

# Catalytic effect of different reactor materials under subcritical water conditions: decarboxylation of cysteic acid into taurine

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**Abstract.** In order to understand the influence of reactor materials on the catalytic effect for a particular reaction, the decomposition of cysteic acid from Ni/Fe-based alloy reactors under subcritical water conditions was examined. Experiments were carried out in three batch reactors made of Inconel 625, Hastelloy C-22 and SUS 316 over temperatures of 200 to 300 °C. The highest amount of eluted metals was found for SUS 316. The results demonstrated that reactor materials contribute to the resulting product. Under the tested conditions, cysteic acid decomposes readily with SUS 316. However, the Ni-based materials (Inconel 625 and Hastelloy C-22) show better resistance to metal elution. It was found that among the materials used in this work, SUS 316 gave the highest reaction rate constant of 0.1934 s<sup>-1</sup>. The same results were obtained at temperatures of 260 and 300 °C. Investigation of the Arrhenius activation energy revealed that the highest activation energy was for Hastelloy C-22 (109 kJ/mol), followed by Inconel 625 (90 kJ/mol) and SUS 316 (70 kJ/mol). The decomposition rate of cysteic acid was found to follow the results for the trend of the eluted metals. Therefore, it can be concluded that the decomposition of cysteic acid was catalyzed by the elution of heavy metals from the surface of the reactor. The highest amount of taurine from the decarboxylation of cysteic acid was obtained from SUS 316.

## 1. Introduction

Supercritical fluid technology (SFT) is of significant scientific and technological importance, and has been extensively demonstrated to be one of the most effective media for a large number of processes. Water at subcritical conditions has been used as a solvent in natural extraction [1–3], the recovery of useful materials from organic wastes [4,5], depolymerization [6,7], chemical reactions [8,9] and organic synthesis [10–12] due to its high ion product. Supercritical water conditions can be applied for the complete oxidation of organic waste [13,14]. Alternatively, supercritical CO<sub>2</sub> has been used for various purposes, such as the recycling of precious metals [15], leaf oil extraction and quinone analysis, among others [16]. As SFT simultaneously uses extreme temperatures and pressures, consequently, chemical corrosion increases [17,18]. The corrosion of various types of materials under high temperature and pressure conditions has been investigated intensively [19–22]. These types of corrosion could be hazardous and their presence in the products is not desirable. Conversely, the

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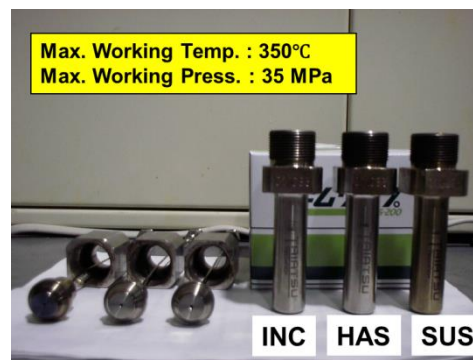
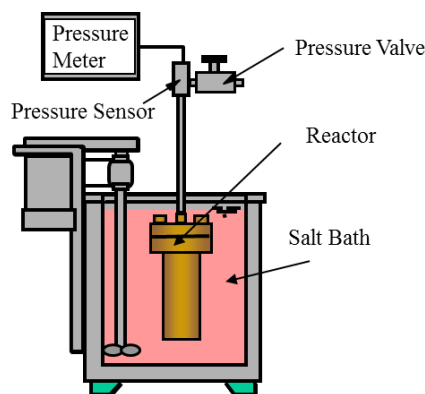
corrosion may act as a catalyst for some reactions. Therefore, selection of the reactor material and reaction conditions is crucial and special attention should be paid when applying SFT.

Under subcritical water conditions and different reactor materials, a small amount of metals (i.e., Fe, Ni, Cr, Mn and Mo) was found to be eluted during the reaction [17]. Although their presence is still within the acceptable environmental limit, these metals, as well as reactor materials, might influence the reaction rate of some reactions. Studies on metal elution from Fe/Ni-based reactor materials using water and cysteic acid have been conducted at short reaction times [17,23]. However, detailed investigations of the effects of metal elution on the reaction media are also important. The objective of this research is to investigate the possible catalytic effect on a particular reaction under subcritical conditions using different reactor materials.

In this research, the chemical reaction of interest for studying the catalytic effect under subcritical water conditions is the preparation of taurine from the decarboxylation of cysteic acid. Taurine is one of the most abundant free amino acids in the body and is essential in human metabolism [24]. From the viewpoint of the complete degradation of organic waste, the decarboxylation of cysteic acid is not a rate limiting step compared to acetic acid. However, since cysteic acid is the intermediate product of taurine production, this decarboxylation information is highly useful, especially when considering resource recovery and organic reactions under supercritical fluids (SF) conditions. Reactor materials and the presence of heavy metals under subcritical water conditions during the decarboxylation of cysteic acid are significant factors that might influence taurine production.

## 2. Methods

Experiments were performed in three batch reactor materials made of SUS 316 (consisting of Fe: 65%, Cr: 18%, Ni: 12%, Mn: 1% and Mo: 2%), Hastelloy C-22 (consisting of Ni: 60%, Cr: 20%, Mo: 12.5% and W: 3%) and Inconel 625 (consisting of Ni: 60%, Cr: 20%, Mo: 9% and Fe: 5%), all with the same size of 1 cm ID and 12 cm in height (a volume of 11 ml). The schematic diagram of the batch reactor apparatus is shown in Figure 1. The apparatus (TSC-006, Taiatsu Glass Corp. consists of a stirrer, pressure gauge, molten salt bath (mixture of KNO<sub>3</sub> and NaNO<sub>3</sub>) and the reactor.



**Figure 1.** Schematic diagram of batch reactor apparatus.

The experiments were conducted over a temperature range of 200 to 300 °C with the corresponding saturated vapor pressures (2-9 MPa) and a time range from 2 to 10 min. During a typical run, about 9 ml of 10 mmol/L cysteic acid was charged into the reactor. The reactor was sealed and the air inside was removed by purging with argon gas. The reactor was then immersed into the preheated molten salt at a desired time and temperature. The reaction was stopped by removing the reactor from the salt bath and immersing the reactor in a cold water bath to bring it quickly to room temperature. The experimental procedure was similar to that described by Faisal et al. [6]. The products were analyzed for taurine and other derived products using an amino acid analyzer (LC-10AD, Shimadzu Corp.).

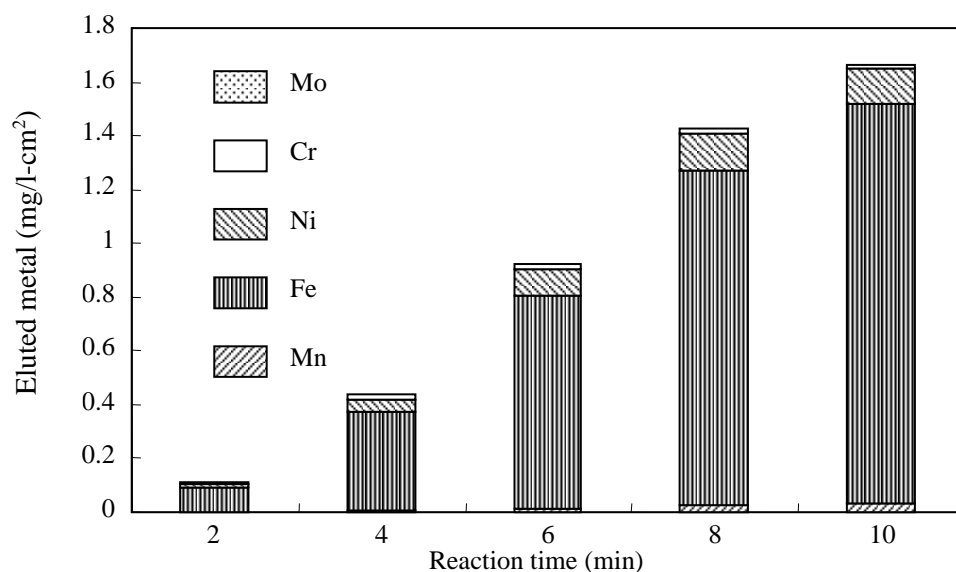
Metal elution was measured using an inductively coupled plasma atomic emission spectrometer (SPS 7700R, Seiko Instrument Inc.).

### 3. Results and discussions

#### 3.1. Effect of reaction time on eluted metals

Figures 2–4 show the effect of reaction time on the amount of metal elution from the various reactor materials (batch, SUS 316, Hastelloy C-22 and Inconel 625) at 260 °C. As can be seen from Figure 2, the eluted metal from SUS 316 was mainly Fe. The amount of eluted Fe is significantly increased with increasing reaction time. Mo was not detected at this temperature; however, a small amount of Cr was detected that was almost stable with increasing reaction time. Ni was detected at an even shorter reaction time and again increased with reaction time. Although Mn was also observed at a short reaction time, a small amount of Mn was detectable after 6 min and increased with reaction time.

Figure 3 shows the effect of reaction time on the amount of metal elution from Inconel 625 at 260 °C. The main eluted metal was Ni, followed by Cr and Mo. The total amount of metal elution was much lower than that for SUS 316. The amount of elution from Inconel 625 follows the trend of SUS 316 except for Fe, in which the trend of eluted Fe was unstable with reaction time. Interestingly, the elution of heavy metals from Inconel 625 was not dominated only by Ni, as a significant amount of Fe was also observed at this condition.



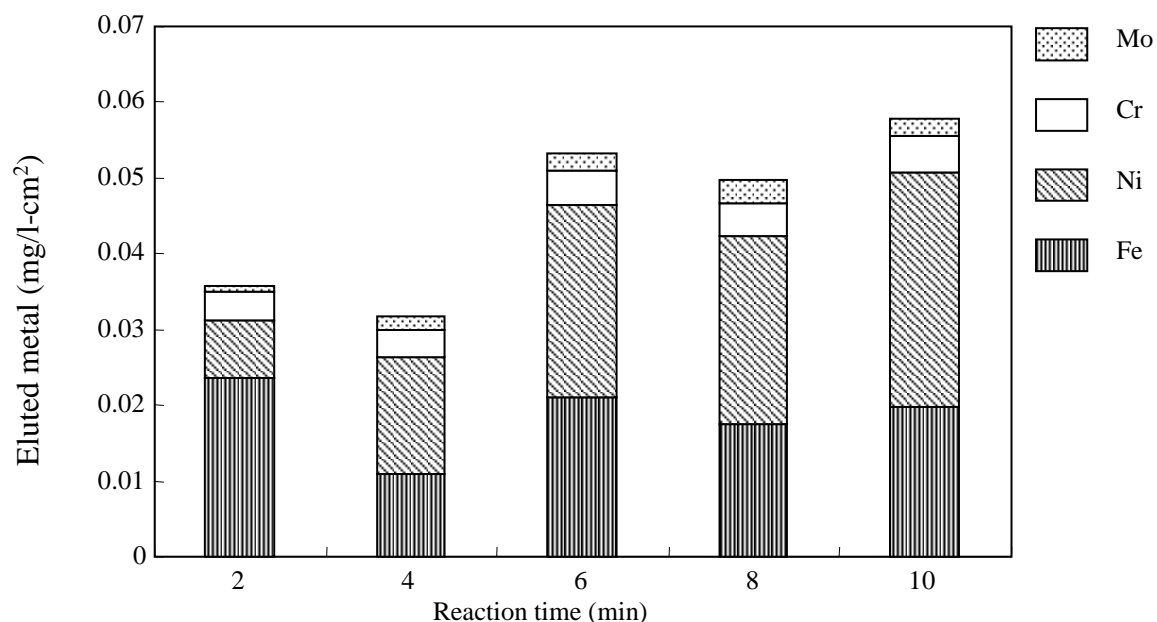
**Figure 2.** Effect of reaction time on the amount of metal elution from SUS 316 at 260 °C.

The amount of metal elution from Hastelloy C-22 at 260 °C at various reaction times is shown in Figure 4. A significant amount of Ni was observed from Hastelloy C-22 over the reaction time of 4–10 min. Cr and Mo were detectable and almost stable with reaction time, while W was not detected even after 10 min of reaction time. This observation allows us to conclude that the total eluted metals from SUS 316 were higher than Hastelloy C-22 or Inconel 625. It was also found that the total amount of elution in cysteic acid solution was higher than that in water [23]. Moreover, the erratic behavior of metal elution under SF conditions in water and cysteic acid was also different.

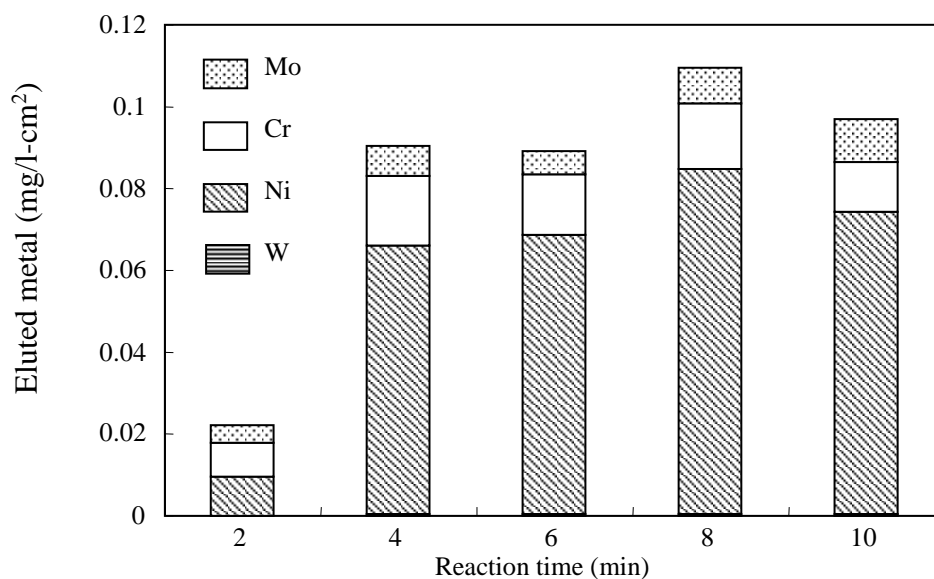
#### 3.2. Effect of reactor materials on decomposition rate of cysteic acid

Figure 5 shows the time course for the decomposition of cysteic acid at 280 °C. The results show that the decomposition of cysteic acid was higher for SUS 316 compared with Hastelloy C-22 and Inconel 625. Among the materials used in this work, SUS 316 gives the highest reaction rate constant ( $k$ ) of

$0.1934 \text{ s}^{-1}$ . The same results were obtained at temperatures of 280 and 300 °C. It was found that the amount of eluted metals follows the decomposition rate of cysteic acid. The presence of these metals



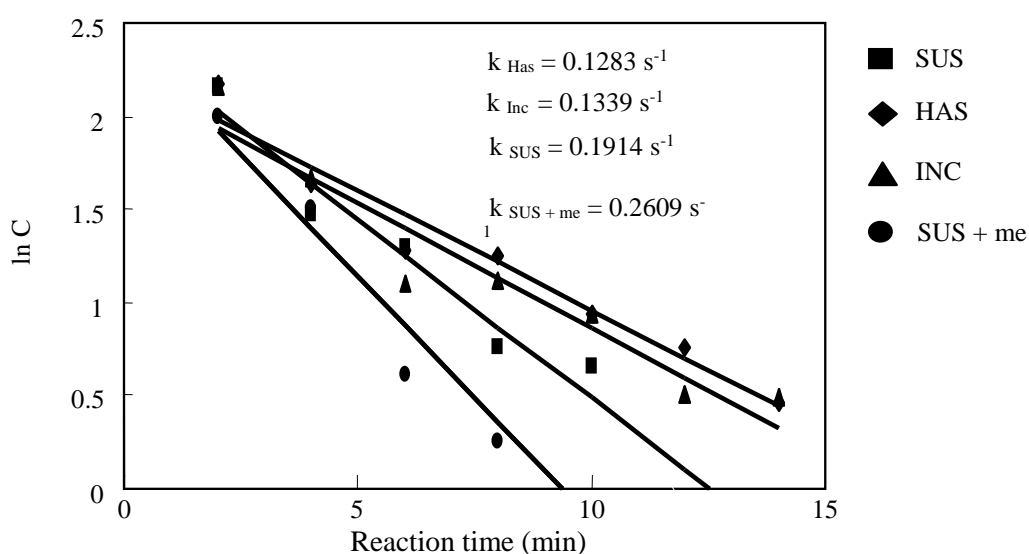
**Figure 3.** Effect of reaction time on the amount of metal elution from Inconel 625 at 260 °C.



**Figure 4.** Effect of reaction time on the amount of metal elution from Hastelloy C-22 at 260 °C.

might affect the acceleration of chain reactions in transforming organic compounds into other chemical compounds. Therefore, it can be concluded that the decomposition of cysteic acid was catalyzed by the metals eluted from the reactor surface. The chemical reaction in SUS 316 was faster than in Inconel 625 or Hastelloy C-22. In addition, to prove that the reactor materials affect the reaction, one piece of SUS 316 metal was added into the SUS 316 reactor (20 cm<sup>2</sup>). As can be seen from Figure 5, the increased surface area (SUS + metal) strongly affects the decomposition rate of cysteic acid. The reaction rate constant of SUS + metal was  $0.2609 \text{ s}^{-1}$ . However, the current results

indicated that increased surface area was not favorable for taurine production. This finding agreed well with the observation of Belsky et al. [25], who reported that the rate of reaction at sub-supercritical fluid conditions was found to depend significantly on the materials of the reactor. Houser and Liu [10] also examined the role of different reactor materials in high-temperature reactions. They reported that chloride attacked the metal walls of the reactor to produce metal chlorides and these compounds may act as catalysts for the decomposition reactions. In fact, both the metal wall and the eluted metals had a catalytic effect on the reaction. In addition, preliminary experiments also revealed that the use of new reactors produced different results from those obtained from reactors that have been used at least once. It was observed that the new reactors, especially on SUS 316, led to a higher decomposition of cysteic acid and a higher amount of eluted heavy metals. High Fe elution, which produced yellowish decomposition products, was observed for the first run. Consequently, all the reactors used in this study were seasoned in order to eliminate these effects.



**Figure 5.** Time course for decomposition of cysteic acid at 280 °C.

The effect of reactor materials on the reduction of the Arrhenius activation energy ( $E_a$ ) for the first-order decomposition of cysteic acid is summarized in Table 1. These results are obtained from the plot of the three reaction rate constants ( $k$ ) at temperatures of 260, 280 and 300 °C.

**Table 1.** Effect of reactor materials on the reduction of activation energy.

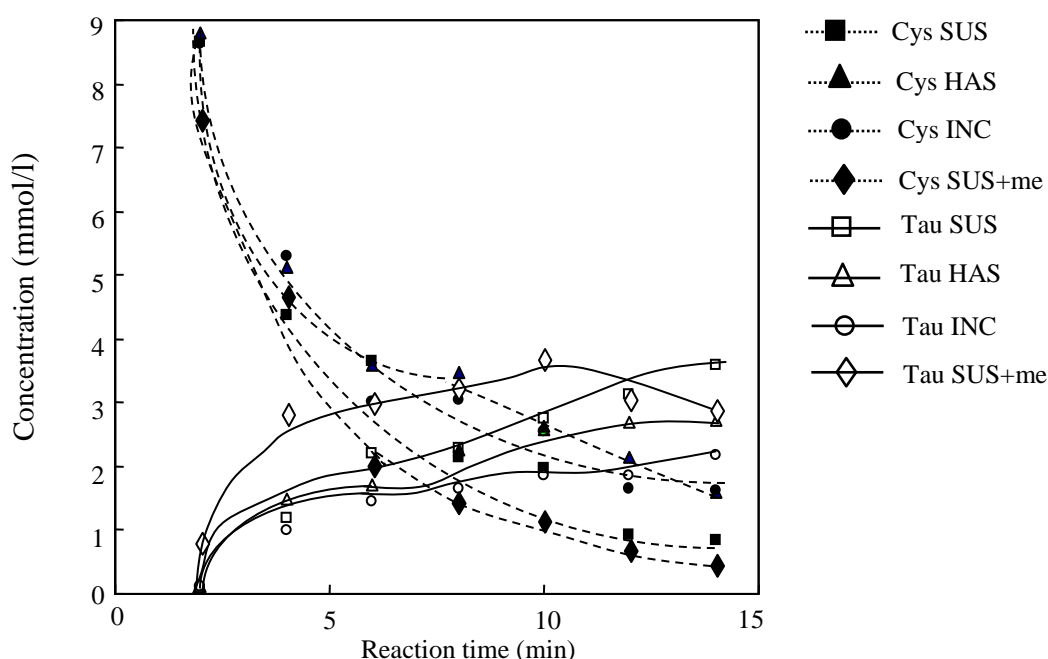
Reactor materials	$k = A \exp(-E_a/RT)$			Activation Energy $E_a$ (kJ/mol)
	260 °C	280 °C	300 °C	
SUS 316	0.1078	0.1914	0.0757	70
Inconel 625	0.0640	0.1339	0.0332	90
Hastelloy C-22	0.0531	0.1283	0.0658	109

The results show that the highest activation energy was for Hastelloy C-22 (109 kJ/mol), followed by Inconel 625 (90 kJ/mol) and SUS 316 (70 kJ/mol). Based on the assumption that the highest  $E_a$  controls the reaction rate, the elution from the reactor surface might increase the reaction rate by helping to break the chemical bonds in reactant molecules. The results suggest that the decomposition reaction in SUS 316 was catalyzed by the SUS 316 material. Compared to Hastelloy C-22, the activation energy was reduced by around 40 kJ/mol. These results agree with the findings of Mingotaud et al. [26]. Their experiments on the effect of the reactor wall of depolymerization of

styrene in supercritical fluid CO<sub>2</sub>/ethanol suggests that a teflon wall improved the yield and the metals itself can interact with the reactants.

### 3.3. Formation of taurine

The effect of reaction time on the formation of taurine from decarboxylation of cysteic acid at 280 °C is illustrated in Figure 6. Cysteic acid started to decompose from 2 min to produce taurine. For all reactor materials, the trend of decarboxylation is almost the same at <4 min of reaction time, after which (>4 min) the trend differs slightly. As can be seen, the formation of taurine increased with increasing reaction time up to 10 min. The highest amount of taurine obtained was from SUS 316, which has the highest metal elution, suggesting that decarboxylation of cysteic acid was catalyzed by the elution, as well as by the reactor wall itself. At 4 min of reaction time, the addition of SUS (Tau SUS+me) results in faster decomposition of cysteic acid, followed by a significant increase in the amount of taurine. However, at these conditions, the formation of taurine decreased after 10 min, while cysteic acid almost completely decomposed at 14 min, indicating that taurine might also decompose into other compounds.



**Figure 6.** Decarboxylation of cysteic acid into taurine at 280 °C with reaction time.

### 4. Conclusions

We examined the influence of reactor materials on the catalytic effect for decarboxylation of cysteic acid into taurine. We demonstrated that reactor materials highly affect the resulting product. Under the tested conditions, cysteic acid decomposes readily in SUS 316, where the highest elution was obtained. The results for the amount of eluted metals show that the elution rate tends to follow the decomposition rate of cysteic acid. Therefore, based on these results, it can be concluded that the decomposition of cysteic acid was catalyzed by the reactor wall and the metals eluted from the reactor surface. The highest amount of taurine from decarboxylation of cysteic acid was obtained from SUS 316. An increase in surface area was also favorable for the decomposition rate of cysteic acid, but does not promote taurine production.

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