

Improvement of Industrial Synthesis of Methyl Methacrylate Application of a Wet Air Oxidation Process (WAO)

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Introduction

A new process in which the blow down from an ammonium sulfate crystallizer is treated in a Wet Air Oxidation (WAO) system has been developed by ATOFINA Italia and USFilter Zimpro Products. The new process has been installed and operated at ATOFINA Italia's methyl methacrylate production facility in Rho, Italy. The new process eliminates the need for off-site disposal of a crystallizer blow down stream, as well as increasing ammonium sulfate recovery.

Methyl Methacrylate Process

Process Description

Methyl methacrylate (MMA) is the most important ester of methacrylic acid. It can be homo- and copolymerised to produce acrylic resins with good strength, transparency and with excellent weather resistance. The first commercial process for making MMA (1930's), the acetone cyanohydrin route, remains the predominant process in use today. In the acetone cyanohydrin route, acetone cyanohydrin reacts with sulfuric acid at low temperature to produce the sulfuric monoester of 2-hydroxy-2-methyl-propionamide, which forms methacrylamide sulphate after exposure to higher temperatures (100° - 140°C). The liquid phase is maintained by using an excess of 0.2 - 0.7 moles of 100% sulfuric acid. The first step of the reaction is strongly exothermic while the rearrangement of the sulfuric ester is endothermic.

During the synthesis of methacrylamide, a portion of the acetone cyanohydrin decomposes to carbon monoxide during the first part of the reaction. Additionally other by-products are formed and react due to the strength of the acid and high temperature in the second step. About 92 - 94% of the acetone cyanohydrin is converted to useful products and 6 - 8% is consumed in the formation of organic by-products (acetone, acetone sulphonates, oligomers, polymers, others). Methacrylamide sulphate is esterified with a mixture of water and methanol to form MMA and an aqueous solution of ammonium hydrogensulphate, sulfuric acid and the organic by-products. The ammonium hydrogensulphate is an unavoidable by-product of the reaction.

By product treatment and disposal options

The most common way to treat the hydrogensulphate by-product is to pyrolyze it at 1000°C - 1100°C to release SO₂, which is then converted into sulfuric acid for reuse in synthesis; no ammonia is recovered. An alternative way to treat the waste acid solution is the neutralization with dry ammonia to produce ammonium sulphate, which is used as a fertilizer. The organic by products coming from the synthesis and the esterification remains in solution and must be purged during the crystallization step to allow the production of good ammonium sulphate crystals. If crystallization is employed, this purge (referred to as crystallizer blowdown) is an unavoidable waste stream of MMA process and its treatment requires some additional production costs.

Possible treatments of the crystallization blow-down are:

- 1) neutralization with ammonia and production of a fertilizer mixture with low content of nitrogen
- 2) pyrolysis to produce SO₂ (and after H₂SO₄)
- 3) biological treatment of the ammonium and the organic by-products
- 4) Wet Air Oxidation of the organic products and neutralization with ammonia to recover ammonium sulphate.

All these processes have their own technical and economic aspects.

Methods 1 and 2 are well known and are usually used by ATOFINA Italia but at high costs. Method 3 has been studied and can be used but a very large amount of water is necessary to dilute the solution at the proper COD and salt concentrations. Additionally, Method 3 results in all the sulfur contained in the purge lost in the discharged waste waters. Method 4 has been tested, developed and an industrial unit has been constructed, and successfully operated by ATOFINA Italy and USFilter Zimpro Products for ATOFINA's methyl methacrylate facility in Rho, Italy.

The choice to invest in a completely new treatment process for the crystallization blow-down came out from the following considerations:

- 1) The agricultural use of industrial by-products is becoming increasingly restricted.
- 2) The alternative choice of incineration is an expensive process with an adverse environmental impact which will create difficulties in obtaining local authorization for gas emissions (NO_x, SO₂).
- 3) The other alternative choice of biological treatment is an expensive process due to the high ammonium salt contained in the purge.
- 4) The use of wet oxidation allows energy recovery as well as a ammonium sulfate recovery while maintaining the lowest environmental impact.

Wet Oxidation: General Background

Wet air oxidation (WAO) is the process of oxidizing organic matter in the presence of liquid water. Any substance that is capable of burning can be wet air oxidized in water. WAO is typically employed as a waste treatment technology when the waste is non-conductive to incineration or biological treatment. It is an ideal process for pretreatment of wastes that are toxic to conventional biological facilities. The WAO process is uniquely suited to the oxidation of concentrated waste liqueurs, slurries, and sludges where the oxygen demanding organic matter is about a few percent of the predominantly water stream (Reference 1).

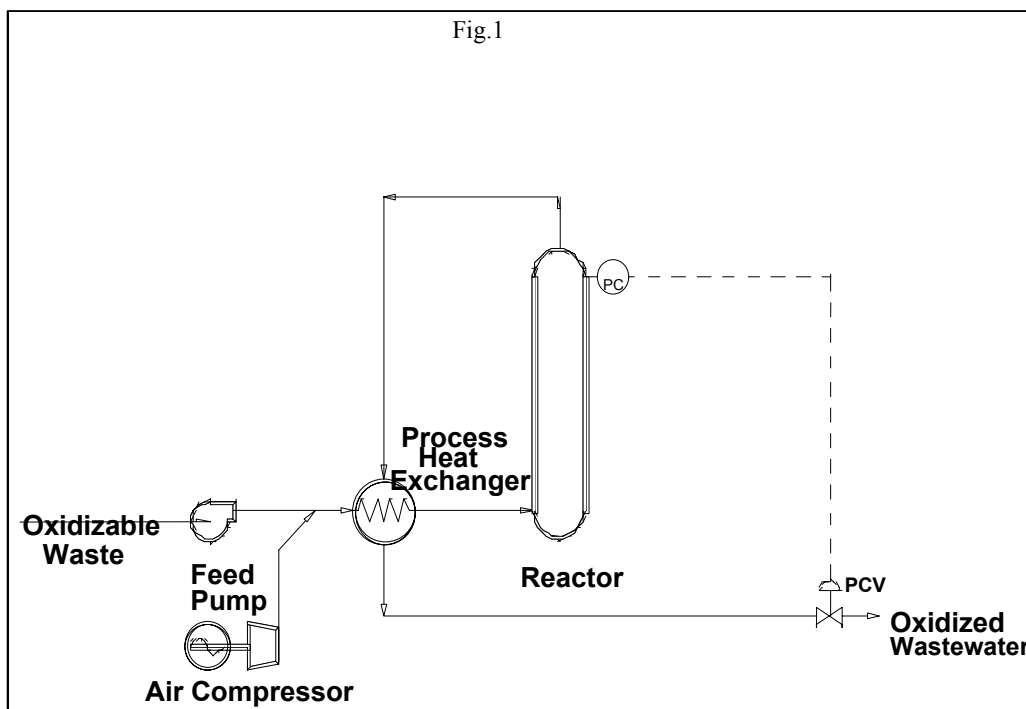
Wet Oxidation Temperature and Application Spectrum:

The wet oxidation reactions take place between 100 and 372°C at elevated pressures to maintain water in the liquid phase. This temperature range can be further subdivided into low (100-200°C), medium (200-260°C), and high temperature (260-320°C) operation. Higher temperature (320-372°C) systems can be designed as well but are rarely used.

Industrial applications of low temperature oxidation (100-200°C) include the thermal conditioning of sludge (TSC) and low strength sulfidic spent caustic treatment. TSC is performed on municipal and pulp/paper industry sludges in the 175-200°C temperature range. Some sulfidic caustics are also treated in this temperature range. Other industrial wastes potentially suitable for low temperature oxidation include cyanide and phosphorous wastes as well as non-chlorinated pesticides.

Medium temperature (200-260°C) oxidation is used for typical ethylene spent caustics, as well as for autothermal TSC, and some industrial wastes. Ethylene spent caustics are derived from sulfidic acid gas washings in the ethylene industry. These wastes are treated in the 200-220°C range. Autothermal sludge conditioning operations occur in the temperature range of 220-260°C as does wet air regeneration of powdered activated carbon for use in wastewater treatment applications. Some other industrial wastes containing phenolic or cresylic compounds can be treated at the high end of this temperature spectrum.

High temperature (260-320°C) oxidation is used for refinery spent caustic, sludge destruction, and most WAO treated industrial wastewaters. High temperature systems are usually designed for less than 290°C operation, which is a transition point for higher strength fabrication conventions. Within the 260-280°C range, refinery spent caustics containing significant concentrations of naphthenic and cresylic acids are treated. Most organic industrial wastes are oxidized in this temperature range as well, including chlorinated pesticides, solvents, pharmaceutical and other organic chemical production wastes. Sludge destruction systems are designed to operate within the higher end of this temperature range (280-320°C) and are employed for complete destruction of municipal, pulp and paper, or other organic sludges.



Simplified General Wet Oxidation Flowscheme

A simple diagram of a general wet oxidation flow-scheme can be seen in Figure 1. The waste is pumped through a high pressure pump; this can be a standard reciprocating diaphragm pump for pure liquid or a more exotic high pressure pump for slurries. The oxygen for oxidation is supplied by either air or pure oxygen and in this general flow scheme an air compressor is shown. The air is combined with the liquid and they pass through a feed/effluent (F/E) heat exchanger (HX) where they are heated to near reaction temperatures. They then flow into the bubble reactor where the exothermic reaction takes place. Usual retention time in the reactor is 1 hour. The oxidized effluent and off gas then pass through the hot side of the F/E HX where they are cooled while simultaneously heating the influent. Auxiliary heaters and coolers are also employed (not shown). Depending on material of construction constraints, steam balance concerns, or other factors, separate heat exchangers rather than an F/E HX may be employed.

The reactor effluent then passes through a pressure control valve which controls the pressure on the WAO system. Proper valve design is critical for this application, as the service can be highly erosive. A separator downstream of the pressure control valve allows the depressurized and cooled vapor to separate from the liquid. The liquid is discharged, typically to conventional biological treatment facilities for final polishing, or to a crystallizer or other downstream system as appropriate. The gas is vented to the plant flare header or a dedicated thermal oxidizer.

General Wet Oxidation Reactions and Chemistry

While air (oxygen) is bubbled through the reactor to provide an economical supply of oxidant, wet oxidation is a liquid phase process and should not be confused with submerged combustion or any of the molten metal/molten salt processes. Oxidation reactions take place in the aqueous environment where the water behaves much like a catalyst and is an integral part of the reaction. It is theorized that the chemistry of wet oxidation involves free radical formation with the oxygen derived radicals attacking the organic compounds and encouraging the formation of organic radicals (Reference 2). The use of catalysts, such as homogeneous Cu^{2+} and Fe^{3+} or their heterogeneous counterparts or even precious metal catalysts, enhance system reactivity and performance (Reference 3-12).

A noteworthy characteristic of wet oxidation chemistry is the formation of carboxylic acids in addition to the primary end-products, CO_2 and H_2O . The yield of these carboxylic acids varies greatly depending on system design, but typically 5-10% of the TOC from the feed remains as carboxylic acids by products, predominantly acetic acid. Carboxylic acids such as acetic acid are readily degradable in conventional biotreatment facilities. The inorganic elements: nitrogen, phosphorous, sulfur, and chlorine which enter the reactor bonded to organic molecules are reacted to NH_3 , PO_4^{3-} , SO_4^{2-} , and Cl^- respectively.

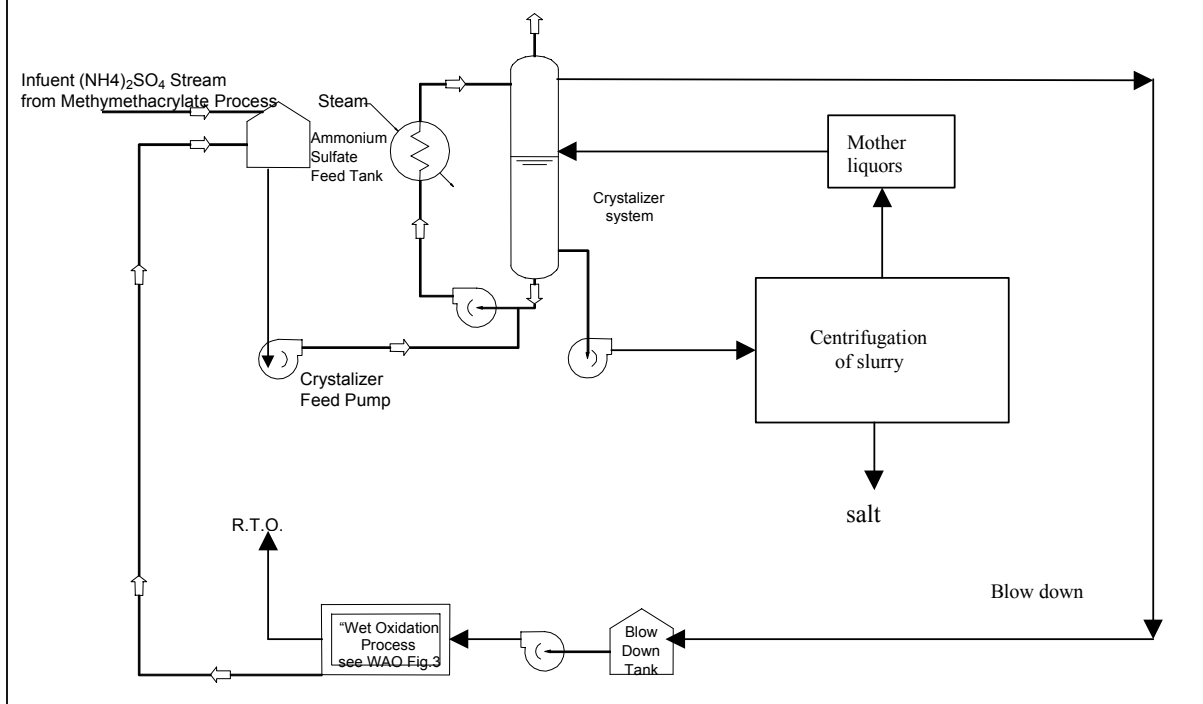
The chemistry of wet oxidation has some advantageous properties with regards to the off-gas produced. The off-gas from a WAO reaction has negligible NO_x , and SO_x ; and negligible particulates. Volatile Organic Compounds (VOC's), such as aldehydes, ketones, and alcohols may be in the off-gas depending on the waste. When VOC's are present, a thermal oxidizer is employed for off-gas treatment.

Application of WAO technology to methyl methacrylate production.

Crystallization of by-product ammonium sulfate

At the ATOFINA Italia's production facility in Rho, near Milan (Italy), it is produced more than 100,000 tons/year of methyl methacrylate (MMA), from acetone cyanohydrin. Almost all this monomer can be utilized for in-house production of several MMA copolymers; these products are then used to prepare granules and sheets. At present, the main by-product of the factory is ammonium sulphate derived from MMA synthesis. For every ton of MMA produced almost 2 tons of this salt is recovered in a crystallization facility. In order to produce good quality crystals, organic by product levels in the crystallizer must be minimized. To remove these organic contaminants from the crystallizer system, a significant blow down (purge) of the mother solution is required. Up until the end of 1998, all the blow-down was treated off-site to produce fertilizers with low nitrogen content, or to produce regenerated sulfuric acid. Both these alternatives were expensive and, in an attempt for significant reduction in production costs, a new process has been developed on-site using WAO to remove organic constituents from the system. Since the beginning of 1999, the ammonium sulphate is produced according to the process flow diagram of Figure 2.

ATOFINA (NH₄)₂SO₄ Crystallizers System Process Flow Diagram (Fig.2)



In this process, a stream of 40 - 45% (by weight), (NH₄)₂SO₄ aqueous solution deriving from the MMA facility, flows into the crystallization feed tank. This tank receives also the treated solution of the WAO unit. The solution is pumped from the feed tank to a system of crystallizers (in the figure is simplified with one single apparatus).

Some organic by-products remain in solution and accumulate in the system. To remove this accumulation, a mother liquor purge stream is removed from the third stage as a blowdown and is sent to a blowdown tank. The blowdown is fed from the tank to the WAO unit for destruction of the organic contaminants.

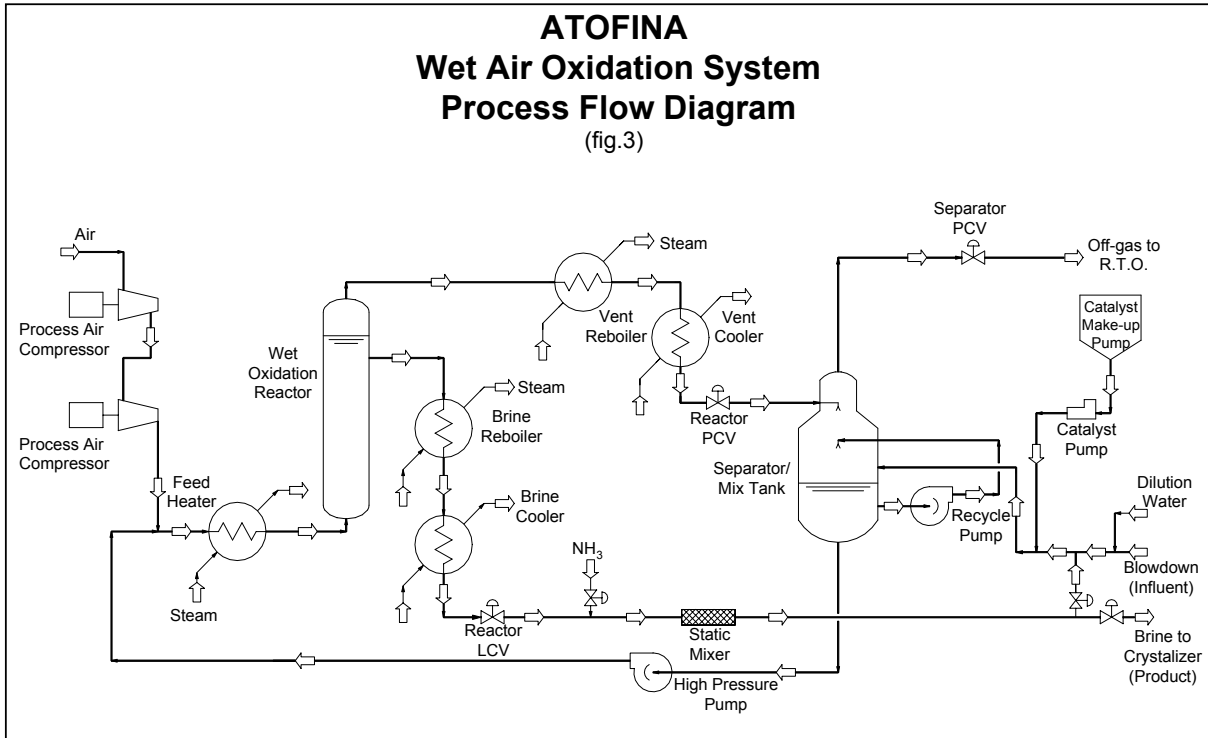
The treated ammonium sulfate stream is then recycled back to the crystallization feed tank. The composition and some characteristics of the blowdown are reported in Table 1.

Table 1: blow-down properties

Water content	30-45%
Ammonium sulphate	15-25%
Ammonium acetone sulphonates (1-; 1,3-)	25-35%
Oligomers of methacrylic acid	1-3%
2-hydroxy-2-methylpropionic acid	1-5%
Other sulphonated organic products	2-5%
Density	>1.2 g/ml
Temperature	About 100°C
Chemical Oxygen Demand	About 400 g/litre

Wet Air Oxidation of the Crystallizer Blow Down

Wet air oxidation of the crystallizer blow down is performed to remove organic contaminants from the system and to recycle the treated ammonium sulfate stream for salt recovery. A process flow diagram is shown in Figure 3.



Flow to the WAO system begins with the crystallizer blowdown stream which is pumped out of the blow down tank to the WAO system as shown in Figure 2. The crystallizer blowdown stream is diluted with several flow streams to reduce its COD value to a level appropriate to the WAO system (<100 g/L). A copper sulfate catalyst solution is added into the diluted crystallizer blowdown in order to enhance the COD destruction efficiency of the WAO system. While not typically used on wastewater WAO systems, a catalyst was used in this system to achieve the high oxidation efficiency that is required in this closed loop application. Since the WAO and the crystallizer are a liquid closed loop system, with only ammonium sulfate crystals and off gas vapor exiting the system, only minor make-up quantities of catalyst is needed.

The various streams and the blowdown stream are contacted in a separator/mix tank where they are blended. From the bottom of the separator/mix tank the diluted and conditioned blowdown flows to the high pressure pump, which pumps the stream to the inlet of the feed heater.

The WAO system requires an adequate quantity of oxygen to achieve the desired treatment objectives. Oxygen is supplied to the WAO system in the form of compressed air by two process air compressors that are connected in series. The discharge flow of the process air compressors is combined with the liquid discharge of high pressure pump before the feed heater. The diluted, conditioned crystallizer blowdown and air mixture enters the tube inlet of the tube and shell feed heater where they are heated with steam.

The hot crystallizer blowdown and air mixture are then directed to the bottom of reactor. The WAO reactor is a vertical cylindrical vessel and as the liquid/gas mixture rises through the reactor oxidation of the organic compounds occurs. The oxidation reactions which occur are exothermic reactions and this heat of reaction raises the temperature of the crystallizer blowdown/air mixture to the operating temperature of 280°C with 117 bar of operating pressure used to maintain the liquid phase. The reactor has a one hour nominal residence time and achieves a 99+% destruction of all organic constituents.

The liquid and vapor phases of the reactor contents separate in the upper portion of the reactor through two outlet connections located at different elevations. The vapor discharge (vent) passes through the vent reboiler which is used to produce steam. This steam is sent to the crystallizer system where it is used as a heat source. The cooled vapor partially condenses in the vent reboiler. The partially cooled vapor and condensate pass through the vent cooler to further cool and condense the reactor vent. The vent stream then passes through the reactor pressure control valve where thermodynamic expansion of the gas is used as a final cooling step. The vapor and vent condensate are discharged into the separator/mix tank where they are gravity separated. The pressure in the separator/mix tank is controlled by a pressure control valve, through which the cooled vent off gas exits. The off gas is then directed to a regenerative thermal oxidizer, which destroys residual and product VOC's before the off gas is discharged to the atmosphere.

The liquid contents of the reactor (brine) are discharge from the reactor via the lower of the two discharge lines. The liquid passes through the brine reboiler which produces steam for the crystallizer system. The cooled brine then passes through the brine cooler for additional cooling before passing through the level control valve. The reactor level control valve is used to maintain the liquid level in the reactor between the two discharge lines within the reactor, allowing phase separation of the vent and brine within the reactor. Phase separation within the reactor is referred to as "hot-separation" and is performed in order to obtain a high concentration of ammonium sulfate in the oxidized brine which is returned to the crystallizer system. Ammonia is added to the oxidized brine for pH control.

The oxidized brine is then returned to the feed tank of the crystallizer system for product recovery. A portion of the pH adjusted brine is also diverted to the separator/mix tank for dilution.

Results

The WAO reactor operates at 280°C with a 1 hour nominal residence time and is aided by the addition of a homogeneous copper sulfate catalyst. The reactor is a vertical bubble reactor with the oxidation of organic constituents occurring in the liquid phase. The performance of the WAO reactor is shown below in Table 2.

Table 2: WAO Reactor performance

	Reactor Inlet	Outlet Brine	Outlet Vent Condense
COD (mg/L)	About 75,000	<600	About 1,300
% Ammonium Sulfate	About 25-30%	45%	None
Volatile acids (mg/L)	About 700	<200	About 710

An overall liquid material balance shows an overall COD destruction of 99+% in the reactor. Since “hot-separation” is utilized, the brine is concentrated before returning to the crystallizer. Additionally, the exothermic nature of the oxidation reaction yields a net energy gain in the WAO system. This energy is transferred to the crystallizer system in the form of steam.

Summary and Conclusions

Elf ATOFINA has incorporated an effective new approach for dealing with the large quantities of unavoidable by-product formed from the MMA production process. By-product ammonium sulfate salt is recovered in high quality form utilizing crystallizers. In order to ensure that the quality of the ammonium sulfate is, and remains, acceptable for agricultural use, a purge stream is utilized. This purge stream, which contains the organic by-product contaminants, passes through a wet oxidation system where the organic contaminants are destroyed and the treated ammonium sulfate returns to the head of the crystallization system.

Wet oxidation is traditionally viewed as a waste treatment technology applied to hazardous wastes and is utilized to make the hazardous waste amenable to conventional biological treatment. While effective in that role, wet oxidation can also be utilized to improve the quality of product. In this application wet oxidation is used as an integral part of the MMA process for producing agriculture grade ammonium sulfate fertilizer.

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