21.6	8.9	7.3	75.2	100.0	75.3	6.6	6.4	12.1	56.6
0.5/850	Feed	59.2	40.8																
	Product	59.2	3.9		27.2		5.0			29.9		14.3	90.4	–	73.7	6.8	–	19.4	66.7
0.5/850	Feed	54.2	40.3	6.7															
	Product	54.2	2.1	0.0	25.2	1.0	8.2	4.2	0.0	30.0	9.2	11.9	94.8	100.0	66.0	10.7	5.5	15.6	62.5

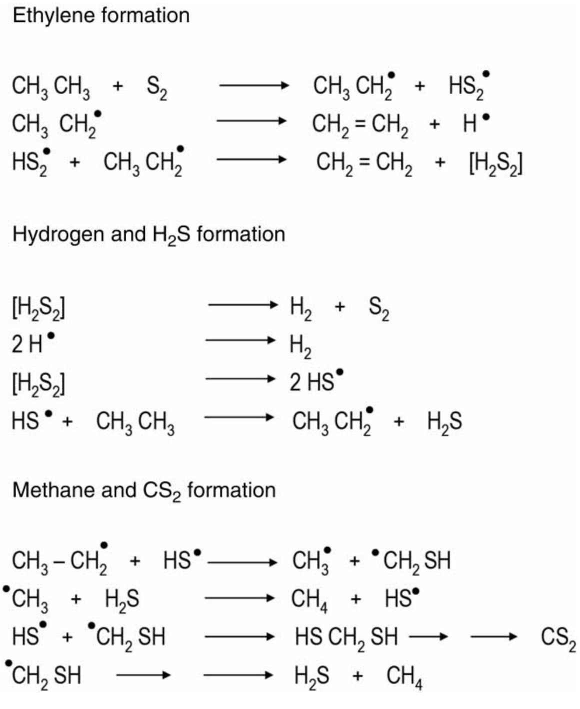
Notes: [a]Calculated from O and C mass balance equations. [b]Calculated on the basis that each mole of C_2H_6 yields two moles of product.

Table 5. Sulfur-promoted conversion of ethane: effect of feed ratio and H_2S.

		Products (moles/100 moles of feed)									Conversion (%)		Selectivity (%)				Yield (%)
t(res) (s)/T °C	Feed/product	N_2	C_2H_6	S_2	C_2H_4	CH_4	CS_2	[C]	H_2S	H_2	C_2H_6	S_2	C_2H_4	CH_4	CS_2	[C]	C_2H_4
0.6/850	Feed	39.7	39.7	4.7													
	Product	55.6	4.7	1.0	31.6	5.4	0.7	0.6	6.0	31.9	88.2	78.7	90.3	7.7	1.0	0.9	79.6
0.6/850	Feed	36.1	59.2	4.7													
	Product	36.1	8.3	1.8	43.4	8.9	0.6	5.5	4.5	48.8	86.0	61.7	85.3	8.7	0.6	5.4	73.3
0.6/850	Feed	15.0	80.3	4.7													
	Product	15.0	13.5	2.3	56.0	11.2	0.5	9.6	3.8	61.9	83.2	48.9	83.8	8.4	0.4	7.2	69.7
0.6/850	Feed	20.2	40.8	4.8					34.1								
	Product	20.2	4.9	0.2	30.3	7.4	1.4	0.8	40.6	29.1	88.0	95.6	84.4	10.3	2.0	1.1	74.3
0.6/850	Feed	13.0	60.1	4.7					22.2								
	Product	13.0	9.6	2.2	44.9	9.3	0.8	1.1	25.5	47.5	84.0	53.2	88.9	9.2	0.8	1.1	74.7

3.3. *Reaction pathways*

Although surface reactions cannot be ruled out when using small reactors, most probably, the quartz reactors used in this study had little influence on the reaction chemistry. Thus, the following discussion will focus on gas-phase reaction pathways. The reactions suggested in Scheme 1 are but a brief summary of the numerous steps that could be written for the sulfur–ethane system and those shown have been chosen to illustrate pathways toward the major products. These pathways should not be viewed as definitive mechanistic information. The stable sulfur allotrope at 800–850 °C is S_2, a species containing two unpaired electrons which, therefore, can initiate a cascade of radical reactions. In addition to the thermal production of ethylene via the standard C–C bond homolysis mechanism (not shown), it is probable that oxidation by S_2 is a major pathway to ethylene (Scheme 1). Interestingly, the proposed intermediate $[H_2S_2]$ can lead either to H_2S or H_2 but, in either case, produce sulfur species which initiate further ethylene-producing reactions.



Scheme 1. Pathways for conversion of ethane to ethylene by S_2.

The production of H_2S or reformation of S_2 is a key difference to ethylene production by partial oxidation of ethane with O_2 because in the oxygen system strong O–H bond formation precludes any further participation of oxygen species, principally water, in ethylene formation. Indeed, the production of water limits ethylene yields because ethylene is readily consumed in steam reforming reactions. Although C–C bond thermolysis could also be invoked to explain the methane production in this work and could, indeed, be the major pathway to methane in this study, Scheme 1 illustrates the possibility of a sulfur-mediated pathway to methane via the ethyl radical. This reaction could also yield a dithiol species that could be oxidized to CS_2. In principle, the production of methane via the ethyl radical should lead to methane and CS_2 in equimolar quantities but the weak C–S bond would result in the preferential formation of carbon species by C–S bond homolysis that form methane via H-abstraction from H_2S or other H-rich species. Indeed, the high yields of ethylene observed in this work are, in part, a consequence of the relatively weak C–S bond as ethyl radicals, even if captured by sulfur radicals, *e.g.* HS, will readily reform the ethyl radical or produce ethylene directly by elimination of H_2S.

3.4. *Sulfur-mediated ethylene production and carbon efficiency*

Depending on the process configuration, a typical steam-cracking plant based on ethane results after ethane recycle in about 75% conversion to ethylene with the remaining carbon ending up as CO_2. In addition, methane is consumed to heat the cracking furnaces, producing further CO_2. Assuming that ethane is recycled in the sulfur process and that an ethylene yield of 75% can be obtained 80–85% of the ethane is converted to ethylene and no external methane is required, since heat demand of all process would be supplied from the oxidation of H_2S and CS_2 with any energy shortfall being made up by co-firing the by-product H_2, CH_4 and H_2S produced in the refinery hydrotreating units. Thus, the only CO_2 resulting from this process is that which arises from the product methane and CS_2 that is recycled to the ethylene furnace. An important aspect of the dedicated ethylene furnace is that it must be operated in a similar regime to the main Claus furnace such that the off-gases can be sent directly to the Claus catalytic converter array. Clark (*12*) gives a comprehensive review of the combustion chemistry of sulfur and carbon species in a Claus-type furnace.

4. Experimental procedures

4.1. *Materials*

Ethane (99.5%) was obtained from Praxair Canada Inc. and elemental sulfur (sublimed, >99.9%) was supplied by Fischer Scientific Canada.

Gas chromatographs, used for the determination of the majority products reported in the data tables, were calibrated with standards obtained from Praxair Canada Inc. and the Scott Specialty Gases Company. In-house calibration mixtures for SO_2 (0.864% in N_2) and for CS_2 (1.7% in N_2) were prepared using standard procedures.

4.2. *Procedure: reagent delivery*

All experiments were conducted in a quartz reactor positioned horizontally in a furnace (Figure 2), the temperature of which could be controlled to ±5 °C. The internal reactor temperature was determined by a K-type thermocouple and by various placements of this thermocouple, the “hot zone” on the reactor was determined in order that inlet feed gas tubes could be positioned at the beginning of the hot zone. Feed ethane, carrier N_2 and other gases were delivered to the reactor using a Linde FM4575 mass flow control console and Brooks 5850E mass flow control modules supplied by Advanced Specialty Gas Equipment, and sulfur was supplied via an LSDS illustrated in Figure 3. Both vapor phase and LSDS were devised for the sulfur feed but only the LSDS provided accurate sulfur delivery.

The LSDS consisted of a 1 L stainless steel pot with a 3 m capillary tube (i.d. 2.5 mm) coiled within it and connected to an outlet valve (Figure 3). The outlet tube was connected via a tee-section to a delivery tube which was heated, insulated and plumbed to the reactor inlet system. With the pot temperature set at 140 °C to avoid the viscous region for liquid sulfur (160–200 °C), N_2 overpressure (up to 414 kPa) was used to force liquid into the capillary tube. A relief valve (Figure 3) allowed for pressure control and as a means of stopping sulfur flow. The outlet capillary

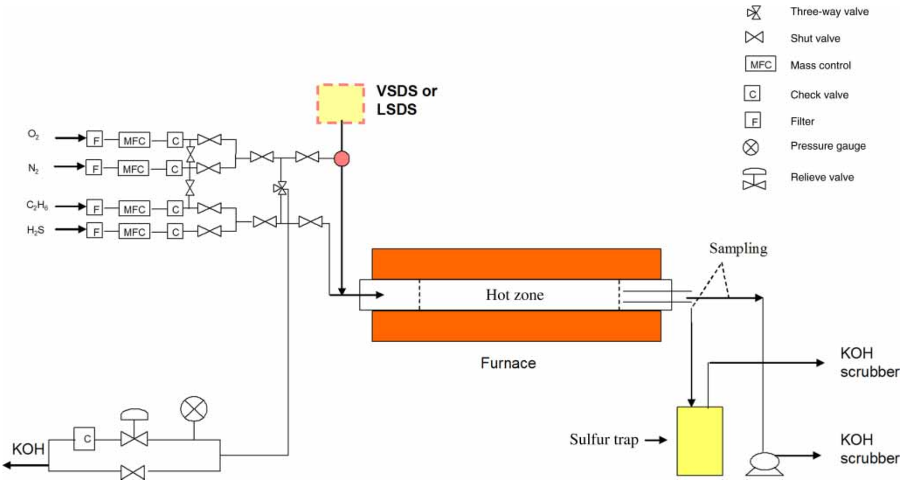


Figure 2. Experimental system for study of oxidative dehydrogenation of ethane.

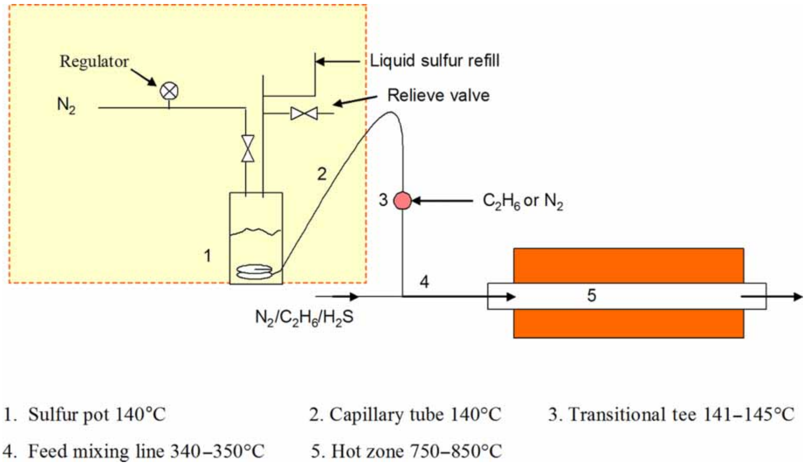
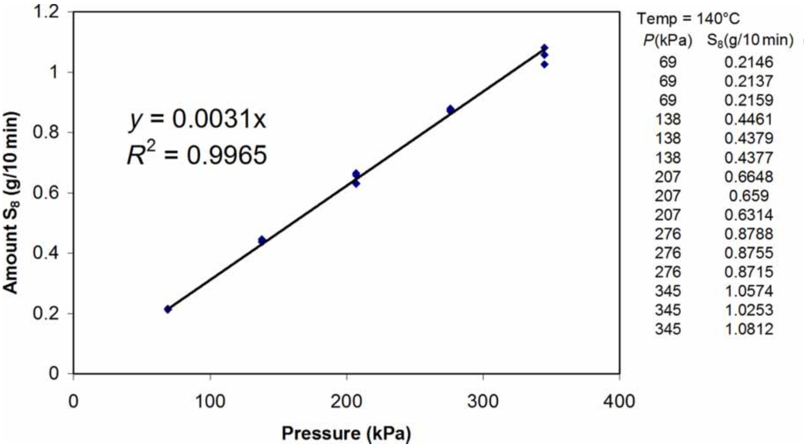


Figure 3. Liquid sulfur delivery system.

was connected to a tee-section (140–145 °C) consisting of a 25.4 mm (OD) to 6.4 mm (OD) reducer and a 4 cm long 25.4 mm (OD) tube extension. The capillary outlet entered the tee-section in such a way as to prevent the liquid sulfur from touching the metal components and for the liquid sulfur to drop vertically into the delivery tube/mixing line (340–350 °C) to vaporize and avoid build up of viscous liquid sulfur near the top of the system. The LSDS was calibrated at various N_2 over-pressures (Figure 4) before each experiment set.

4.3. *General procedure*

The complete system was flushed with N_2 and the reactor temperature was raised to the desired value using a N_2 flow rate equivalent to the following feed flow rates. After the reactor temperature had been attained (ca 1 h), feed gases were introduced and flowed until the product gas composition had stabilized (ca 15 min). Product samples were obtained via a gas syringe from a capillary tube inserted at the end of the hot zone using a pump to withdraw the gas. In addition, gas samples



P(kPa)	S_8(g/10 min)
69	0.2146
69	0.2137
69	0.2159
138	0.4461
138	0.4379
138	0.4377
207	0.6648
207	0.659
207	0.6314
276	0.8788
276	0.8755
276	0.8715
345	1.0574
345	1.0253
345	1.0812

Figure 4. Calibration of liquid sulfur delivered by LSDS.

Aecometric Corporation
Ametek Western Research
AMGAS
Apollo Environmental Systems Ltd.
AXENS
Baker Petrolite
BASF Catalysts LLC
Bechtel Corporation
Black & Veatch Corporation
BP Canada Energy Company
Brimrock Group Inc./Martin Integrated Sulfur Systems
Brimstone STS Ltd.
Canwell Enviro-Industries Ltd.
Champion Technologies Ltd.
Chevron Texaco (Research and Technology)
ConocoPhillips Company/Burlington Resources
Controls Southeast, Inc.
Devon Canada Corporation
EnCana Corporation
Enersul Inc.
ENI S.p.A. – E&P Division
Euro Support BV
ExxonMobil Upstream Research Company
Fluor Corporation
Goar, Allison & Associates, Inc./Air Products
Galvanic Applied Sciences Inc.
HAZCO Environmental & Decommissioning Services
HEC Technologies
Husky Energy Inc.
Innovative Chemical Technologies Canada Ltd. (ICTC)
International Commodities Export Company of Canada Limited (ICEC Canada Ltd.)
IPAC Chemicals Limited
Jacobs Canada Inc./Jacobs Nederland B.V.
KPS Technology & Engineering LLC
Linde Gas and Engineering
Lurgi GmbH
Marsulex Inc.
Nalco Canada
Petro China Southwest Oil and Gasfield Company
Porocel Corporation
Rio Tinto Alcan
Sandvik Process Systems, Inc.
Saudi Arabian Oil Company (Saudi Aramco)/ASC
SemCAMS ULC
Shell Canada Limited
SiiRTEC Nigi S.p.A.
Statoil ASA
Sulfur Recovery Engineering (SRE)
Sulphur Experts Inc. (Western Research)
Sultran Ltd.
Suncor Energy Inc.
TECHNIP
Tecnimont KT S.p.A.
Total
URS Corporation / Washington Division
Virtual Materials Group Inc.
Weatherford International LLC
West Penetone Inc.
WorleyParsons

Figure 5. Alberta Sulphur Research Ltd. member companies 2009–2010.

were taken from the sulfur condenser pot and, in both cases, the gas was flowed through a small cartridge of P_2O_5 to remove sulfur and water (formed in cases where O_2 was used).

4.4. *Gas feed and product analysis*

Gas feed and product analyses were conducted on SRI 8610B gas chromatographs equipped with thermocouple detectors. Hydrocarbons (C_1–C_3) and sulfur-containing compounds (H_2S, SO_2, COS and CS_2), as well as CO_2 were analyzed on a Poropak QS column using He carrier gas. N_2, O_2, CO and H_2 were analyzed on a 5 A molecular sieve column using Ar carrier gas. Multi-point calibrations of the chromatographs were conducted using the gas standards mentioned previously. Three or more gas samples were taken at each condition, or until steady-state data were obtained using a variance of ±5% for the collected data to be deemed representative. This figure was based on the error estimation for all procedures used for gas sampling and analysis. In practice, data variation of less than ±2.5% was achieved.

4.5. *Safety note*

A major product, and in some cases a reactant in this study, was H_2S, a gas which is lethal at concentrations of 750–1000 ppmv for a single breath by an adult. All experimental systems were, therefore, contained in a ventilated area under constant electronic H_2S monitoring with a warning threshold set to 10 ppmv. H_2S supply was also contained in a ventilated area and supplied through an emergency shut down valve system designed to stop gas flow if the 10 ppmv threshold was reached in either the gas storage or experiment containment areas. Hazardous operations review of the experimental procedures was also conducted by our research team before the laboratory study was commenced.

5. Concluding comments

Results obtained in this study demonstrate that it should be possible to design a commercial process for the production of ethylene via sulfur-mediated oxidation of ethane in high selectivity (ca 90%) and yield (ca 75%). Importantly, this process produces very little CO_2 in comparison with the conventional steam-cracking technology. The process could be readily integrated in an oil refinery or into a sour gas processing plant with all off-gases being handled in the Claus sulfur recovery plant and tail gas treatment systems.

Ethylene formation via sulfur oxidation of ethane is a kinetically controlled process. Mechanistically, it is concluded that high selectivity to ethylene is a consequence of the relatively weak C–S bond which favors ethylene production pathways over the formation of products such as CS_2.

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