国外蛋氨酸工业化合成工程技术

1. Introduction

The worldwide demand for amino acids is increasing at between 5 and 10 % per year. The major markets are in animal nutrition (feed additives) and for food additives. The two major amino acids for animal feed additives are DL-Methionine and L-Lysine. Other important amino acids include L-Threonine, L-Leucine and L-Tryptophane.

The reason for using feed additives is the necessity to optimize the diets of animals in order to maximize their growth in weight with any given amount of animal feed. Since the diet of animals may be inadequate in any essential amino acid, protein synthesis cannot proceed beyond the rate at which this amino acid is available. Therefore, this amino acid is called a limiting amino acid.

The 10 essential amino acids that have to be provided in pig diets are: lysine, threonine, tryptophane, methionine (and cysteine), isoleucine, histidine, valine, arginine, phenylalanine (and tyrosine). Most cereal grains are limiting in Lysine, Tryptophane and Threonine. Therefore, these amino acids are of particular importance when evaluating feed ingredients and feed composition.

Methionine and Lysine are the two amino acids most commonly added to animal diets, especially for poultry and pig diets, cattle (cows) and turkeys. The amino acids Threonine and Tryptophane may in the future also be added, provided these amino acids become available in feed grade at competitive prices.

The increasing affluence of the population is expressed in strongly increasing demand for food and especially meat. This involves significant growth in the market for feed additives and feed.

2. Utilization of DL-Methionine

The animal and human metabolism is capable of inter-changing the D-and L-form of Methionine into each other. Therefore, both forms can be utilized as feed additive (essential amino acid) without the requirement of delivering the optically active natural L-form.

Consequently, DL-Methione (the racemic mixture) is added as feed and food supplement and thus chemical synthesis (which yields the racemic mixture) is the synthesis method of choice.

3. Chemical Synthesis of DL-Methionine

The industrial synthesis of DL-Methionine utilizes Acrolein as starting compound. This Acrolein is reacted (addition at the double bond) with Methylmercaptane at ambient modest temperatures with base catalysis.

Acrolein + Methylmercaptane -------------. Intermediate 1 (Aldehyde)

The resulting Aldehyde is reacted with NaCN and NH4HCO3 in aqueous solution at ca 90 C to form a Hydantoin.

Intermediate 1 (Aldehyde) + NaCN + NH4HCO3 -------. Intermediate 2 (Hydantoin)

This Hydantoin is furthermore reacted with NaOH or K2CO3 under pressure at ca 180 C and, after acidification or after CO2-treatment, converted into the free DL-Methionine.

Intermediate 2 (Hydantoin) + NaOH or K2CO3 ----------. DL-Methionine

4. Chemical alternatives to DL-Methionine

In the USA, a chemical alternative (substitute) is used besides DL-Methionine in the feed additive industry.

This alternative compound is MHA (Methionine-Hydroxy-Analogon = Methionine-hydroxybutyric acid).

5. DL-Methionine Specifications

DL-Methionine is synthesized and supplied to consumers (feed compounders, industrial users) at purity levels exceeding 99 %.

Moreover, solid DL-Methionine is supplied with high bulk density and good flow properties as crystalline powder to ascertain high dosing accuracy and homogeneity of the resulting mixture.

DL-Methionine may also be supplied to the feed compounders and the animal rearing industry as liquid in order to facilitate certain applications and mixing operations.

For cattle and cows (which are ruminants), DL-Methionine may be supplied in granular coated form as rumen-stable particles to improve the amino acid supply to the small intestine where the amino acids are absorbed.

Otherwise, in ruminants, the amino acids are metabolized and degraded by the microorganisms in the rumen.

6. Separation of the Racemic Mixture

D-and L-Methionine may be produced by separation of the two isomers at the hydantoin stage of the synthesis. Enzymatic hydrolysis by stereo-specifically acting hydantoinases (enzymes) is used to obtain the two separate forms of D-and L-Methionine.

7. Technology and Process Know-how

The industrial synthesis of DL-Methionine involves the handling of several noxious or toxic compounds (NaCN, CH3SH) and includes aggressive reaction mixtures. Moreover, aldehydes are prone to undesired side reactions.

The synthesis requires specific process know-how as well as the utilization of appropriately designed equipment, which is manufactured with special alloys for the cladding of reactors and

critical piping parts.

Special consideration has to be given to process control and safety as well as the purification of the resulting product. Closed loops of reaction and environmental protection are of importance.

The technology, process and equipment know-how for industrial DL-Methionine synthesis and separation of the racemic mixture as well as the knowledge about purification and formulation of the final product are available from specialized German company. Several specialized equipment producers in Germany and Switzerland are competent suppliers of equipment and process technology.

Further details of the process for DL-Methionine production and product specifications can be provided.

8. Raw Materials/Battery Limits:

Propene (propene, propylene) for synthesis of acrolein

Methane and ammonia for synthesis of HCN

Methanol and hydrogen sulphide for synthesis of methylmercaptane

Ammonium carbonate for hydantoin synthesis (Recycling)

Emissions-and effluent control (no environmental burden)

Steam generation

Pressure air generation

9. Investment and Capacity:

A manufacturing plant with .world-scale-capacity produces 50 000 tons-per-year of DL-Methionine and requires investment (production technology and purification, without utilities and civil construction, without land area) of ca. 35 million Euro.

Due to special expertise in micro-reaction-technology, RTM and affiliated companies can provide manufacturing units starting from 1000 tons-per-year (at investment in technology and purification, without utilities and land) of ca. 2.0 million Euro (for a 1000 tons-per-year unit). Specific investment per annual capacity decreases with increase in capacity.

10. Environment:

The manufacturing facilities are completely contained and all emissions and effluents are controlled and made innocuous. In addition, the facility can be established as a carbon-neutral operation.